

Bonding of Supported Chromium during Thermal Activation of the $\text{CrO}_x/\text{SiO}_2$ (Phillips) Ethylene Polymerization Catalyst

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An active surface science model for the Phillips ethylene polymerization catalyst has been prepared by impregnating aqueous CrO_3 on a flat silicon(100) substrate covered by amorphous silica. Using a combination of X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and Rutherford backscattering spectrometry, we studied the effect of calcination on the state of the supported chromium. Depending on the calcination temperature and the initial Cr loading of the catalyst, two processes are observed. The impregnated chromate anchors to the silica surface in an esterification reaction with the surface silanol groups of the support. The saturation coverage of these surface chromates is 2.4 Cr/nm^2 for a calcination temperature of 450°C . Superficial, not anchored, chromate slowly desorbs from the flat silica surface. Under crowded conditions a portion of the surface chromates also desorb if the calcination temperature is increased, while low Cr loadings ($>1 \text{ Cr/nm}^2$) are stable up to the highest calcination temperature in our experiments (730°C). The silica-bound surface chromates are monochromates exclusively, independent of the initial loading or calcination temperature.

Introduction

Highly dispersed chromium oxide supported on silica is an industrially important catalyst for ethylene polymerization. The well-known Phillips catalyst^{1,2} produces roughly one-third of the world supply of linear high-density polyethylene. It consists of less than 1 wt % Cr, impregnated commonly as an aqueous solution of CrO_3 or Cr(III) salts on high surface area silica ($\pm 300 \text{ m}^2/\text{g}$), which corresponds to about 0.4 Cr/nm^2 only. The catalyst is activated through calcination in dry air or oxygen and polymerizes ethylene, e.g., in a loop reactor at 35 bar and 110°C in isobutane slurry (Phillips Process).

Despite continuous and extensive research for more than 40 years now, there is little understanding of the Phillips catalyst on a molecular level. The reason for this lies probably in the complex redox and coordination chemistry of chromium in combination with the heterogeneous silica surfaces. As a result the supported chromium may be present on the support in a mixture of different valences and coordination environments, depending on the exact preparation. The nature of the silica support (e.g., specific surface area, porosity, and concentration of surface hydroxyls), the Cr loading, the activation method (e.g., maximum temperature, heating rate, total calcination time, and calcination atmosphere), and further chemical treatments (e.g., reduction with C_2H_4 , CO, H_2 , or metal alkyls, temperature, etc.) all influence the chemical state of the supported chromium. Consequently, results obtained by different groups are difficult to compare, and there is still controversy about the state of the supported chromium species after activation.

There is a general consensus that during calcination the supported chromium can anchor to the silica support in an esterification reaction with the surface hydroxyl groups, yielding surface chromate(VI) species. The maximum amount of chromate that is anchored to the support is limited by the amount

of hydroxyls available and will decrease with increasing temperature (if lower valent chromium precursors have been impregnated, the chromium will be oxidized during the calcination). If a fully hydroxylized silica is used, the saturation coverage at 425°C is about $1.8\text{--}2.3 \text{ Cr/nm}^2$ and the excess chrome is converted to chromium(III) oxide.¹ The structure of the surface chromate, namely, the degree of polymerization, remained disputed in the literature over the years. Indirect evidence has been deduced from measuring the change in hydroxyl population upon binding of the chromium or by the reverse reaction, stripping of anchored chromium using hydrogen chloride.^{1,3–5} The general trend in these experiments is that chromate anchors to the silica surface initially as monochromate while high calcination temperatures and loadings encourage the formation of dichromates.

In the 1990s the molecular structure of anchored chromium on various supports has been intensively studied with spectroscopic techniques such as Raman or UV–vis spectroscopy.^{6,7} Again it is difficult to compare because the surface area of the substrate varies strongly and their hydroxyl population remains unknown. For silica supports both monochromate (on a precalcined Cab-O-Sil) and dichromate (on a precalcined sol–gel silica) have been found to be the main species after calcination. Again high chromium loading and calcination temperatures are believed to favor the formation of surface dichromates. However, these very conditions also favor the formation of Cr_2O_3 , which can also form surface chromates. This makes the assignment of surface dichromates questionable, since the employed techniques, Raman and diffuse reflectance UV–vis spectroscopy, do not discriminate between chromates on a silica or chromia surface.

Ultra-high-vacuum spectroscopic techniques are potentially very powerful for the desired microscopic characterization of catalysts in general, as they provide direct information originating from the atoms and molecules on the surface. To use these techniques at their full potential, we have chosen to prepare

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a flat model catalyst with a conducting structural support (Si[100]) covered with a thin film of amorphous silica.

Replacing the high surface area, nonconducting materials such as silica, alumina, and titania by their thin-film analogues offers several advantages.

With respect to X-ray photoelectron spectroscopy (XPS) and other surface spectroscopies the most obvious advantage is that the surface probed in the spectrometer is identical to the catalytic active surface in the reactor. This makes correlation between the catalytic activity and surface characterization straightforward. In addition the thin oxide support has sufficient conductivity to minimize the deleterious effects of sample charging on XPS, Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) measurements.

The active phase is deposited onto the model surface from a homogeneously thick evaporation layer, resulting in a homogeneous catalyst loading on the nanometer scale. The wide distribution of pore sizes in a silica gel results in equally large variation of catalyst loading and dispersion. The superior definition of the active phase on the model catalyst improves the resolution of, e.g., photoelectron peaks.

Our surface science model is prepared on flat silicon single crystals with (100) surface orientation, which are covered with a flat layer of amorphous silica. This support is impregnated with aqueous CrO_3 using the spin-coating technique,^{8–10} which gives control over Cr loading and mimics the conventional pore volume impregnation used in industry for high surface area silica gels. This model catalyst shows a realistic catalytic activity for ethylene polymerization.¹¹ The scope of this paper is to look at the calcination (activation) of the Phillips catalyst on a molecular scale, using our flat model catalyst and surface science techniques.

Experimental Section

Preparation of the $\text{Cr}_{\text{ox}}/\text{SiO}_2/\text{Si}(100)$ Model. The experimental details have been published in our first publication.¹² Briefly $\text{CrO}_3/\text{SiO}_2/\text{Si}(100)$ model catalysts with a Cr loading between 0.4 and 10 Cr/nm^2 were prepared from aqueous CrO_3 (0.4–10 mmol/l) using spin-coating impregnation at 2800 rpm in dry nitrogen. The samples were calcined in a homemade preparation chamber that is directly connected to a VG-Escalab 200 spectrometer. Heating occurred stepwise in 100 K steps starting at 150 °C up to the desired calcination temperature. Each plateau was held for 1/2 h to allow thermal equilibration of the reactor.

XPS. XPS measurements were done with a background pressure of 5×10^{-10} mbar using an aluminum anode (Al $\text{K}\alpha = 1486.3$ eV) operating at 510 VA. Chromium(VI) oxide decomposes rapidly (within a few minutes) when exposed to X-rays. To minimize the effect of this degradation, individual scans of the Cr 2p were added until the damage became visible in the spectra. All binding energies are referred to the Si 2p at 103.3 eV (SiO_2) to correct for charging (<1 eV). Intensities are normalized to the total Si 2p area.

SIMS. SIMS was performed in a VG Ionex system equipped with a VG 12-12S quadrupole mass spectrometer and a VG FAB61 fast atom bombardment electron impact source. The base pressure of the analyzing chamber was 1×10^{-9} mbar. Samples were transported to this separate chamber using a sealed transfer vessel. A 5 keV Ar^+ ion beam was used for all spectra. Charge compensation by a low-energy electron flood gun was not necessary. The blank sample was measured using dynamic SIMS with a beam current density of about $3 \mu\text{A}/\text{cm}^2$, enhancing the secondary ion yield to ensure the detection of all Si_iO_x

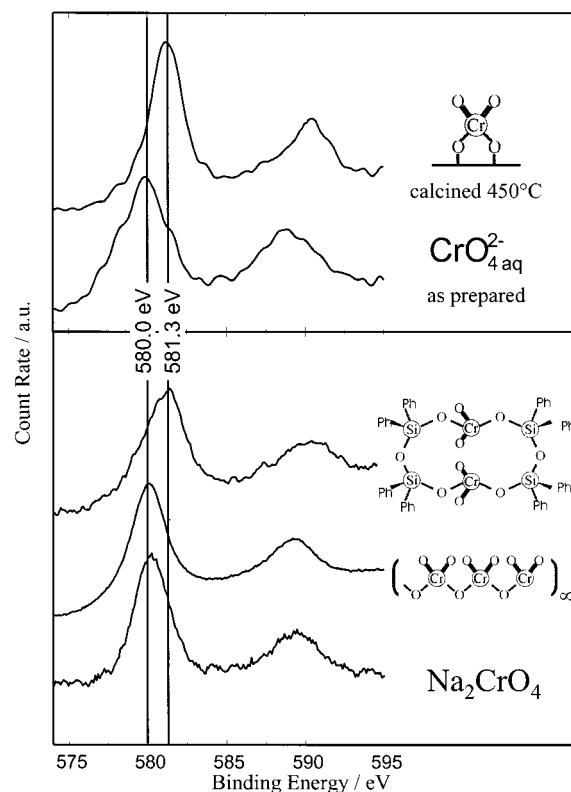


Figure 1. Shift in binding energy of the Cr $2p_{3/2}$ peak of a $\text{Cr}_{\text{ox}}/\text{SiO}_2/\text{Si}(100)$ model catalyst upon calcination in He/O_2 at 400 °C (top) and of CrO_3 or Na_2CrO_4 upon esterification to a siloxanediol (bottom).

fragments. Spectra of the Cr-loaded samples were taken under quasi-static conditions, applying beam current densities of approximately 50 nA/cm^2 to avoid rapid surface damage. The target bias was adjusted for maximum intensity of mass 100 (CrO_3^-) and 136 (Si_2O_5^-) signals in negative SIMS. The displayed spectra are normalized to the 136 amu signal.

Rutherford Backscattering Spectrometry (RBS). Samples for RBS were prepared in a quartz tube reactor described in ref 11. RBS spectra were measured with an incident beam of 2 MeV He^+ , produced with the AVF cyclotron at the Eindhoven University of Technology.¹³ Details concerning beam optics and detectors have been published in ref 14. The overall energy resolution was measured to be 22 keV. We adopted a scattering geometry with the incoming beam directed 5° from the surface normal and a scattering angle of 150° . We assume that the cross-sections are accurate within 4%.

Results and Interpretation

XPS. The X-ray photoelectron spectra in Figure 1 show the Cr 2p emission of $\text{Cr}_{\text{ox}}/\text{SiO}_2/\text{Si}(100)$ models and of three Cr(VI) references. After spin-coating impregnation of 1 CrO_3/nm^2 , the Cr 2p maximum appears at 580.0 eV, the same binding energy that we measured for bulk CrO_3 or alkali-metal chromates. Upon calcination at 450 °C the binding energy increases to 581.3 eV. This binding energy is in excellent agreement with the 581.6 eV (with Si 2p = 103.5 eV) measured by Merryfield et al.¹⁵ for a 1.1 wt % Cr/SiO_2 (0.42 Cr/nm^2) catalyst calcined in dry air at 650 °C. Moreover, we measured a siloxane ester of chromic acid ($[\text{CrO}_2(\text{OSi}(\text{C}_6\text{H}_5)_2\text{OSi}(\text{C}_6\text{H}_5)_2\text{O}]_2$)¹⁶ as a reference for surface chromium(VI) esters, which turned out to have the same Cr $2p_{3/2}$ binding energy as the anchored chromate(VI) on silica. Thus, we conclude that the shift in Cr $2p_{3/2}$ binding energy proves the anchoring of Cr to our $\text{SiO}_2/\text{Si}(100)$

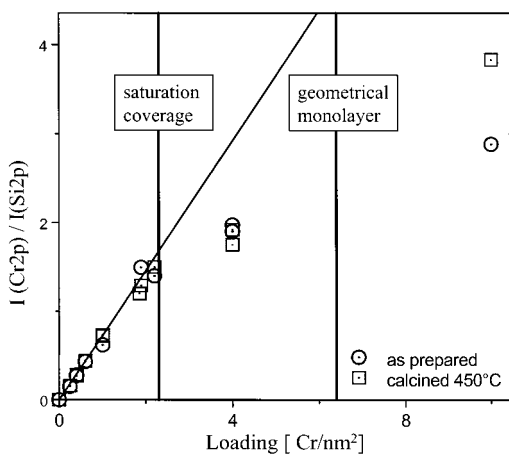


Figure 2. The normalized Cr 2p intensity grows linearly with increasing loading up to a saturation coverage of 2.3 Cr/nm² both on the impregnated catalyst and after calcination at 450 °C, indicating molecular dispersion of the deposited chromium at low loadings.

model support upon calcination. The high binding energy of surface chromate is a unique feature of the silica support, whereas chromate on other oxidic supports such as Al₂O₃¹⁷ or SnO₂¹⁸ shows Cr 2p_{3/2} maxima close to 580 eV.

The intensity of the Cr 2p emission for a given chromium loading is a measure of the dispersion of Cr on the silica surface. Figure 2 shows the intensity of the Cr 2p emission as a function of the chromium loading. For low loadings both the hydrated (as spin-coated) and the dehydrated (calcined at 450 °C) catalysts show the expected linear correlation indicative of molecular dispersion. The extreme solubility of chromium trioxide in water prevents the formation of particles on the hydrated catalyst; after calcination the chromium is expected to anchor to the support, which ensures molecular dispersion. Indeed, the molecular dispersion of the calcined catalyst ends at about 2 Cr/nm², which is in nice agreement with the 1.8–2.3 Cr/nm² reported by McDaniel for fully hydroxylized silicas.¹ While on high surface area silicas the superficial chromium is converted to Cr₂O₃, the XPS shows a different behavior for our flat model catalyst as illustrated in Figure 3. Model catalysts with 4 Cr/nm² initial loading are calcined at 450 °C. The hydrated catalyst (after spin-coating impregnation) shows a broad Cr 2p emission with a Cr 2p_{3/2} peak at 580 eV. After 5 min at 450 °C the Cr 2p_{3/2} peak has split into two components with a peak maximum at 581.0 eV (assigned to surface chromates) and a shoulder at about 578 eV (assigned to reduced chrome clusters). After 30 min of calcination at 450 °C the low binding energy shoulder has disappeared and the surface chromium peak has shifted toward 581.4 eV, indicating that the catalyst now features only chromate species anchored to the silica support. The surface area or the Cr 2p emission corresponds to 2.3 Cr/nm², implying that 1.7 Cr/nm² is no longer detectable with XPS. Increasing the calcination temperature results in a further decrease of integrated Cr 2p intensity (Figure 4), whereas the peak shape and position remain unchanged. The same peak shape and position are found for all samples measured in our experimental window (loading 0.4–4 Cr/nm², calcination temperature 450–730 °C), meaning that XPS detects only one type of anchored chromium on our model catalyst. The apparent loading (determined from the integrated Cr 2p intensity) of a series of catalysts with varying initial loading is plotted as a function of calcination temperature in Figure 5. While at high initial loadings the Cr 2p intensity decreases with increasing calcination temperature, at low initial loadings the Cr 2p intensity remains constant. In our view the most probable explanation for these observations is that surface

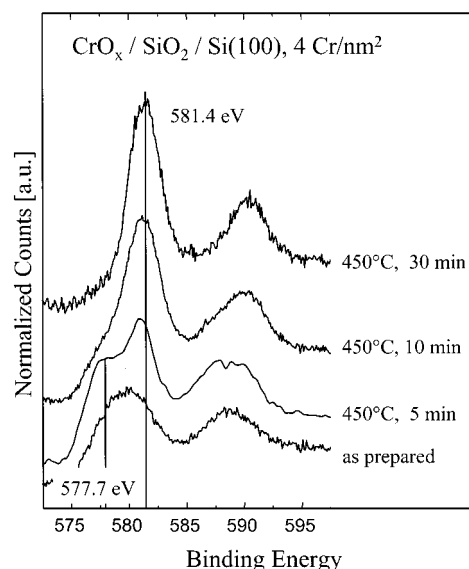


Figure 3. Upon calcination at 450 °C the Cr 2p emission of a catalyst with 4 Cr/nm² impregnated loading splits into two components: One at 577.7 eV is assigned to Cr₂O₃ clusters, which disappears with increasing calcination time. Simultaneously the other peak increases in intensity and moves toward 581.4 eV. It is assigned to chromate anchored to the silica surface. After 30 min only 2.4 Cr/nm² remains detectable with XPS.

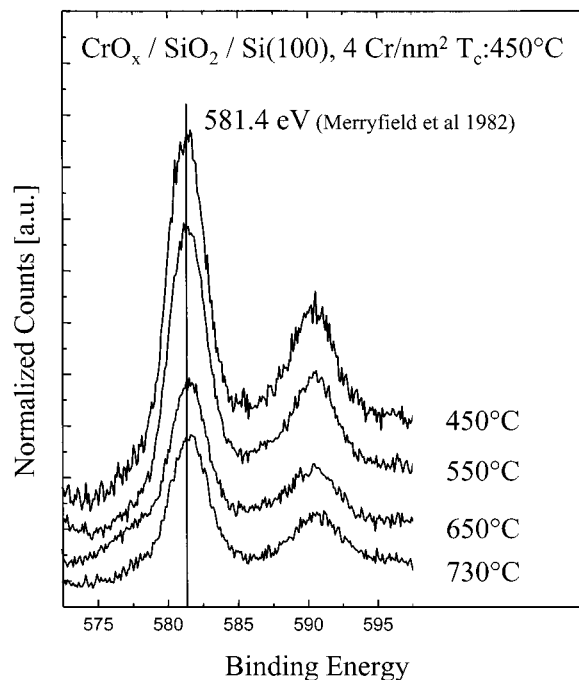


Figure 4. Cr 2p spectra of model catalysts with an initial loading of 2 Cr/nm². Increasing the calcination temperature leads to a further decrease in intensity to 1 Cr/nm² after 730 °C, while the peak shape and position remain constant. We attribute the decrease of Cr 2p intensity to desorption of chromate.

chromates can desorb from crowded silica surfaces and from the surfaces of chromium oxide clusters.

RBS. Rutherford backscattering is used to clarify whether chromium really desorbs from the silica support upon calcination as it allows us to quantify the total amount of chromium on our model catalyst regardless of dispersion. A model catalyst wafer was loaded with 10 Cr/nm². One piece was measured as prepared, a second after calcination at 550 °C. A third piece was placed parallel to a blank silica wafer at about 1 mm distance, and both were also calcined at 550 °C. The RBS

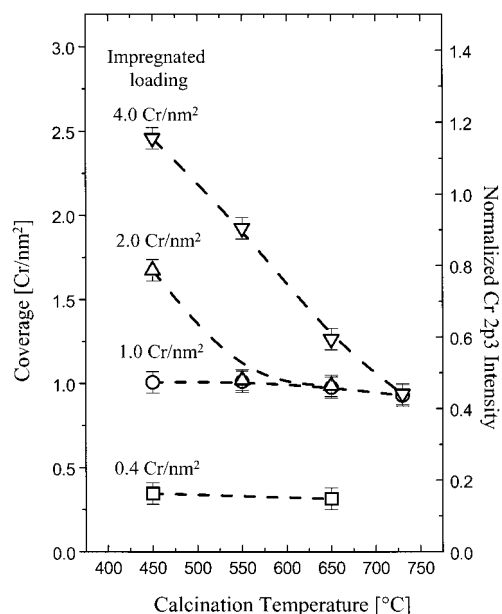


Figure 5. Leftover Cr coverage for different impregnated loadings and calcination temperatures. Desorption of chromate during thermal activation is most pronounced for high initial loadings and for high calcination temperatures. Low loadings (below 1 Cr/nm²) are unaffected.

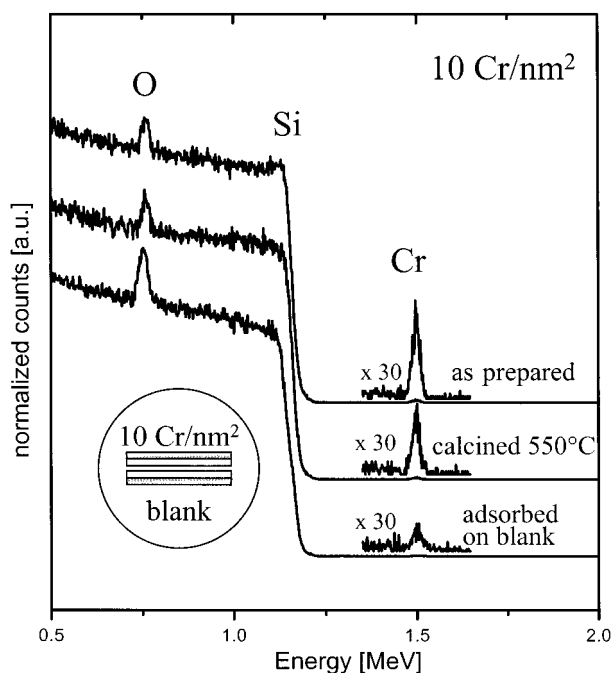


Figure 6. RBS proves that chromate can indeed desorb from the model catalyst during thermal activation. A wafer with 10 Cr/nm² loading features 7.0 Cr/nm² after calcination at 550 °C. The desorbing chromate readily readsorbs on an empty silica surface placed opposite the loaded wafer.

spectra shown in Figure 6 show the hydrated, calcined, and initially blank silica wafer (top to bottom). Obviously the chromium-loaded wafer has lost some of its chromium loading through desorption. A large portion of the desorbed chromium can be found back on the blank silica wafer, implying that the chromium has a very high sticking probability. While the formation of volatile high-valent oxides is common for molybdenum and tungsten, chromium(VI) oxide is much less stable. Thermodynamically (bulk) CrO₃ decomposes to α -Cr₂O₃ below 200 °C even in an oxygen atmosphere. However, calcination at higher temperatures leads to formation of mobile surface

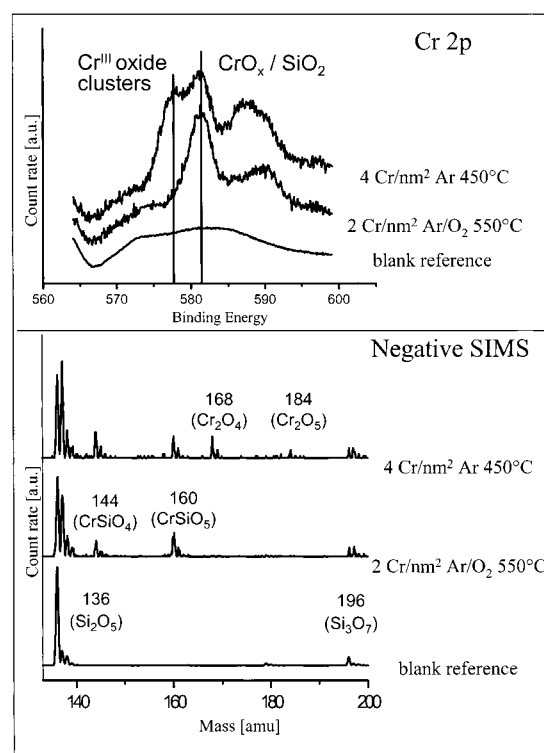


Figure 7. Cr 2p spectra and negative SIMS spectra of two model catalysts and a blank reference. The blank (bottom) shows only Si_xO_y fragments; on a chromium-loaded catalyst Si_xCr_yO_z fragments appear after thermal activation (Ar/O₂). If desorption of chromium is made impossible (in oxygen-free argon), also Cr₂O_x clusters can be detected. In combination this is strong evidence that chromate anchors to the silica surface as a monomer (see the text).

chromates (on the Cr₂O₃ cluster or crystallite surface).^{19,20} When physical mixtures of bulk chromium compounds and empty support are calcined above 500 °C, surface chromate can be detected on the previously unloaded support.²¹

While Jozwick et al.²¹ believe that redispersion of chromium on a support surface or from bulk oxide onto a support surface occurs via surface diffusion or surface wetting, Haber et al.²² favor transport via gaseous CrO₃. It is still possible that surface diffusion plays an important role in the redispersion of chromium on silica; however, our experiments show that transport through the gas phase is also significant.

SIMS. SIMS was used to elucidate the structure of the surface chromate, which is anchored to the silica surface. Only this chromate is a precursor of the active site for ethylene polymerization as bulk chromium compounds fail to show any activity. Figure 7 shows the XPS and SIMS spectra of two model catalysts and a blank reference. One catalyst has been prepared as the standard catalyst for our polymerization test: initial loading 2 Cr/nm², calcination with maximum 550 °C in 20% oxygen/argon. The Cr 2p emission of the catalyst shows as expected only one signal for anchored chromate. The second catalyst has an initial loading of 4 Cr/nm² and is heated to 450 °C in the absence of oxygen. This pretreatment leads to a catalyst with both anchored chromate and reduced chromium as the loading exceeds the saturation coverage of the silica support. The XPS spectrum shows a Cr 2p^{3/2} peak at 581.4 eV with a pronounced shoulder at about 577.7 eV close to the 577.6 eV found by Merryfield et al.¹⁵ for highly dispersed chromium-(III) oxide on silica. The negative SIMS spectrum of the blank wafer (calcined at 550 °C) (bottom) shows only two fragments at 136 and 196 amu, which we assign to Si₂O₅⁻ and Si₃O₇⁻, respectively. The calcined catalyst (2 Cr/nm², O₂/Ar 550 °C)

shows two additional fragments with masses 144 and 160 amu; we identify these as CrSiO_4^- and CrSiO_5^- . The second catalyst (4 Cr/nm², Ar 450 °C) shows again two additional fragments at 168 and 184 amu assigned as Cr_2O_4^- and Cr_2O_5^- . Note that the chromium-loaded catalysts also show a strong signal at 137 amu ($\text{Si}_2\text{O}_5\text{H}^-$) indicative of residual surface hydroxyls. This mass is absent on the pure silica because the spectra have been obtained with a much higher ion current to detect all possible Si_xO_y fragments, which results in rapid removal of the surface atoms.

The key observation is that the calcined catalyst, which features exclusively surface chromates, shows only $\text{Cr}_1\text{Si}_1\text{O}_x$ fragments. Yet, on the second sample, where a part of the chromium was forced to form clusters, Cr_2O_x fragments are easily detectable. In our view this is strong evidence that chromate can only anchor to the silica surface as a monomer. If dimeric species were formed on the silica surface, they would have been detected with SIMS.

Discussion

A $\text{CrO}_x/\text{SiO}_2/\text{Si}(100)$ model catalyst prepared by spin-coating impregnation from aqueous chromic acid has been studied using XPS, SIMS, and RBS, aiming at a molecular description of the calcination process of the Phillips catalyst. In many ways our model catalyst behaves as its industrial counterpart. Upon calcination the supported chromate forms surface esters consuming surface hydroxyl groups of the silica support. The saturation coverage of chromate, which can be anchored to the silica support in such a fashion, depends on the amount of available surface hydroxyls and decreases with calcination temperature. However, unlike on porous high surface area silicas, we do not observe the transformation of excess chromate to Cr_2O_3 at temperatures above 450 °C on our model catalyst. Instead it desorbs from the silica surface (note that if a second surface is nearby, most of the chromium will readsorb there). As a consequence, with calcination above 450 °C we prepare catalysts which expose only silica surface—no chromium clusters—and all chromium we observe using XPS and SIMS is anchored to surface silanols. All Cr_2O_3 -free catalyst showed the same $\text{Cr}2p_{3/2}$ binding energy at 581.4 eV, which we assigned to monochromate species, on the basis of our SIMS findings.

In our earlier publication²³ we presented XPS data for a series of model catalysts calcined at 400 °C. We observed anchored chromate at low loading. Upon increasing loading, a shoulder at low binding energy grew, which we assigned to Cr_2O_3 clusters. Parallel to the development of the Cr_2O_3 clusters, we observed a downward shift of the “anchored chromate” signal. We explained this downward shift as a result of the superposition of two anchored chromate species, assigning them to mono- (581.4 eV) and dichromate (580.6 eV). While we cannot completely rule out a silica-bound dichromate species after low-temperature calcination (400 °C), we believe now that the second chromate species is actually bound to the Cr_2O_3 surface. Prolonged calcination at 450 °C leads to the disappearance of the Cr_2O_3 clusters and simultaneously to an upward shift of the “anchored chromate” peak toward its final value, 581.4 eV. Surface chromates on Cr_2O_3 might also explain other sightings of anchored dichromate in the literature such as Weckhuysen et al.^{6,24}

The silica-bound monochromate is the only detectable chromium species on our standard polymerization catalyst^{11,25} after calcination at 550 °C with an initial loading of 2 Cr/nm². This catalyst shows a respectable catalytic activity, while bulk chromium oxide is notoriously inactive for ethylene polymer-

ization. Our catalyst polymerizes ethylene at 160 °C and atmospheric pressure to yield polymer films of up to 500 nm thickness with a pseudoturnover frequency of 2.5 s⁻¹ (molecules of ethylene per atom of chrome per second).

Conclusions

Studying the calcination behavior of chromium oxide supported on silica using a flat silica substrate and a combination of complementary surface science techniques is a powerful way to monitor the bonding of the supported chromium during calcination, the necessary pretreatment to activate the catalyst for ethylene polymerization. The model catalyst mimics the industrial Phillips catalyst close enough to claim relevance; it starts out as a 2-dimensional aqueous solution of hydrated chromate that anchors to the silica surface, consuming surface silanol groups. We profit from its defined surface and its conductivity. The most significant difference between the surface science model and its high surface area match is the absence of pores or internal surface. This feature greatly facilitates the qualitative and quantitative interpretation of our data; however, if desorption and readsorption of the supported chromium come into play, it will immediately disappear from the model catalyst, taken away by the gas stream, while on porous silica this process is obscured by readsorption. This will lead to differences between the surfaces of the model and industrial catalysts, which have to be taken into account to avoid oversimplified extrapolations. On the other hand, this also gives us an opportunity to look at desorption and readsorption as a mechanism for redispersion of the active phase on the silica surface or between support particles.

We indeed observe chromate desorption from the model catalyst, in particular at high Cr loading (far above the nominal Cr loading of the Phillips catalyst) and at high calcination temperatures. Chromate desorbs most easily from small chromium oxide clusters and from crowded silica surfaces, while isolated surface chromates (on the silica surface) are stable during high-temperature calcination. Inside the pores of a high surface area silica gel, the chromate can readily readsorb and will eventually produce more stable Cr_2O_3 crystallites. The silica-bound monochromate, however, forms the active sites during ethylene polymerization.

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