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An XPS Study of the Phillips Cr/Silica Polymerization Catalyst

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The Phillips Cr/silica polymerization catalyst has been examined by means of X-ray photoelectron spectroscopy and chemical methods, and the results have been compared to activity measurements from a high-pressure autoclave. Only Cr(VI) was found after O_2 at 600–800°C, but CO at 350°C cleanly reduced this to Cr(II). On contact with ethylene, which increased the binding energy slightly, the divalent material became an active polymerization catalyst. Reducing Cr(VI) with ethylene produced similar results. This indicates Cr(II) as the active precursor and that its electron density is decreased by the ethylene.

INTRODUCTION

Although an unusually wide variety of researchers have studied the Cr/silica system for over 25 years, opinions of the active site on the Phillips polymerization catalyst are still equally diverse. In fact, every valence from Cr(II) to Cr(VI) has been proposed as the active site, either alone or in combination with another valence. The confusion has been compounded by the simultaneous presence of several oxidation states, and by the fact that most workers studied preparations and used conditions bearing little resemblance to the highly active commercial systems.

The original catalyst (*1*) consisted (and still does) of hexavalent chromium, but the discoverers quickly realized that reduction occurred on contact with ethylene, leaving a lower oxidation state as the active species. Since incomplete reduction leads to a strong and sharp ESR signal from a small presence of Cr(V), it was perhaps inevitable that this signal would be studied almost to the exclusion of other techniques, including polymerization itself (*2–4*). Many workers, not surprisingly, found a correlation between the signal intensity and polymerization activity (usually measured by vacuum line techniques rather than the high-pressure commercial autoclaves), and thus concluded that Cr(V) was the active species (*5–16*). Others found no correlation (*17*), or an inverse one, concluding that Cr(IV) must be the correct valence (*18*). Still others decided that the active site (*19–23*), and also the ESR signal (*21*), was not an intermediate valence but a combination of Cr(III) and Cr(VI).

Finally, Krauss and Stach (*24–26*), and others (*27–31*), actually measured the average oxidation state by a pulse titration technique. They found that reduction stopped when the average valence approached 2.0, that this catalyst was highly active, and that it had no Cr(V) ESR signal. Although the evidence for Cr(II) was direct, and the catalysts used were like those used commercially, the issue has apparently not been settled because the most recent reports now lean toward Cr(III) as the active species (*32, 33*). This is based on the finding that the catalyst's activity passes through a maximum as the severity of the reduction is increased. This "optimum reduction" argument for Cr(III) has usually been applied without knowledge of the average oxidation state, and not under commercial conditions. Indeed, the most convincing evidence that Cr(III) can polymerize ethylene has come from Kazanski (*34*), a former advocate of Cr(V) (*11*), who found that trivalent salts impregnated on silica, such as $CrCl_3$, and calcined under vacuum, were active.

Notably absent in this deluge of speculation about valence has been some concrete

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data from X-ray photoelectron spectroscopy. For although two XPS studies of Cr/silica have been reported (*35, 36*) many questions still remain concerning the commercial catalyst, because both works examined preparations so highly loaded with CrO_3 that the dominating feature turned out to be the thermal decomposition of bulk CrO_3 into bulk Cr_2O_3. For example, Cimino *et al.* (*35*), investigating Cr densities as high as 6.3 Cr/nm^2, reported XPS signals from Cr(VI) and Cr(III), whereas at a more typically commercial loading of 0.6 Cr/nm^2 almost no signal was found. Similarly, Best *et al.* (*36*) reported Cr(VI) and Cr(III) signals from a preparation having over 6 Cr/nm^2. On reduction in carbon monoxide at 300°C some evidence for Cr(II) was also seen in the XPS, but no attempt was made to correlate this signal with the polymerization activity or to examine it in the presence of ethylene.

In this study we have used XPS to characterize the commercial Cr/silica polymerization catalyst. Loadings were kept at a low 0.4 Cr/nm^2 to cut down on extraneous signal, and the choice of silica and calcining conditions represent near optimum activity based on years of commercial experience. Samples were also titrated with pulses of CO or O_2 to determine the average oxidation states and this information was correlated with activity measurements in a high-pressure autoclave.

EXPERIMENTAL

Materials

The catalyst studied in this investigation was typical of those used commercially in the Phillips process for ethylene polymerization. Davison 952 microspheroidal silica, having a surface area of about 280 m^2/g and a porosity of 1.6 cm^3/g, was impregnated with an aqueous solution of chromium (III) acetate. After being dried on a hot plate with stirring, the blue-green catalyst contained 1.1 wt% chromium (0.42 Cr/nm^2).

To activate the catalyst, about 10 g was fluidized in a dry air or oxygen stream for several hours at 800–900°C, or whatever temperature was desired. A quartz tube was used with a sintered glass disk to support the sample, which was raised to temperature at 400°C/hr with the flow rate through the bed at 1 cm/sec. Gases were predried through activated alumina or, where possible, CO-reduced Cr/silica.

To make samples containing only Cr(VI), the raw catalyst was calcined in dry oxygen at 600–900°C for 2–5 hr. Subsequent reduction in dry carbon monoxide at 300–400°C for 30–60 min resulted in near quantitative conversion to Cr(II). Samples containing only Cr(III) were obtained by calcining the raw catalyst in N_2, or wet N_2; sometimes $CrCl_3$/silica was substituted for the acetate preparation according to the method of Kazanski and co-workers (*34*).

For reference materials in the XPS work the following commercially available compounds were used: $CrF_3 \cdot 3.5H_2O$ and Cr_2O_3 from Matheson, Coleman and Bell; CrO_3 from Mallinckrodt; and CrF_2 (90%) and chromium metal foil from Ventron. The 0.02-mm foil was sputtered with argon before the spectrum was taken.

Pulse Titration Studies

To determine the average oxidation state after reduction, oxidized samples containing only hexavalent chromium were titrated with pulses of carbon monoxide at various temperatures. A helium stream, purified through a column of CO-reduced Cr/silica pellets, passed through the sample and into an HP-5750 gas chromatograph equipped with TC cell and disk integrator. At 300–800°C each CO pulse (or a portion of it) was converted to CO_2, which could be separated from CO by a silica gel column installed downstream from the sample. Usually no more CO_2 evolved after the third or fourth pulse. Titration back to Cr(VI) provided a secondary check of the oxidation state.

Polymerization

Activity tests were conducted at 100 to 110°C in a 2-liter stirred autoclave. A pressurized jacket filled with boiling alcohol held the internal temperature of the reactor constant to within 0.5°C. First, about 0.05 g of the catalyst was charged under dry N_2, then 1 liter of liquid isobutane diluent (vapor pressure = 250–300 psig), and finally ethylene was supplied on demand at 550 psig until about 250 g of solid polyethylene had been made. Under these conditions the polymer does not go into solution but remains as a slurry. The rate of polymerization was followed by monitoring the ethylene flow with a calibrated rotameter. Isobutane and ethylene stock were Phillips polymerization grade, further prepurified through activated alumina and, in the case of isobutane, through a CO-reduced Cr/silica column.

XPS Instrumentation

Two electron spectrometers were used for the XPS studies: Perkin–Elmer instruments Phi-548 and Phi-550, with Mg$K\alpha$ radiation (1253.6 eV). Both were interfaced to a Hewlett–Packard 21MX computer for data acquisition and manipulation. The instruments were operated at about 2×10^{-9} Torr, with the sample being introduced from a prechamber at 1×10^{-7} Torr. Since samples were typically charged only about 4 eV, no attempt was made to eliminate charging. The reported binding energies have been referenced to Au $4f(7/2)$ as 84.0 eV. Referencing was performed after a complete set of spectra had been obtained. A thin film of Au was evaporated onto the sample and another set of spectra was then taken. On the supported samples binding energies were referenced to the Si $2p$ peak at 103.5 eV, as determined relative to gold.

XPS Sample Pretreatment

After being calcined in a fluidized bed, as has already been described, most samples were mounted in the spectrometer by means of double-faced sticky tape. This was accomplished in a glove box filled with dry argon where the catalyst was dusted into the mount and then sealed in a prechamber connectable to the instrument (*37*). In this way the sample was introduced into the spectrometer without being exposed to the atmosphere.

Another procedure was also used in a few cases. The virgin catalyst was hydraulically pressed into a 6-mm opening on the mount. Then once in the antechamber, the disk and mount were treated in flowing gas before being evacuated, and introduced directly into the spectrometer. Of course this second method would be expected to be the cleaner of the two, but no difference in the spectra was noticed.

RESULTS AND DISCUSSION

In past studies of valence on the Cr/silica system one difficulty has often been the simultaneous presence of several oxidation states. To avoid this problem we tried to prepare three "pure" samples, that is, where all of the chromium was in one valence, Cr(VI), Cr(III), or Cr(II). This allows for cleaner XPS data and more direct interpretation of polymerization results.

Polymerization with Cr(VI)/Silica

By calcining Cr/silica in dry O_2 at 800–900°C, a bright orange catalyst resulted in which all of the chromium (within experimental error) was found, by titration with Fe(II) to the Ferroin endpoint, to be in the hexavalent state. This material was very active for the polymerization of ethylene in the high-pressure autoclave at 100–110°C, producing several thousand grams of polyethylene per gram of catalyst within an hour. Figure 1 plots the rate of the polymerization reaction against time for a typical run. The catalyst was not active immediately but gradually came alive after a dormant period, or induction time (*38, 39*), which could last from a few minutes to over an hour depending on conditions. Then the

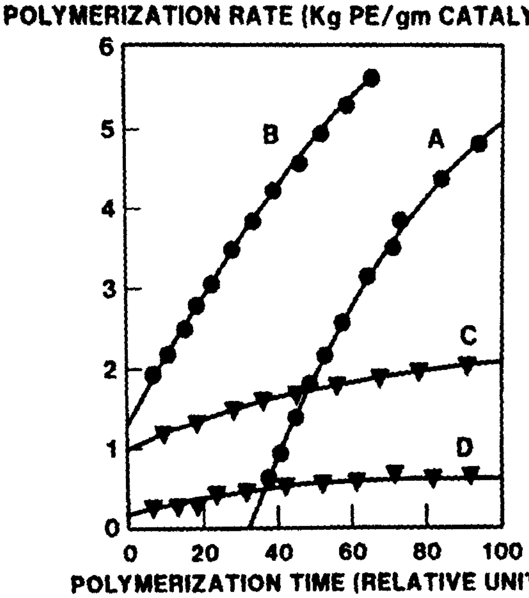


FIG. 1. Polymerization rate of Cr/silica calcined in (A) O_2 at 850°C, (B) then CO at 350°C, (C) then CO at 500°C, (D) then CO at 700°C. Run at 105°C, 550 psig, in isobutane.

rate increased during the next hour or two before finally leveling off or even slowly declining.

The induction time became shorter with increasing calcining temperature, reactor temperature, and ethylene concentration (*38, 39*). The optimum calcining temperature was 900°C, just short of sintering. Below 900°C the induction time became longer, until by 500°C the polymerization rate had declined by an order of magnitude. As the reactor temperature was decreased from 100°C the induction became longer, until by about 50°C the activity became negligible in comparison. Increasing the polymerization temperature to 150°C (by putting the polymer into solution using a cyclohexane solvent) eliminated the induction time and also the gradual rise in activity. Instead the rate held almost constant during the run.

That catalysts initially containing only Cr(VI) were active does not imply that the active center was hexavalent because the chromium is known to be reduced by the ethylene (or perhaps even by the solvent). Formaldehyde has been identified as the product (*27*). The induction time probably corresponds to the initial reduction of Cr(VI) to the lower-valent active species, or perhaps to the desorption of by-products (*38–40*). This explains the extreme dependence of the activity on temperature and pressure. This interpretation agrees with that of Zakharov and Ermakov (*40*) who found that the number of active sites also increases with time, paralleling the increase in activity.

Polymerization with Cr(II)/Silica

This reduction from Cr(VI) to the lower-valent active form can also be accomplished outside of the reactor using reducing agents other than ethylene. For example, if the Cr(VI) catalyst described above is treated with dry carbon monoxide at about 350°C, and then cooled in argon, a pale green catalyst is obtained which turns light blue on exposure to N_2 indicating a weak chemisorption. As would be expected this material has an improved and less variable activity for ethylene polymerization.

Many previous workers (*24–31*) have examined this CO-reduced catalyst and those who have measured the average oxidation state agree that it quickly approaches 2.0. Our own experiments have also confirmed this point, not by titration with CO which is slow at 350°C compared to the pulse lifetime, but by titrating the CO-reduced catalyst with pulses of oxygen. At 500°C and above the reduction becomes rapid enough to measure directly by pulse titration, but the average oxidation state does not decrease further. Since Cr(I) or Cr(0) are unlikely under these conditions (*30*), this suggests that the chromium is converted almost quantitatively to Cr(II). And because at least about 15% of the chromium (*10*) on this catalyst is thought to polymerize ethylene, one concludes that the Cr(II) form is active.

Figure 1 also shows the kinetics of polymerization for Cr(II)/silica. Actually the maximum rates observed were not much different from that of its Cr(VI) precursor and the polymer obtained was also very similar. However, the induction time was completely eliminated. The gradual increase in rate was again noticed, and even the slope was approximately the same. Unlike the Cr(VI) catalyst, however, the CO-reduced material did not lose much activity as the reactor temperature was decreased. Even at 25°C it had no induction time and good activity.

These facts strongly suggest that the induction time corresponds to reduction of Cr(VI) by ethylene, probably to Cr(II). The gradual increase in rate may be due to a slow initiation reaction; that is, the first ethylene molecule may be incorporated more slowly than succeeding ones. These observations emphasize the difficulty of comparing the activities of different Cr/silica catalysts. Often researchers unfamiliar with the complexity of these kinetics have drawn conclusions from single experiments conducted at low pressure (<1 atm) and low temperature (25°C). In our experience, it is unreliable to make such comparisons merely on the basis of the initial rate of polymerization, particularly if the ethylene also serves as a reducing agent.

The dependence of the activity of the catalyst on its initial calcining temperature, as was observed with the Cr(VI)/silica samples, was again found with Cr(II) samples. For example, samples calcined in O_2 at 800°C, then in CO at 350°C, were considerably more active than those calcined in O_2 at 400°C, then in CO at 350°C. This suggests that the phenomenon is not related to reduction of the chromium. Instead we believe that the hydroxyl population on silica somehow interferes with polymerization (*47*).

Polymerization with Cr(III)/Silica

For comparison, an attempt was also made to prepare a catalyst containing only Cr(III). Cr(VI)/silica is easily reduced to the trivalent form by a number of reducing agents, particularly if moisture is present or formed (*28–31*). However, the reduction is rarely clean; Cr(VI) or Cr(II) or Cr(V) are usually also present (*34*). This makes it difficult to assign the activity to any one of these species. Therefore the method of Kazanski and co-workers (*34*) was used instead. That is, a trivalent chromium salt was impregnated onto the silica in the absence of air and then the preparation was calcined in N_2. $CrCl_3$ was chosen as the salt because the chloride anion is unlikely to oxidize or reduce the chromium during the calcining.

Two activations were made, one in N_2 to 300°C, and another in N_2 to 700°C. Titration with Fe(II) solution indicated no Cr(VI) on either sample. Titration with $AgNO_3$ indicated no chloride on the 700°C sample, but that about 15% still remained on the 300°C sample. Neither preparation produced any measurable amount of polymer when tested at 105°C. The 700°C sample was even tested again in the presence of an alkylating agent, but again no polymer resulted.

When a dead Cr(III) catalyst is obtained, one is never sure whether the lack of activity stems from the Cr(III) valence itself, or just a poor dispersion of the Cr compared to those catalysts described above, which were made by reducing the monodispersed surface Cr(VI). Therefore in the following experiments $CrCl_3$/silica was also treated with CO. The first experiment, done in the pulse reactor, confirmed that some trivalent Cr could indeed be reduced to the divalent form. A few pulses of CO at 600°C quickly dropped the average oxidation state to 2.5. In the second experiment, $CrCl_3$/silica was heated to 650°C in CO, cooled in N_2, and then tested for polymerization activity in the high-pressure autoclave. It produced 755 g polyethylene (PE)/g catalyst in a 90-min run in which the rate gradually increased. Thus either (1) the dispersion was not bad enough to kill the catalyst, or (2) reduction to Cr(II) itself causes a redistribution. These results are contrary to those reported by Kazanski and co-workers (*34*), who obtained the highest activity from Cr(III) and found a decline in activity upon reduction in CO.

Of course, had $CrCl_3$/silica been calcined in O_2, a much more active system would have been obtained due to the formation of monodispersed Cr(VI). Or conversely, had large crystallites of α-Cr_2O_3 formed, it would have been very difficult to either oxidize or reduce the chromium. As in the bulk (*48*), the formation of crystalline Cr_2O_3 on silica is favored by the presence of a trace of Cr(VI) to act as a flux.

In another experiment the silica support was calcined at 800°C to achieve the benefit of dehydroxylation, and then it was impregnated with anhydrous $CrCl_3$ in THF. After a mild calcining at 300°C in N_2 to remove the solvent, the sample was tested for polymerization activity in an autoclave. Again it had none.

Optimum Reduction

Sometimes researchers have noted that the activity of Cr(VI)/silica passes through a maximum as the catalyst is reduced either as a function of time or temperature (*14, 15, 32–34*). Beyond this maximum the activity dies as the reducing treatment becomes more severe, implying that the active species is some intermediate between Cr(VI) and Cr(II). This "optimum reduction" argument is indirect and has often been applied without knowledge of the average oxidation state.

We too have observed this behavior; it is illustrated in Fig. 1. As the Cr(VI)/silica catalyst (after O_2 at 850°C) was reduced in CO at progressively higher temperatures, its activity fell quickly until by 850°C it was only marginally active. For a half-hour reduction treatment the optimum reduction temperature was in the vicinity of 350°C. However, this optimum activity could not have been due to a change in oxidation state because it was nearly constant at 2.0.

Instead the effect may be due to rearrangement of the chromium, perhaps some form of clumping, rendering it less coordinatively unsaturated. The loss of coordinative unsaturation has been confirmed by Zecchina *et al.* (*28*) in chemisorption measurements in a static system, and again in these laboratories in a flow apparatus. Figure 2 shows the amount of CO chemisorbed when pulses were passed through the catalyst at −78°C. The catalyst had first been calcined in O_2 at 850°C, then reduced 1 hr in CO at the temperature indicated. After reduction at 300°C nearly two CO molecules were adsorbed per chromium, but as the reduction temperature was increased the chemisorption decreased until it reached less than 0.3 CO/Cr after reduction at 800°C. However, chemisorption of O_2 at −78°C, which was irreversible, held constant near 1.0 O_2/Cr at all reduction temperatures. This suggests an easy conversion back to Cr(VI), even at −78°C. The clumping was not severe enough to be detected by X-ray diffraction. The Cr(III)/silica samples prepared from $CrCl_3$ adsorbed only traces of CO.

XPS of Cr(VI)/Silica

Figure 3A shows the Cr 2*p* spectrum of a catalyst calcined in flowing dry air at 650°C

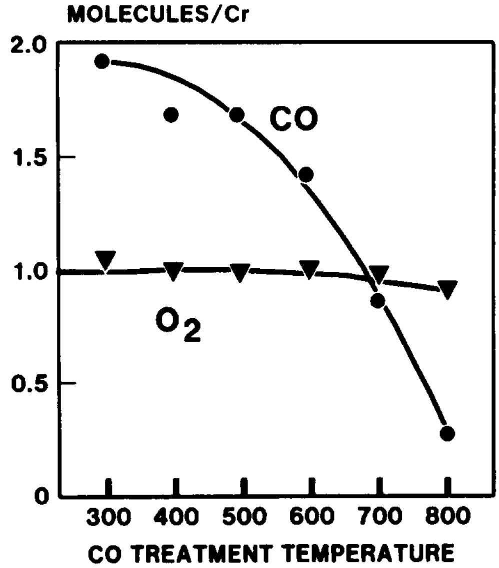


FIG. 2. Chemisorption at −78°C of CO or O_2 on Cr/silica calcined in O_2 at 850°C, then CO reduced at temperature shown.

for 1 hr before being introduced directly into the spectrometer. As in the polymerization studies, this treatment produced a bright orange catalyst in which all of the chromium was hexavalent. The spectrum was obtained quickly (in 30 min rather than the normal 2 hr) to minimize the gradual photoreduction which later became visible with prolonged exposure to X rays. Table 1 shows the results of this experiment. The binding energy of the Cr $2p(3/2)$ peak was found to be 581.6 eV and the spin orbit splitting was 9.0 eV. The intensity ratio of Cr $2p(3/2)$ to Cr $2p(1/2)$ was typical of hexavalent chromium. When the experiment was repeated with a chromium loading almost three times greater, but still below the saturation coverage, nearly identical results were obtained (Cr $2p(3/2) = 581.7$ eV).

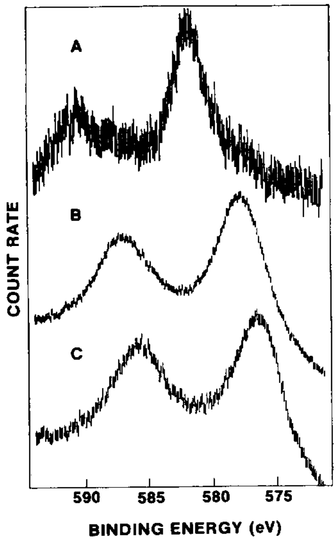


FIG. 3. X-Ray photoelectron spectrum of (A) Cr(VI)/silica, (B) Cr(III)/silica, (C) Cr(II)/silica.

This value is a full 1.3 eV higher than that reported by Cimino *et al.* (*35*) and by Best *et al.* (*36*) for Cr(VI)/silica. However, our findings for bulk compounds, such as CrO_3 and others, agree quite well with those reported by Cimino *et al.* (*35*) and others (*41, 42*). These data are summarized in Table 2. Therefore the discrepancy between Cr(VI)/silica binding energies is not just a matter of calibration. The most probable explanation is that their catalysts were so heavily loaded with CrO_3 (9 wt% Cr or 6.3 Cr/nm^2), that they obtained measurements on bulk CrO_3 rather than monodispersed surface Cr(VI). These loadings were far above the hexavalent saturation coverage (*49*). In contrast, this study usually employed the typical commercial loading of only 0.4 Cr/nm^2. Actually, such an increase in the binding energy is not unexpected when the chromium becomes isolated on the silica surface, since the contribution of extra atomic relaxation energy is lower than it would be in a CrO_3 lattice. The binding energies of other chromium species also exhibit similar shifts when they become supported. A similar effect has been observed for metals isolated in a silica lattice (*43*) and supported on polymer supports (*44, 45*).

XPS of Cr(II) and Cr(III)/Silica

XPS measurements were also made on the CO-reduced catalyst described earlier, that is, Cr(II)/silica. Since this catalyst is extremely sensitive to air, its pale blue

TABLE 1

X-Ray Photoelectron Spectroscopy of Cr/Silica Catalysts

Sample[a]	2p(3/2) peak			Spin orbit splitting (eV)
	Position[b] (eV)	Width[c] (eV)	Intensity[d] (eV)	
Cr(VI)/silica (O_2, 600°C)	581.6	3.7	2.7	9.0
Cr(III)/silica (wet N_2, 300°C)	577.6	4.9	2.7	9.5
Cr(II)/silica (O_2, 800°C; CO, 300°C)	576.6	5.0	2.8	9.6

[a] All three samples were started with Cr(III) acetate on silica, 0.4 Cr/nm^2.

[b] Binding energy.

[c] Full width at half-maximum.

[d] Surface coverage of Cr (Si 2p = 100). Includes corrections for photoionization cross sections. Chromium intensities were difficult to measure due to nonlinear background over the region.

color after introduction into the spectrometer by means of the glove box technique was a good indication that the transfer was accomplished without contamination. Figure 3C shows the Cr 2p doublet obtained, and again the binding energies and other values are tabulated in Table 1. The Cr 2p(3/2) peak was found at 576.6 eV.

To obtain the spectrum of Cr(III)/silica, the choice of which sample to study presented a problem. A poorly dispersed Cr(III)/silica would probably just resemble bulk Cr_2O_3, and thus not be of much interest for comparison to Cr(II)/silica. Therefore, to discourage the formation of large Cr_2O_3 crystallites, a low calcination temperature was chosen (300°C). However, this ruled out the $CrCl_3$/silica catalyst stud-

TABLE 2

X-Ray Photoelectron Spectroscopy of Bulk Chromium Compounds

Compound	Reference	2p(3/2) peak		Spin orbit splitting (eV)
		Position[a] (eV)	Width[b] (eV)	
CrO_3	This study	579.1	2.9	9.1
	Okamoto *et al.* (*42*)	580.3	2.8	9.1
	Cimino *et al.* (*35*)	579.9	1.6	9.0
	Allen *et al.* (*41*)	578.3	2.3	8.7
Cr_2O_3	This study	576.2	3.5	9.8
	Okamoto *et al.* (*42*)	576.6	3.6	9.8
	Cimino *et al.* (*35*)	576.8	3.0	9.6
	Allen *et al.* (*41*)	576.8	3.0	9.7
Cr metal	This study	574.4	2.8	9.3
	Okamoto *et al.* (*42*)	574.5	nd	9.1
CrF_3[c]	This study	579.4	3.7	9.9
	Okamoto *et al.* (*42*)	579.2	3.6	9.9
CrF_2[c]	This study	578.1	4.3	9.6

[a] Binding energies. Corrected to Au 4f(7/2) as 84.0 eV or C 1s as 285.0 eV.

[b] Full width at half-maximum.

[c] Composition verified by X-ray diffraction.

ied earlier because at 300°C some chloride still remained which would probably affect the binding energy. Instead we decided to use the same starting material studied in previous experiments, Cr(III) acetate on silica, only calcined in wet N_2 at 300°C. The wet N_2 was used to help hydrolyze away the acetate and, at the same time, to prevent it from reducing the chromium. After this treatment no evidence of residual acetate was found in the infrared spectrum of the catalyst, nor was any Cr(VI) present, nor did the sample have any polymerization activity. The X-ray photoelectron spectrum is shown in Fig. 3B and again the numerical data are tabulated in Table 1. The Cr $2p(3/2)$ peak was found at 577.6 eV.

Since, as we have seen, the binding energies of the supported chromium species cannot be compared directly to those of the bulk compounds, we have chosen to compare shifts in binding energies to determine the oxidation state on Cr/silica catalysts. From the data for bulk compounds in Table 2 we find a 2.9- to 3.7-eV difference between the oxides of Cr(VI) and Cr(III). To compare Cr(III) to Cr(II), we studied the bulk fluorides, CrF_3 and CrF_2, which show a shift of 1.3 eV. Although the absolute binding energies of fluorides would not be comparable to those of the oxides, the shifts should be typical. Thus on the supported catalysts one would expect a decrease in binding energy of between 4.2 and 5.0 eV as the valence decreases from Cr(VI) to Cr(II).

This behavior agrees quite nicely with that actually observed, which is summarized in Table 1. The total shift from Cr(VI)/silica to Cr(II)/silica was 5.0 eV. That from Cr(VI)/silica to Cr(III)/silica was 4.0 eV and that from Cr(III) to Cr(II) was 1.0 eV. The intensities of the three signals, also listed in Table 1, show that these three "pure" samples had about the same high dispersion of chromium on the silica. This is a good confirmation that none of the samples contained chromium in a "bulk" state. In contrast, the $CrCl_3$/samples exhibited a lower intensity (1.8–2.3) due probably to some clumping.

Addition of Ethylene

The X-ray photoelectron spectrum of Cr(II)/silica was also taken after exposure to ethylene. Since, as noted earlier, the catalyst has no induction time, it began to polymerize the ethylene vigorously on contact (1 atm at 25°C). In a commercial system several thousand grams of polymer would normally be produced per gram of catalyst before the reaction would be killed with oxygen, water, or perhaps alcohol. However, in this experiment the reaction was stopped by pumping out the ethylene after a productivity of only about 1 g/g. Otherwise the catalyst becomes hidden in the polymer.

Since a kill agent was not used, there is a possibility that the chromium still contained a live polymer chain, as has been reported by Krauss (*26*). However, this is by no means certain since the chain terminates on its own, possibly by β-elimination, to yield an α-olefin (*38, 39, 47*). This termination reaction is very important commercially because it determines the molecular weight of the polymer produced. The rate of the autotermination reaction at 100°C is several times per second per site. However, we know that as the temperature is decreased, the lifetime of the chain becomes longer, and at 25°C it is quite conceivable that it could exist long enough to be studied by XPS. Otherwise it would probably still be coordinated to the active site as an α-olefin.

The XPS scan of this catalyst, before and after addition of ethylene, is shown in Fig. 4. The ethylene caused a broadening and an increase in binding energy of 0.4 eV, that is, Cr $2p(3/2)$ was found at 577.0 eV. This indicates decreased electron density on the chromium and thus agrees with other data suggesting the chain is negative relative to chromium (*38*). Of course one would like to believe that this shift is due to a live polyethylene chain growing from each chromium. However, we must remember that

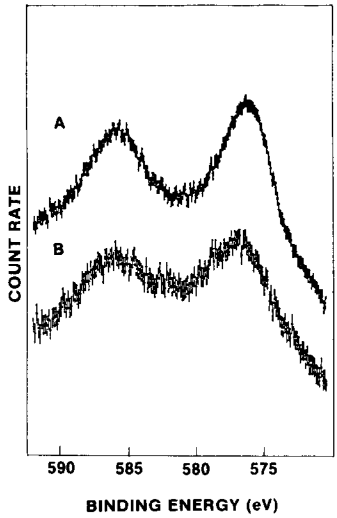


FIG. 4. X-Ray photoelectron spectrum of Cr(II)/silica (A) before, and (B) after exposure to ethylene.

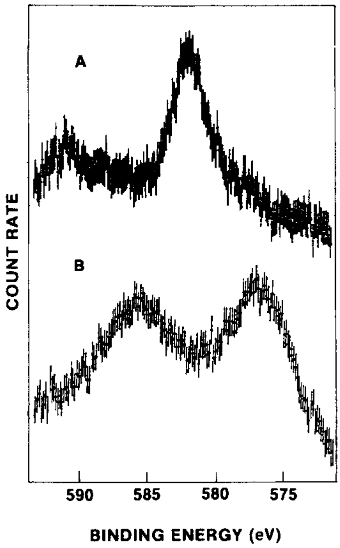


FIG. 5. X-Ray photoelectron spectrum of Cr(VI)/silica (A) before, and (B) after exposure to ethylene.

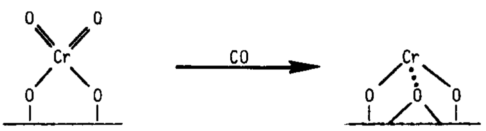
possibly only about 20% of the chromium might be active in polymerization (*38*), whereas all sites strongly chemisorb ethylene. Therefore the measured shift in binding energy may be due as much to simple chemisorption as to polymerization.

In the commercial operation the reduction from Cr(VI) is accomplished not with CO, but with ethylene itself in the reactor. Therefore the following XPS experiment was done to imitate the process. A Cr(VI)/silica catalyst, calcined in O_2 at 850°C, was exposed to 1 atm of flowing ethylene at 100°C. Nothing happened immediately so the temperature was raised until at 160°C a strongly exothermic reaction was noted. Within a minute the temperature had surged to 180°C, so at this point the ethylene was flushed out with argon and the catalyst cooled to 25°C. After another brief exposure to ethylene, this time at 25–30°C, the catalyst was evacuated and mounted in the spectrometer. Again the productivity was about 1 g/g.

Figure 5 shows the X-ray photoelectron spectrum of this catalyst before and after addition of ethylene. It closely resembles that obtained from Cr(II) + ethylene; the Cr $2p(3/2)$ peak was found at 577.1 eV. This again suggests reduction from Cr(VI) to Cr(II) by ethylene, and that the electron density on the Cr(II) is decreased by ethylene.

CONCLUSIONS

These results support what was concluded from other techniques long ago (*26*). The Phillips catalyst starts with a monodispersed chromate (or perhaps dichromate) individually attached to a highly dehydroxylated silica surface. This phase, probably tetrahedrally coordinated like many other Cr(VI) compounds, is then reduced by CO, ethylene, or perhaps other agents, to a highly coordinatively unsaturated, isolated, divalent species, capable of accepting ethylene into its coordination sphere and polymerizing it. Assuming that octahedral coordination is possible for Cr(II), an expansion of the coordination number is even conceivable.



When ethylene is used as the reducing agent, the induction time corresponds to this reduction. The activity of the catalyst is inversely related to the hydroxyl population on the silica, suggesting that it may interfere, perhaps by coordination, with the active species or oxidation of it.

From these experiments we can say only that the precursor of the active site is divalent. We cannot tell exactly what states the active chromium takes during polymerization. The XPS results indicate a decrease in electron density (a partial oxidation) on the chromium after exposure to ethylene, but whether this reflects initiation by active sites, or merely chemisorption on inactive ones, is unknown.

By choosing divalent chromium as the active precursor on the commercial catalyst we do not mean to imply that it is the only valence which can polymerize ethylene. There are many modifications of the basic Cr/silica recipe and it may be possible that other valences, under certain conditions, can also polymerize olefins to a limited extent. In fact, we are convinced that in another catalyst system the active species is Cr(I) (*46*). We also note that in the many previous studies where the active valence was reported to be higher than Cr(II), the Cr/silica preparations examined often bore little resemblance to the commercial Phillips catalyst, and the activities reported were usually insignificant by commercial standards.

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