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The X-Ray Photoelectron Spectra of Heterogeneous Catalysts
II. The Chromia–Silica Catalyst System[1]

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The X-ray photoelectron spectra of a series of chromia–silica catalysts (containing ~8% Cr) have been recorded. The Cr $2p_{\frac{1}{2},\frac{3}{2}}$ and O 1*s* binding energies have been monitored as a function of calcination temperature, and the change from Cr(VI) to Cr(III) has been followed as the temperature is increased. A dramatic enhancement in the intensity of the Cr 2*p* peaks at 500°C is attributed to a dispersion change in which α-Cr_2O_3 concentrates on the surface of the silica support. Treatment of the catalysts with CO generates chromium sites which possess Cr 2*p* binding energies lower than those of Cr(III). This observation is consistent with the formation of Cr(II), a species which is probably the active catalyst site. The concentration of Cr(II) decreases upon exposure of the reduced catalyst to NO at 300°C. These results are discussed in the light of other studies which have been carried out on these catalysts.

INTRODUCTION

Supported chromium oxide catalysts have a wide variety of applications including ethylene polymerization (*2*) and oxidation–reduction reactions between environmentally important molecules such as CO and NO (*3*). In recent years, many efforts have involved the characterization of these catalysts in an attempt to sort out the appropriate reaction mechanisms. Volumetric titrations to determine the bulk oxidation state of the chromium routinely used in conjunction with infrared and electron paramagnetic resonance spectroscopy have provided much information dealing with these questions. However, these techniques have also revealed that the chromia system is highly complex, and, as a result, many ambiguities have arisen concerning the state of the catalyst throughout its various reaction histories.

One controversial aspect concerns the oxidation state of the chromia which is present as a result of reaction with CO and NO. In relation to treatment of the catalyst with these two gases, both singularly and as a mixture, a wide range of chromium oxidation states from II to V have been proposed. As a possible tool to gather additional information concerning this aspect, we have used X-ray photoelectron spectroscopy (XPS or ESCA), the application of which to catalytic problems has previously been discussed by Delgass *et al.* (*4*), to investigate the surface during various stages and conditions of reaction of the chromia catalyst with carbon monoxide and nitric oxide. While our XPS results do not provide any additional information on the recently proposed mechanisms of the reactions between carbon monoxide and nitric oxide over chromia catalysts (*5*), they do enable us to investigate the nature of the catalyst surface.

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The study was conducted in essentially two parts, the first of which involved the calcination process and included monitoring the Cr 2*p*, O 1*s*, and Si 2*p* binding energies as well as detecting dispersion changes which occurred as the calcination temperature was varied. The second part deals with reactions of the catalyst with CO and NO. These gases were reacted with the catalyst individually, as a 1:1 mixture, and were cycled one after another. After each stage, the Cr 2*p*, Si 2*p*, and O 1*s* binding energy spectra were recorded.

EXPERIMENTAL METHODS

The supported samples were prepared using conventional impregnation techniques. A quantity of CrO_3 which was sufficient to produce samples containing 8% chromium was dissolved in an aqueous slurry of silica (Cab-O-Sil, grade M-5); the resulting mixture was stirred for approximately 30 min and was allowed to stand in order that the chromia–silica solid would settle out. After approximately 10 h the aqueous supernatant liquid was siphoned off, and the remaining residue was allowed to evaporate to dryness. As will be discussed later, the XPS spectra of the calcinated samples showed great differences in dispersion when this procedure was altered. All samples were then dried in an oven at 250°C for a period of 24 h. The resulting powder was then pressed at 843.0 kg/cm^2 to a 22-mm-diameter, 0.1–0.2-mm-thick selfsupporting catalyst disk. To study the effect of calcination temperature, the sample disks were heated in air to 300, 400, 500, 550, or 600°C for a period of 4 h.

In the studies involving reaction of the chromia surface with gaseous CO (Matheson, 99.5% minimum purity) and NO (Matheson, 99.0% minimum purity), exposure to the atmosphere following reaction was minimized. The calcined disk was placed in a porcelain boat which was in turn inserted into a horizontal glass tube which could be sealed by attaching vacuum stopcocks to each end. The entire reaction tube was then placed inside a tube furnace and was heated to a temperature of 300°C for 3 h. Using this apparatus, the gas or gas mixture was allowed to flow over the disk at a rate of 20 ml/min by opening the stopcocks. Following reaction, the glass tube was evacuated and placed via a vacuum port into a dry oxygen-free glove box which was attached to the XPS spectrometer. The spectra were obtained in a vacuum which approached 10^{-8} Torr.

Binding energy spectra were recorded using a Hewlett–Packard 5950A ESCA spectrometer. The Al$K\alpha_{1,2}$ line (1486.6 eV) was used as the excitation source. The catalyst disks were placed in a recessed gold-plated copper blank which was in turn attached to the end of the instrument sample probe. An electron "flood-gun" was used to minimize surface charging effects (*6*).

As has been discussed previously (*7*), the binding energies of a supported catalyst can be internally referenced to some suitable binding energy line of the support. This procedure is desirable if differences in surface charging effects between different catalyst samples are to be minimized. In the present work, the Cr 2*p* and O 1*s* binding energies were referenced to a Si 2*p* binding energy (*8*, *9*) of 103.7 eV for the silica support. A C 1*s* value of 285.0 eV (*10*) for the surface carbon contaminant was used (*8*, *9*) in the energy calibration of the latter spectrum.

RESULTS AND DISCUSSION

The discussion of the results can be divided conveniently into the following two parts: (i) evidence of changes in oxidation state and dispersion which occur as a result of different calcination temperatures and (ii) evidence of changes on the surface of the catalyst after reaction with CO and NO.

The XPS of the Calcined Catalysts

The appropriate Cr $2p_{3/2}$ and O $1s$ binding energies for the catalyst before and after calcination are presented in Table 1, and typical spectra are illustrated in Fig. 1. An analysis of these spectra shows that, for the noncalcined samples, the chromium species are predominantly in the Cr(VI) oxidation state. When these samples are heated to higher temperatures there is a shift of the Cr $2p$ peaks to lower energies, with the Cr(III) state predominating at temperatures of 500°C and above.

We have obtained a Cr $2p_{3/2}$ binding energy of 580.4 eV for the noncalcined sample which contains mainly Cr(VI) and a binding energy of 577.1 eV for the sample calcined at 500°C (Table 1). Allen and coworkers (*11*, *12*) have measured Cr $2p$ binding energies for a variety of different chromium compounds. If we reference their data (*11*, *12*) to the commonly accepted (*10*) gold reference of 83.8 eV, then the corresponding Cr $2p_{3/2}$ binding energies for CrO_3, CrO_4^{2-}, $Cr_2O_7^{2-}$, and Cr_2O_3 are 578.1, 579.5, 579.2, and 576.6 eV, respectively. In comparing these values with our experimental data, we note that, while the samples calcined at high temperature only differ from the Cr $2p_{3/2}$ energy of bulk Cr_2O_3 by 0.5 eV, the noncalcined sample is considerably different from CrO_3. In fact, the experimental values correlate quite well with the Cr $2p_{3/2}$ energies of chromate and dichromate (*11*, *12*). This observation tends to support the proposed chromate and/or dichromate structure of chromia on silica (*13*, *14*) although unfortunately it is not possible to distinguish between the two by XPS.

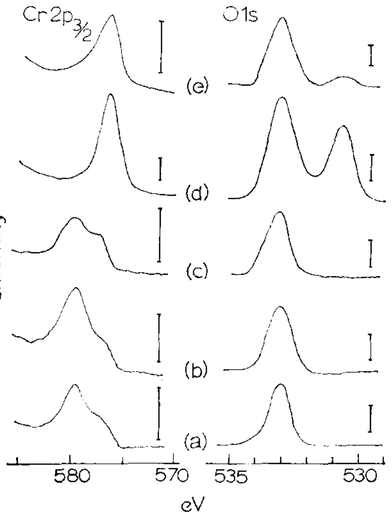

FIG. 1. The Cr $2p_{3/2}$ and O $1s$ binding energy spectra of chromia–silica catalysts after calcination at different temperatures: (a) not calcined; (b) 300°C; (c) 400°C; (d) 500°C; (e) 600°C. The length of the vertical line to the right hand side of each spectral trace indicates the intensity scale: Cr $2p_{3/2}$, 350 cpm; O $1s$, 4000 cpm.

TABLE 1

Chromium $2p$ and Oxygen $1s$ Binding Energies of Chromia–Silica Catalysts before and after Calcination

Calcination temperature °C	Cr[a]		O $1s$[a]
	$2p_{1/2}$	$2p_{3/2}$	
Not Calcined	588.6 (3.7)	580.4 (3.7)	533.1 (1.6)[c]
300	588.4 (3.8)[b]	579.9 577.5 (3.7)	533.2 (1.4)[c]
400	587.7 (4.2)[b]	579.9 577.4 (4.3)	533.1 (1.8)
500	587.1 (3.5)	577.1 (3.1)	533.2 (1.6)[c] 530.7 (1.3)
550	587.1 (3.5)	577.1 (3.1)	533.1 (1.6) 530.7 (1.3)
600	587.1 (3.5)	577.1 (2.9)	533.1 (1.9)[c] 530.7[d]

[a] Full width at half-maximum (fwhm) values given in parentheses; energies in eV.

[b] Resolution into two components due to presence of Cr(VI) and Cr(III) species less apparent than with more intense Cr $2p_{3/2}$ peaks.

[c] This O $1s$ binding energy is mainly due to the silica support.

[d] Very weak peak.

The aforementioned results resemble in one respect those which have previously been reported for the La_2O_3–Cr_2O_3 catalyst system (*15*), namely, that measurements of Cr $2p$ binding energies of the calcined catalysts show only the presence of Cr(VI) and Cr(III) species on the surface. Our Cr $2p_{3/2}$ binding energies (Table 1) agree closely with those reported for the La_2O_3–Cr_2O_3 system (*i.e.*, Cr(VI) ~580 eV and Cr(III) ~577 eV). (*15*).

In addition to the binding energy shifts which establish the presence of Cr(VI) and/or Cr(III) species, a very dramatic increase in the intensity of the Cr *2p* peaks occurs for the sample calcined at 500°C (Table 1 and Fig. 1). Further characteristics of this particular sample include the appearance of an additional O 1*s* peak at 530.7 eV (believed to be the result of crystalline Cr_2O_3) and an equally dramatic decrease in the intensity of the Si *2p* peak. We found this change to be evident on samples containing between 5 and 15% chromium. Through efforts to reproduce this effect, we found that both the calcination temperature and the procedure we used to prepare the catalyst were critical. Apparently, this intensity change occurs only over a narrow temperature range of approximately 20°C, and, by about 550°C, this intensity enhancement had largely disappeared. Furthermore, it was found that when samples which had been calcined at 500°C were reheated in air at a lower temperature (4 h at 300°C), this dispersion change was reversed.

This structural change has also been reported for unsupported chromia by using different characterization procedures (*16–18*). Dyne *et al.* (*16*) have noted from X-ray diffraction patterns that, when a chromia gel prepared from chromium nitrate is heated in hydrogen to 400°C, the sample changes from an amorphous state to that of a crystalline form of α-Cr_2O_3. Through a detailed analysis of the resulting X-ray powder pattern and the X-ray line broadening thereof, they found that, when the holding temperature was lowered as little as 8° below 400°C, no crystallization occurred. When the samples were held at temperatures between 400 and 450°C, crystallites which have dimensions less than 100 Å in the *a* direction appeared to be essentially spherical, whereas those crystallites greater than 100 Å in the *a* direction tended to grow to platelets having diameters about twice their thickness. As a result of their X-ray and electron microscopy data, they concluded (*16*) that these samples can be "considered to be microcrystalline chromia supported on amorphous chromia." A further characteristic of this structural change is a decrease in surface area.

Our own X-ray diffraction studies of powdered supported samples, although not as detailed as those just mentioned, give similar results. At temperatures below 400°C, only amorphous chromia is present. At temperatures above 400°C, the degree of crystallinity steadily increases, although much of the sample apparently remains amorphous. In addition to the results noted by Dyne *et al.* (*16*), we have found that, as the temperature is increased past 500°C, the relative amount of the crystalline phase appears to decrease, and the samples once more take on a more amorphous character. This result correlates nicely with the related XPS data on these same samples.

McDaniel and Burwell (*17*) have also noted a variety of conditions which cause this structural change. Although the temperatures reported in these studies are somewhat lower than those indicated by our data, this is not disturbing due to the difference in sample preparation and the possible effects of the support.

The interpretation of the XPS data (Table 1 and Fig. 1) in the light of the preceding discussion is now appropriate. Since peak intensities in XPS are directly related to surface concentration, the observed Cr *2p* intensities can be, at least, qualitatively related to the concentration of chromium on the surface. As the larger platelets of Cr_2O_3 form at approximately 500°C and grow to cover the surface, we would expect that the surface concentration of chromium could be greater than that of the initially prepared sample. In addition, this change should be accompanied by a decrease in the relative intensity of the Si *2p* peak, since the environmental effect of the silica should be correspondingly reduced. This is in fact observed. Furthermore, the formation of a very high surface concentration of Cr_2O_3 should result in the appearance of an associated O 1*s* binding energy. This peak should be located at ~530.8 eV, since Allen *et al.* (*11*) have established that, for Cr_2O_3, the binding energy difference $\Delta E(\mathrm{Cr}\ 2p_{\frac{3}{2}}\text{–O}\ 1s)$ is 46.3 eV. The O 1*s* peak that we observe at 530.7 eV (Table 1 and Fig. 1) is clearly this particular binding energy, its intensity behavior closely mirroring that observed for the Cr $2p_{\frac{3}{2}}$ peak at 577.1 eV. The decrease in intensity of both the Cr 2*p* (577.1 eV) and O 1*s* (530.7 eV) binding energies, as the calcination temperature is raised above 500°C, can be explained by the reconversion of crystalline Cr_2O_3 to a more amorphous form with an accompanying dispersion change. With chromia once again being in a more highly dispersed state, the Cr 2*p* (577.1 eV) and O 1*s* (530.7 eV) peaks decrease in intensity.

Although reproducible results were noted on samples containing between 5 and 15% chromium, we found that the degree of crystallinity was very dependent upon sample preparation. Using different volumes of water and/or using heat to speed the evaporation process, the dispersion change was either enhanced or found to be nonexistent. McDaniel and Burwell (*17*) have reported that different drying temperatures produce very marked effects in the degree of crystallinity of unsupported chromium. These workers have related the amount of excess oxygen to drying temperature and crystallinity. Samples dried at 25°C were found to have no excess oxygen and remained amorphous when heated in helium at 300–500°C. However, amorphous samples dried at 85 and 135°C were converted to a crystalline form when heated to 450°C in helium or 350°C in oxygen. Other studies which have noted similar results include those by Weller and Voltz (*18*).

De Angelis has recently reported (*19*) some interesting results concerning the possibility that surface reduction of CrO_3 and silica-supported CrO_3 may occur during the recording of XPS spectra. In our work, we found no evidence that such a reduction process had occurred to any great extent. This is not unexpected since our data were recorded with a type of spectrometer different than that utilized by De Angelis (*19*), and the duration of our data accumulation was usually less than that for which the amount of X-ray induced reduction was very great (*19*). With a spectrometer which uses monochromated X-rays (as in our work), it is very likely that X-ray damage will be less than that experienced with an instrument which does not monochromate the incident radiation.

The XPS of the Catalysts after Treatment with Carbon Monoxide and Nitric Oxide

Measurements were made of the Cr 2*p* and O 1*s* binding energies of the catalysts after they had been reacted separately with CO and NO and with 1:1 mixtures of these two gases. The spectra were monitored after reaction at 300°C for a period of 3 h. The experimental conditions under which the binding energies were measured (a pressure of $\sim 10^{-8}$ Torr) do not of course correspond to the conditions which prevailed during measurments of the infrared spectra of NO and CO adsorbed on silica-supported chromia (*20–23*). Accordingly, although we are unable to monitor the nature of the reversibly adsorbed species, this technique is suited to an investigation of the nature of the chromium species which are present. In addition, it should be emphasized that reactions between the CO-reduced catalysts and NO were carried out at 300°C, whereas most data (*21–23*) in the literature pertain to reactions at room temperature or below.

When catalyst samples which have been calcined at 500°C are reacted with CO, a shoulder appears at ~576.4 eV on the low binding energy side of the Cr $2p_{\frac{3}{2}}$ peak due to Cr(III) (Fig. 2). By measuring the separation between the related Cr 2*p* peaks of Cr (VI) and Cr(III) species (Table 1), it is apparent that the average binding energy shift per unit change in oxidation number is ~0.8 eV. If this linear relationship persists in going from supported Cr(III) to Cr(II) oxide, then the observed Cr $2p_{\frac{3}{2}}$ energy of 576.4 eV is consistent with the presence of Cr(II). Some support for this contention is provided by the results of Haber *et al.* (*24*) on tungsten oxides produced by the partial reduction of WO_3. A linear relationship was observed between the W $4f_{7/2}$ binding energy and the metal oxidation number. If we qualitatively relate the intensity of the shoulder at 576.4 eV to the concentration of Cr(II) present, this indicates that, while considerable amounts are generated in samples which had been calcined at temperatures of 500°C and above, samples that were not calcined or were calcined at 300°C showed very little chromium reduction.

Because of the very high reactivity of any Cr(II) species, it is necessary to guard against oxidation during sample handling. Samples which were exposed to the atmosphere for even short periods of time show the Cr(II) to be absent. As a check on our experimental design, we reacted a catalyst with CO in the sample handling chamber of the instrument. Before reaction, the surface was "cleaned" by argon ion bombardment and then reacted with CO at 300°C for approximately 30 min. The chromium spectrum in this case did not differ significantly from that produced using the other procedure. By measuring the C 1*s* binding energy after "cleaning" and again after reaction with CO, we observed a peak at 289.1 eV which was not present before reaction. This peak can be attributed to the formation of a carbonate species. Samples not "cleaned" also show a C 1*s* peak at 285.0 eV which is the result of a carbon layer chemisorbed on the surface.

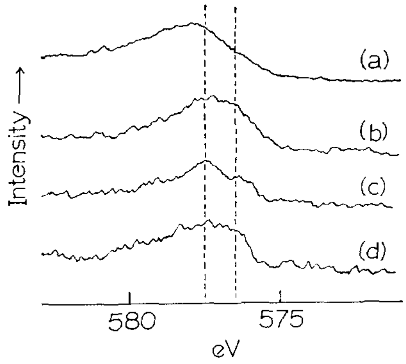

FIG. 2. The Cr $2p_{\frac{3}{2}}$ binding energy spectra of a chromia–silica catalyst upon treatment with CO and NO: (a) catalyst after calcination at 500°C; (b) calcined catalyst after treatment with CO; (c) catalyst from b after treatment with NO; (d) catalyst from c after further treatment with CO.

Although the lower oxidation state is also produced when NO is passed over the catalyst at 300°C, the degree of reduction is much less than in the case of CO. Reaction of NO with the samples calcined at temperatures below 500°C produced very small amounts of Cr(II). These results support those of Shelef and co-workers (*3*) who concluded that CO is a better reducing agent than NO.

The catalysts which had been treated with NO exhibited a N 1*s* binding energy peak at 400.2 eV, a value which is characteristic of NO when adsorbed on metals or metal oxides (*25*, *26*). However, the intensity of this peak was rather low, so that we did not pursue a detailed study of the N 1*s* spectra of these systems. Consistent with the low concentration of Cr(II) species which were generated when the catalysts were reacted with NO, we did not detect any significant amounts of the oxidation byproducts, NO_2^- or NO_3^-, on the catalyst surface.

When the catalyst was reacted with a 1:1 mixture of CO and NO at 300°C for 3 h, the results obtained were quite similar to those obtained for reaction with CO. Using the same criteria to correlate binding energy with oxidation state, the concentration of Cr(II) is quite appreciable, approaching that of the Cr(III) species. However, while the N 1*s* spectrum was similar to that described above, the C 1*s* spectrum showed a greatly reduced carbonate peak. Although much controversy has existed concerning the oxidation state of catalytically active chromium, our results certainly support those models which require the formation of the divalent state. By measuring the uptake of oxygen by fully reduced samples, Zecchina *et al.* (*13*) have found that catalysts with loadings up to 0.5% show oxidation states between 2.05 and 2.15. These conclusions may also be relevant to the chromia catalysts used in ethylene polymerization. Thus, Krauss *et al.* (*27–29*) have also shown that the oxidation state in CO-reduced samples is near 2, and that a linear correlation exists between catalyst activity and the concentration of the divalent species. On the other hand, Eley and co-workers (*30*) remain confident that Cr(V) is the active species in these polymerization catalysts, based on their results of activity as a function of the reduction time by ethylene, whereas Przhevalskaya *et al.* (*31*) believe that coordinatively unsaturated Cr(III) is responsible for the catalytic activity.

In light of the fact that CO tends to be a better reducing agent than NO, we became interested in following the reversibility of these redox processes when CO and NO gases were cycled over the catalyst surface. The results of these efforts are apparent in the Cr 2*p* spectra as shown in Fig. 2. The sample which had first been treated with CO, was oxidized when reacted with NO for a 3-h time period at 300°C, as noted by a lowered intensity of the Cr(II) peak. When this sample was subsequently retreated with CO for 3 h at 300°C, reduction was again noted.

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