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Surface States on a Chromia Catalyst[1]

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Experiments were performed on pressed pellets of microcrystalline chromia, using measurements of adsorption, temperature-programmed desorption, and electrical conductivity. From the electrical conductivity measurements, a donor surface state was identified and calculated to be at an energy of 0.3 eV above the valence band. (Presumably, the bulk valence band is the Cr^{3+} band of the semiconductor.) It was concluded that this donor surface state is associated with the same coordinatively unsaturated surface Cr^{3+} ions that have been shown in other work to be the catalytically active centers on the catalyst. Studies of oxygen adsorption, CO adsorption, and CO oxidation are presented. The results are consistent with, but provide new details regarding, the accepted models of oxidation catalysis over chromia.

INTRODUCTION

Semiconducting chromium oxide (Cr_2O_3) seems unique as an oxidation catalyst. In most commercially useful oxidation catalysts, lattice oxygen is exchanged with the reactants during the oxidation process (*1*). In the case of chromia, evidence exists that lattice oxygen is not involved in the oxidation activity (*2*). The evidence is the sharp saturation of the adsorption of both reducing agents and oxygen over the catalysts, as described in Refs. (*2–4*), for example, and as described below in these studies. In a few less effective oxidation catalysts ionosorbed oxygen, (i.e., oxygen formed by electron capture from the bands of the bulk catalyst) is the active intermediate. An example of a catalyst where the active oxygen usually is ionosorbed oxygen would be zinc oxide (*5*). However, in the case of chromia, evidence exists that the adsorbed reactants are not in the ionosorbed form. The conclusion that neither oxygen nor reducing agents are dominantly ionosorbed on chromia is drawn because both oxygen and reducing agents are adsorbed to more than 0.1 monolayer coverage (*3*, *4*, *6*, *7*), whereas ionosorption stops at the order of 10^{-3} to 10^{-2} monolayers (*8*), as pointed out by Burwell *et al.* (*7*). Chromia appears unique as a catalyst because the above complications do not enter—all reactants are adsorbed by bonding to localized sites at the surface.

Although its adsorption characteristics seem independent of energy-band effects, chromia is nonetheless a reasonably well-behaved *p*-type semiconductor, so sensitive electrical measurements can be made. Therefore, we considered it of interest to study the catalytic behavior using electrical "surface state" measurements to monitor the interaction between the reactants and the active sites (the surface states) on the chromia surface.

To investigate the electrical effects as the surface states interact with adsorbates, one needs to use a form of the catalyst that can be expected to have meaningful semiconductor properties. Thus, in the present studies we chose the microcrystalline chro-

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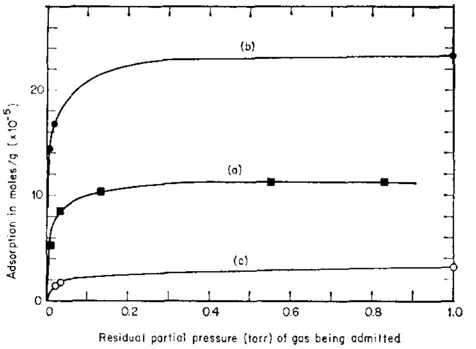

FIG. 1. Adsorption of O_2 and CO on Cr_2O_3 at 410°C. (a) Adsorption of O_2 on CO-treated surface (1.8×10^{-5} moles CO_2/g Cr_2O_3 produced during adsorption). (b) Consumption of CO because of adsorbed oxygen (the CO_2 produced is trapped out). (c) CO adsorbed on sample during (b).

mia phase rather than the more hydrated amorphous chromia (*7*). Burwell *et al.* (*7*) and Carruthers and Sing (*9*) have provided recipes for preparation of microcrystalline chromia. To further define the properties of the chromia as a *p*-type semiconductor, we have doped our material with magnesium acceptors. Only with such a well-defined bulk doping can the theory of conductance of pressed powder pellets be used (*10*). Chromia as a semiconductor has been studied by Elyutin *et al.* (*11*), by Cogan and Lonergan (*12*), and by Cajacaru (*13*). Cogan and Lonergan measured the conductance versus temperature for calcined chromia with magnesium present and obtained activation energies of 0.36, 0.44, and 0.52 eV, corresponding to 1, 0.1%, and zero added magnesium. Doped with 1% magnesium, the resistivity is 2×10^2 ohm cm for a sintered pellet. Cojacaru (*13*) concludes that the *p*-type conductivity of the chromia arises by a hopping mechanism in a Cr^{3+}/Cr^{4+} band. In other words, the conductivity arises because some of the bulk chromium ions in the solid are in the 4+ valent state, and these unoccupied levels in the band act as holes that can hop from one lattice chromium ion to the next through the solid. The activation energy of the conductivity, determined, for example, by Cogan and Lonergan (*12*), is then related to the energy of activation of the "hole" as it moves through the lattice. Cojacaru bases this conclusion on his observation that the Seebeck coefficient is independent of temperature up to 280°C, suggesting that the hole density is constant and, therefore, the variation of conductance in this temperature range must be associated with an activated mobility. As discussed below, this same redox couple, Cr^{3+}/Cr^{4+}, when present at the surface, is considered to dominate the catalytic behavior. Therefore, the correctness of this interpretation of the conductivity becomes critical in the analysis of electrical measurements versus catalytic behavior.

The form of adsorbed O_2 and CO on chromia has been reasonably well established, although it depends to some extent on the hydroxylation of the chromia surface. The studies of McDaniel and Burwell (*14*), Davydov and co-workers (*15–17*), and Zecchina and co-workers (*18*) most clearly show the form of the adsorbed species. Oxygen is adsorbed on a "clean" surface of chromia by bonding to the chromium ions at the surface; below room temperature, a $Cr\text{–}O_2$ bond is formed; above about 300°C, the oxygen is completely dissociated; and between about room temperature and 300°C, there is a transition region where oxygen bonded to the surface chromium sites can be in many forms, depending on the temperature and the degree of hydroxylation. CO adsorbed on a "clean" chromia surface at room temperature is found (*18*) to be removable without reaction. Zecchina and his co-workers (*18*) suggest a bond between the CO and the chromium site that is primarily a σ-bond with little π contribution. The adsorption of CO on an oxygen-covered surface at room temperature results in no change in the infrared spectrum (*16*). Beyond 100°C, CO_2 bands begin to appear, and the oxygen bands begin to change their character. Beyond 300°C, most oxygen bands are removed.

The objective of the present study of the interaction of oxygen and CO with the surface states on the chromia using electrical conductivity measurements is threefold: (a) to show how the surface states associated with the chromia surface atoms are affected by the adsorption of gaseous reactant species, (b) to show how conductance measurements can be used to follow the interactions between reactants and surface states, (c) to provide new information about the catalytic reaction between oxygen and CO on the chromium oxide surface.

EXPERIMENTAL DETAILS

The chromia was prepared essentially in accordance with the recipes of Burwell *et al.* (*7*) and Carruthers and Sing (*9*). From a solution 0.1 *M* chromium nitrate and 10^{-3} *M* magnesium nitrate, a gel was slowly precipitated with ammonium hydroxide. After centrifuging about 30% of the volume was gel, so, assuming random distribution of the Mg, we can assume about 0.3% Mg doping of the resulting chromia. The gel was heated in vacuum to 250°C for 1 hr, then warmed slowly to 350°C, maintained there for 1 hr, then heated further in vacuum to 450°C. The heating rate was 5°C/min. Pellets of the resulting powder, 0.5 g, were pressed, pressure contacts were applied, and the sample was mounted in a vacuum system/reaction chamber.

In addition to a four-point electrical conductivity measurement, the apparatus included a mass spectrometer for temperature-programmed desorption (TPD). In general, the procedure was to admit aliquots of gas and measure the amount adsorbed, the amount reacted, and the corresponding conductance changes.

Most of the work was done at one of three temperatures, 400°C, room temperature, and −130°C. As described above, it is expected that the measurements at 400°C and −130°C will provide definite forms of adsorbed oxygen (atomic and molecular, respectively). Electrical conductivity measurements were possible between 400°C and room temperature, but the conductance became too low below room temperature.

Studies focused primarily on the adsorption of oxygen and CO, but a few studies were made with NH_3 as the reducing agent. In general, the sample was pretreated by cycling between oxygen and the reducing agent of interest at 400°C, then was evacuated at 400°C to about 10^{-6}–10^{-7} Torr. This is similar to the pretreatments used by Zecchina *et al.* (*18*) and is contrasted to the 600°C outgassing pretreatment used by Davydov *et al.* (*15–17*). As described below, the 400°C pretreatment never results in complete outgassing of the reducing agent. We did not investigate the pretreatment of Davydov *et al.*, so we do not know whether this pretreatment results in a thoroughly outgassed chromia surface.

RESULTS

Adsorption at 400°C

Figure 1 shows the adsorption/pressure curves for CO and oxygen on chromia at 410°C. The sample is initially pretreated as described above, ending with a CO treatment at 5 Torr CO and evacuation for 0.5 hr. Following this, aliquots of oxygen are admitted (curve a): In the early stages of the run, aliquots corresponding to 0.05 or 0.5 Torr of initial pressure, and in later stages, aliquots of 1 Torr initial pressure were admitted. Until more than 5×10^{-5} moles of oxygen have been adsorbed, the admitted oxygen is essentially all consumed. A small residual pressure of oxygen (as indicated on the abscissa), plus a small amount of CO_2 (0.9×10^{-5} moles produced *in toto*, as indicated in the figure caption) remains in the gas phase. We conclude that the CO_2 comes from oxidation of residual CO present on the surface after the pretreatment. Curve b of Fig. 1 shows the

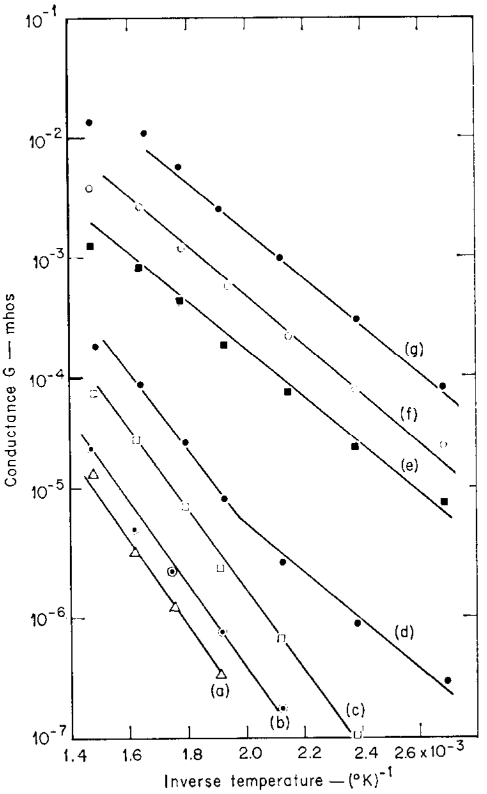

FIG. 2. Temperature dependence of the conductance. (a) After 400°C exposure to 5 Torr CO and evacuation; (b) through (f) after integrated O_2 adsorption at 400°C of 4×10^{-7}, 1.2×10^{-6}, 5×10^{-6}, 2×10^{-5}, 10^{-4} moles/g catalyst; (g) after exposure to 2 Torr O_2.

consumption of CO that is admitted immediately following the adsorption of oxygen shown in curve a. CO "consumption" includes both adsorbed CO and CO_2 that is desorbed into the gas phase. After each aliquot of CO is admitted, the CO_2 is measured, then removed. Curve c shows the difference between the CO consumed and the CO_2 returned to the gas phase and thus represents the amount of CO that is left on the surface. The amount thus measured agrees with the amount of CO_2 produced upon subsequent oxygen adsorption as in curve a. From the results of Fig. 1, we conclude that about 10^{-4} moles of oxygen/g Cr_2O_3 become adsorbed in a manner closely approximating the Langmuir adsorption isotherm; about 2×10^{-4} moles of CO react with this to produce CO_2, and about 2×10^{-5} moles of CO become adsorbed in the early stages of this reaction.

Figure 2 shows the Arrhenius plot of the conductance G versus inverse temperature with varying amounts of adsorbed oxygen on the surface. Curve a shows the results after the CO pretreatment and evacuation. A slope corresponding to about 0.7 ± 0.03 eV is obtained under these conditions. Curves b to f show the results after aliquots of oxygen are adsorbed onto the surface, and curve g shows the results with the full oxygen coverage. In all cases, the gases are admitted at 400°C, and the conductance/temperature measurements are made after evacuation. The solid lines as drawn suggest that the Arrhenius slope changes somewhat abruptly after several aliquots of oxygen are admitted. However, other similar runs do not always reproduce the abruptness of the shift in activation energy. However, the initial and final slopes with and without oxygen present on the surface always show a behavior similar to that of Fig. 2. The Arrhenius slope for the surface saturated with oxygen is found to be 0.40 ± 0.03 eV. In other experiments (not shown), the Arrhenius slope after an NH_3 treatment and evacuation at 400°C is of the order of 1.0 eV.

In Fig. 3, curve a, the conductance at 400°C is plotted as a function of oxygen coverage as aliquots of oxygen are admitted; in curves b and c, the conductance is plotted as a function of residual oxygen during its subsequent removal by CO. Curve b contains the data taken immediately after the run of curve a. Unfortunatey, too great an aliquot of CO was admitted at the end point of curve b and the remaining oxygen was removed in its entirety. Curve c shows results analogous to curve b on another sample, where the coverage range of interest was explored in more detail. The results of Fig. 3 suggest no significant difference in the conductance/

adsorbed oxygen relationship whether oxygen is being added to a "clean" surface or whether oxygen is being removed by reaction with CO. To a reasonable approximation, the conductance appears to vary as the cube of the surface coverage by oxygen. At present, we attach no theoretical significance to this relationship; the theoretical analysis of conductance variation with coverage and temperature is very complex at low coverages.

Adsorption at −130°C

The adsorption of oxygen in the molecular form on a surface that has been "cleaned" by CO at 400°C, evacuated, and cooled to −130°C, is similar to that of Fig. 1, except that at the low temperature no CO_2 appears in the gas phase. The adsorption saturates at a slightly higher coverage than indicated in Fig. 1, but some of this oxygen is removable by subsequent evacuation.

After the surface has been saturated thus with oxygen, CO can be adsorbed as indicated in Fig. 4, Curve a, displacing some adsorbed oxygen as indicated in curve b. Again, the adsorption of CO saturates rather abruptly; however, at this low temperature, the adsorption of CO is substantially less than that observed at 400°C. Specifically, the adsorption of CO is now closer to one-half the coverage of the previously adsorbed oxygen. From curve b it is observed that until the CO adsorption is almost complete, negligible oxygen is displaced by the adsorbing CO. As the CO adsorption saturates, however, the displacement of oxygen abruptly becomes 1 oxygen molecule displaced/CO molecule adsorbed. The displaced oxygen comes off as O_2, not as CO_2.

Temperature-programmed desorption (TPD) measurements have been made of the desorption of oxygen after the adsorption of a monolayer. In this case, the measurements were made after "cleaning" the sample at 400°C, using NH_3 rather than CO as in the results so far reported. We found that up to 50°C only oxygen gas is desorbed, the integrated desorption to 50°C begin 1.8×10^{-5} mole/g. Beyond 60°C, primarily nitrogen and N_2O are desorbed. Integrated from 60 to 150°C, 0.3×10^{-5} mole/g are desorbed; integrated to 400°C, 3×10^{-5} mole/g of gas are desorbed, including some water vapor. The lack of well-defined surface species when NH_3 is the reducing agent prompted us to concentrate on CO in the rest of our studies.

In these low-temperature measurements,

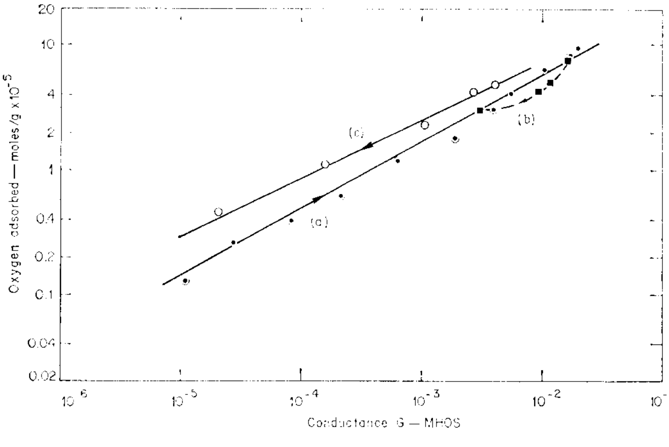

FIG. 3. Variation of conductance with oxygen coverage (400°C). (a) Oxygen adsorption; (b) removal by CO reaction; (c) removal curve from another sample.

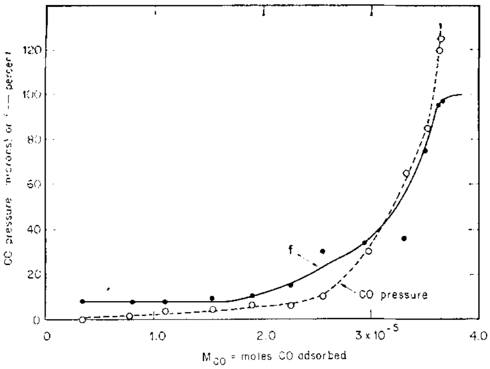

FIG. 4. Adsorption of CO on a 0.5 g sample of O_2-covered chromia (7.6×10^{-5} moles O_2 on surface). CO pressure, (– –). $f = (\Delta M_{O_2}/\Delta M_{CO_2}) \times 100\%$, the number of moles or oxygen displaced per mole CO adsorbed. $T = -135°C$.

the conductance was too low for a reliable measurement in the apparatus as designed.

Adsorption at Room Temperature

If a sample "cleaned" by CO at 400°C is evacuated and cooled to room temperature, and oxygen is adsorbed, negligible CO or CO_2 is found in the gas phase. The adsorption of oxygen is slightly less than the adsorption at −130°C. Table 1 summarizes the adsorption of oxygen, the subsequent consumption of CO, and the adsorption CO on a clean surface for the three temperatures studied extensively in this work. At 23°C, as at −130°C, the consumption of CO subsequent to oxygen adsorption is much lower than the original oxygen adsorption. This suggests that the O_2 is in the same nonreactive molecular form at room temperature as at low temperature. Also, neither CO_2 nor displaced oxygen is observed in the gas phase during the CO consumption measurements. On a clean surface, on the other hand, the adsorption of CO is very high, higher than the adsorption of oxygen under any conditions.

At room temperature, the conductance is measurable. This case is of particular interest because the above results and the work of others (*12*) indicate that at this temperature the oxygen is present in the molecular form. Thus, measurements of conductance changes at room temperature can give information about the interaction of molecular oxygen and subsequently adsorbed CO with the surface states. We found that the adsorption of oxygen at room temperature increases the conductance substantially. The conductance, at the limit of measurement (less than 10^{-10} mhos) increases to 10^{-7} mhos upon adsorption of a saturated coverage of oxygen. The TPD curve for oxygen that had been adsorbed on a "clean" surface showed no oxygen desorption. Small amounts of CO_2 were desorbed as the temperature was increased.

Adsorption of CO over a saturated layer of adsorbed oxygen at room temperature affects neither the electrical conductance nor the coverage of adsorbed oxygen—no oxygen is observed in the gas phase subsequent to the CO adsorption. The TPD curve for CO adsorbed over oxygen showed CO being desorbed to 100°C (at this temperature the species CO and CO_2 were desorbed in equal quantities), then beyond that temperature, the gas ·desorbed was increasingly in the form of CO_2.

In another experiment, oxygen was adsorbed at 400°C in an attempt to form dissociated oxygen atoms, the temperature was lowered to room temperature, and CO was subsequently adsorbed. In this case, also, there was no influence on the conductance from the adsorption of the CO. Again, no CO_2 was evolved during the CO adsorption process.

The adsorption of CO on a "clean" surface (Table 1) saturated at about 19×10^{-5} moles of adsorption at 4 Torr of CO pressure. Negligible CO_2 or O_2 was evolved. Evacuation of the sample resulted in the desorption of 10^{-4} moles of this CO at room temperature. A subsequent TPD measurement results in the further desorption of 7×10^{-5} moles of CO, with a single symmetric peak maximized at 175°C using a

0.75°C/sec heating rate. This suggests an activation energy E for desorption of the order of 1 eV, as determined by the formula of Redhead (*19*):

$$E/RT_p = (\nu T_p/\beta)\exp(-E/RT_p), \quad (1)$$

with ν a frequency factor assumed $10^{13}\ \mathrm{sec}^{-1}$, β the heating rate, and T_p the temperature of the peak. It should be emphasized that this peak consisted solely of CO; no CO_2 was desorbed.

DISCUSSION

The adsorption characteristics of oxygen are consistent with the observations of others as reported in the literature (*3*). The BET surface area for our samples was about 60 m^2/g, consistent with the results of others using similar recipes for preparation (*7, 9*). From Fig. 1 about 1 molecule of oxygen/100 Å^2 is adsorbed at saturation. Burwell *et al.* found that for samples prepared similarly 1.6 molecules of oxygen are adsorbed/100 Å^2. The Langmuir isotherm shape of the oxygen adsorption curves suggests fairly homogeneous adsorption sites and certainly precludes lattice oxygen effects.

We conclude with Burwell *et al.* (*7*), that the oxygen interacts with Cr^{3+} during adsorption rather than being reduced by electrons from a valence band. One cannot rationalize such high oxygen coverages if ionosorption occurs associated with an accumulation layer in the valence band. The main concern in this work is the interpretation of the Arrhenius slopes of the conductance G versus inverse temperature (Fig. 2) in terms of the energy levels of surface states. In earlier work (*10*) it was shown that when the activation energy is associated with current carriers crossing a surface barrier, the slope represents the energy level of the surface state relative to the band edge. That is, for a p-type material:

$$G = A\mu\exp\{-(E_1 - E_{\mathrm{vs}})/kT\}, \quad (2)$$

where E_1 is the surface state energy, E_{vs} the energy of the "valence band" edge, A a temperature-insensitive constant, and μ the mobility of the holes. In the present case, the mobility of the holes was extracted from the preexponential constant because, according to Cojacaru (*13*), the mobility is activated. As discussed in the introduction, with 0.3% Mg acceptors the mobility should have an activation energy about 0.4 eV, so,

$$G = A\mu_0\exp\{-(E_1 - E_{\mathrm{vs}} + 0.4)/kT\}. \quad (3)$$

TABLE 1

Values of Oxygen and CO Consumption (moles/g catalyst) as Measured on a Typical Sample

	400°C	23°C	−130°C
O_2 adsorbed	11.2×10^{-5}	13.2×10^{-5}	15.6×10^{-5}
Subsequent CO adsorption	23	4 to 6	7.2
CO adsorbed on "clean" surface	2	19 ± 3	—

An error in our estimate of the bulk doping could lead at most to a ±0.1 eV error in the values of $E_1 - E_{\mathrm{vs}}$ calculated below. Presumably the actual error from this cause is much less than 0.1 eV.

The Arrhenius slope, when the surface is saturated with oxygen at 400°C or room temperature, is 0.4 eV (Fig. 2), the activation energy we associate with the bulk mobility. Thus, with oxygen present on the surface, we can assume that the bands are flat, and the conductance/temperature characteristic is that associated with bulk chromia (doped with magnesium). That is, with oxygen present on the surface acting as an acceptor species, holes may be injected to the chromia but certainly holes are not extracted from the chromia by any residual donor surface states.

The interpretation of the Arrhenius slope after a CO pretreatment at 400°C is not so simple and is more interesting. The large decrease in conductance associated with the oxygen removal indicates an active donor surface state that captures holes. The slope of the Arrhenius plot with the clean surface is 0.7 eV, and from Eq. (3), we suggest that the donor level is about 0.3 eV above the valence band edge, E_{vs}.

The chemical groups giving rise to the donor levels are of particular concern. As has been discussed by others (*11–14*), with oxygen on the surface, simple groups of the form $Cr^{4+}–O_2^-$ and $Cr^{4+}–O^-$, as well as more complicated groups at intermediate temperatures. Only one or two sites/100 Å^2 actively adsorb oxygen. In these studies we find the donor levels at the surface completely disappear upon oxygen adsorption (the conductance in Fig. 2 increases to that expected for bulk Cr_2O_3). Thus we suggest that the same sites that are active in forming donor–acceptor complexes with oxygen (i.e., the active Cr^{3+}) are active in donating electrons to the valence band of the Cr_2O_3. When combined with oxygen, these active sites are no longer donors, and the bands become flat.

Two other possibilities for the identity of the donor levels are to be considered. One possibility is donors associated with lattice oxide ions at the surface. However, these are considered less likely than Cr^{3+} levels because the adsorption of only about 0.1 monolayer of oxygen, just enough to passivate the active Cr sites, eliminates the donors. The other possibility for the donors is Cr–CO bonding orbitals associated with the residual CO on the surface. From the curves of adsorption of CO at 400°C, we conclude that, at most, the residual CO occupies only the order of 10 to 20% of the active chromium surface states. Thus, the surface outgassed at 400°C should have a substantial density of coordinatively unsaturated Cr^{3+} available. Now the σ bond between the residual CO and the chromium surface atom should tend to stabilize the electrons in bonding orbitals in the complex, that is, should tend to lower their energy level and make them less effective as a donor. Thus, the remaining Cr^{3+} valence electrons should provide donor levels at a higher energy than the levels of the Cr^{3+}–CO complex.

It is of particular interest that the energy of these donor sites, which we will henceforth attribute to coordinatively unsaturated surface Cr^{3+} ions, is 0.3 eV above the valence band. By the accepted model (*13*) the valence band is attributed to bulk Cr^{3+} levels. Thus, apparently, the energy level of the valence electron on the surface Cr^{3+} is 0.3 eV higher than the bulk Cr^{3+} ion because at the surface the ion is coordinatively unsaturated.

It may be of interest that the shift in cationic surface levels on a strictly ionic compound should be to a lower level according to the Madelung model (*18*), while the experimental observations indicate an upward shift of the level. The observed upward shift of the energy level is presumably associated primarily with a covalent character of the bulk Cr–O bonds.

The observations after CO adsorption can be briefly summarized. Apparently CO does not affect the conductivity except by removal of oxygen. Specifically, the adsorption of CO on a "clean" surface at room temperature had no effect on the conductivity of the chromia. This result is surprising, as one would perhaps expect a Cr^{3+}–CO group to be ineffective as a donor compared with the unbonded Cr^{3+} and certainly one would expect an energy level shift. It may be that, with the low adsorption energy (the CO desorbs again readily), the donation of electrons to the valence band from the Cr^{3+} is energetically more favorable than CO adsorption, so enough sites remain unoccupied (by CO) to provide the observed electrical effects.

With ammonia adsorption, an Arrhenius slope of about 1 eV obtains, indicating that a more active donor is generated. The donor may be associated, for example, with hydrogen atoms at the surface or with NH groups. The resulting donor by Eq. (2) apparently has a surface state energy level

0.6 eV above the energy level of the valence band of the semiconductor.

Although the main object of this work was to show the value of electrical studies, we can also perhaps glean some new information about Cr_2O_3 as an oxidation catalyst from the studies of adsorption and reaction of CO and O_2. The low coverage of CO when adsorbed at low temperature on an oxygen-covered surface, the observation that the CO does not displace the adsorbed oxygen, and the observation that it does not change the charge on the adsorbed oxygen, are all consistent with the weak CO–catalyst bond. It is not clear at this time whether the apparent 1:2 ratio of $CO:O_2$ during adsorption at $-130°C$ is of significance. It may be related to the formation of carbonate-like groups as suggested by Davydox *et al.*, (*15–17*) but a plausible structure is not obvious. It is of interest that the appearance of CO_2 occurs only at temperatures above 100°C, at which temperature it can be assumed that the molecular oxygen is being dissociated to atomic oxygen. This is consistent with the low reactivity of O_2^- in other CO oxidation studies (*5*). Another point of interest is the observation that when chromia is heated with an adsorbed monolayer of molecular oxygen, desorption of oxygen is not observed in a TPD experiment. This is consistent, of course, with the fact that the number of oxygen molecules adsorbed at high temperature is the same as adsorbed at low temperature. Perhaps the $Cr–O_2^-$ species forms a 2×2 array converting to a 1×1 structure over chromium atoms at higher temperature. On the other hand, if we assume with Burwell *et al.* (*3*) that only about 16% of the surface chromium atoms are active, then the reason why only half the sites are occupied at low temperature is not easily explained.

CONCLUSIONS

The results of this study are consistent with those of earlier studies showing that complexes such as $Cr–O_2$, Cr–O can be formed on the chromia surface, where the Cr in these complexes is a coordinatively unsaturated surface cation. In addition, some weakly bonded CO can be adsorbed on an oxygen-covered surface at room temperature or below. We have found that the Cr–CO bond has a dissociation energy of the order of 1 eV and, consistent with other work, that the $Cr–O_2$ complex transforms to the Cr–O complex approximately 150°C, the latter oxygen form being able to react with CO to form CO_2 at high temperatures. We find from conductance measurements that a donor surface state level is present on a surface with low oxygen and low CO coverage. The donor level is about 0.3 eV above the "valence band" where the valence band is presumably the bulk Cr^{3+} band. We conclude that the level is due to the coordinatively unsaturated Cr^{3+} surface ions, with the difference in energy between bulk and surface Cr^{3+} levels resulting from the absence of oxygen ligands at the surface sites.

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