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An Infrared Spectroscopy Study of Carbon Monoxide Adsorption on α-Chromia Surfaces: Probing Oxidation States of Coordinatively Unsaturated Surface Cations

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CO adsorption on thermoevacuated, H_2-reduced and O_2-treated α-chromia surfaces was studied by IR spectroscopy in the temperature range 77–298 K. Coordinatively unsaturated (cus) Cr^{3+} cation sites, probably in 3-coordinate and to a much lesser extent 5-coordinate states, are the adsorption sites on H_2-reduced α-Cr_2O_3. The surface containing excess oxygen also exposes cus Cr^{4+} and Cr^{5+} sites. An empirical procedure is described which permits the determination of oxidation state and coordination number of the cus surface sites. This procedure is based on a correlation between C–O stretching frequency and electric field strength exerted by the cation. The latter is calculated from Pauling's strength of the electrostatic bond and effective ionic radii, both of which take the cation coordination into account. © 1986 Academic Press, Inc.

INTRODUCTION

The surface chemistry of chromia has been the subject of considerable research interest in the past (*1*). High-surface-area materials exist in either amorphous or microcrystalline form (*1, 2*) depending on the preparation conditions, and these forms have been shown to differ in their catalytic properties (*3*). After exposure to water vapor, the chromia surface is terminated by hydroxyl groups which can be removed by thermal treatment. This leads to condensation of adjacent hydroxyl groups, desorption of water, and exposure of coordinatively unsaturated (cus) Cr^{3+} and O^{2-}ions (*1*). Reduction of Cr^{3+} to Cr^{2+} in bulk α-Cr_2O_3 is extremely difficult, but may be possible at sufficiently high temperatures for surface cus Cr^{3+} (*1*). Oxygen is adsorbed rather strongly on the chromia surface. This excess oxygen was thought to bind to cus Cr^{3+} sites as follows (*1, 4*):

$$Cr^{3+}\square + O_2 \rightarrow Cr^{4+}O_2^{-}. \qquad (1)$$

However, Zecchina *et al.* (*5*) have demonstrated that O_2 adsorption is dissociative at room temperature and that $\equiv Cr{=}O$ groups are formed. At higher temperatures oxygen chemisorption is more complex and presumably also leads to formation of Cr^{5+} and Cr^{6+} in the surface (*4, 5*). Hence, depending on the pretreatment conditions, α-Cr_2O_3 can expose a large variety of sites which differ in chromium oxidation state, coordination number, and the nature and distribution of ligands (O^{2-} or OH^-, depending on degree of hydroxylation).

Carbon monoxide adsorption has frequently been used for the characterization of chromia surfaces (*1, 6–10*). Burwell *et al.* (*1*) have suggested coordination of CO to cus Cr^{3+} on surfaces which did not contain any excess oxygen:

$$Cr^{3+}\square + CO \rightarrow Cr^{3+} \leftarrow CO, \qquad (2)$$

and they considered the amount of CO adsorbed under suitable conditions as a measure of the number of cus Cr^{3+} sites present. Zecchina *et al.* (*9*) have confirmed this view by their IR-spectroscopic studies. They observed a coverage-dependent

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C–O stretching band at 2178–2184 cm^{-1} (shift to lower frequency as coverage increased). After room temperature evacuation, the residual absorption band was located at 2184 cm^{-1} and was asymmetric toward lower frequencies. This band was assigned to a $Cr^{3+} \leftarrow CO$ surface complex with the Cr^{3+} ion being anchored to four surface atoms (O^{2-} and OH^-). The authors speculated that the coverage-dependence of the band position and the tailing of the band might result from intermolecular interactions and from site inhomogeneities.

Recently, Scarano *et al.* (*11, 12*) have analyzed in detail the IR spectra of CO adsorbed on microcrystalline α-chromia (after H_2 treatments to remove excess oxygen). Using isotope dilution (^{12}CO in ^{13}CO), they demonstrated that the position of the carbonyl band is in fact influenced by intermolecular interactions. These are dynamic and static in character. The dynamic interactions are entirely due to dipole–dipole coupling, which leads to a shift of the carbonyl band to higher frequency ($\Delta\nu(CO) > 0$). The static effect is also called "chemical" in that it is thought to be analogous to an inductive effect whereby a CO molecule adsorbed on a cus chromium site reduces the electron acceptor strength of a neighboring site. This effect leads to a shift of the carbonyl band position to lower frequency ($\Delta\nu(CO) < 0$) and, as experimentally observed, overcompensates the dynamic high-frequency shift. Analogous results have been reported by Tsyganenko *et al.* (*13*) for the adsorption of CO on zinc oxide. In conclusion, the band position extrapolated to zero-coverage (experimentally observed at 2184 cm^{-1}) should be unperturbed by intermolecular interactions and may be considered as characteristic of the coordination interaction. Scarano *et al.* (*11, 12*) suggested that CO molecules giving rise to this absorption should be adsorbed on cus Cr^{3+} in trigonal positions; i.e., the Cr^{3+} ions have three oxygen ligands. We will use the notation Cr^{3+}_{3c}, where the subscript indicates the coordination number of the cus cation by oxygen ions.

An additional CO band, which was assigned to CO coordinated to Cr^{3+}_{5c} on prismatic faces, was observed at 2162 cm^{-1} at low temperatures (*11, 12*).

To the best of our knowledge, IR spectra of CO adsorbed on α-chromia surfaces containing excess oxygen have not been reported in the literature. The present work is therefore devoted to an IR-spectroscopic study of CO adsorption on α-chromia after different reductive and oxidative pretreatments. An attempt is made to determine oxidation states and the coordination situation of the cus Cr^{x+} sites. The basis for this approach is the frequently reported dependence of the carbonyl stretching frequency on the electric field strength which the coordination center exerts on the C≡O molecule (*14–20*).

EXPERIMENTAL

Materials

α-Cr_2O_3 was provided by Degussa (West Germany). It was prepared by flame hydrolysis from the chloride. Its purity was 99.9%. The oxide had a N_2 BET surface area of 44 m^2 g^{-1}, and was microcrystalline as shown by the electron micrographs of Fig. 1. The particle morphology is very similar to that described by Scarano *et al.* (*12*), in that the particles typically show irregular octagonal contours which are consistent with a hexagonal prismatic habit of the majority of the microcrystals (*12*). As with the work of Scarano *et al.* (*12*), the exposed faces appear to be flat and well developed and should preferentially consist of the basal hexagonal (0001) and the prismatic $(10\bar{1}0)$ faces. For geometric models of these faces, see Refs. (*9, 11, 12, 14*).

The other oxides used, namely MgO, CeO_2, TiO_2, Al_2O_3, and SiO_2–Al_2O_3, were the same as those used earlier (*15, 16*). The gases O_2, H_2, and CO used were from Linde AG (West Germany) and had a nominal purity of 99.997%. H_2 and CO were

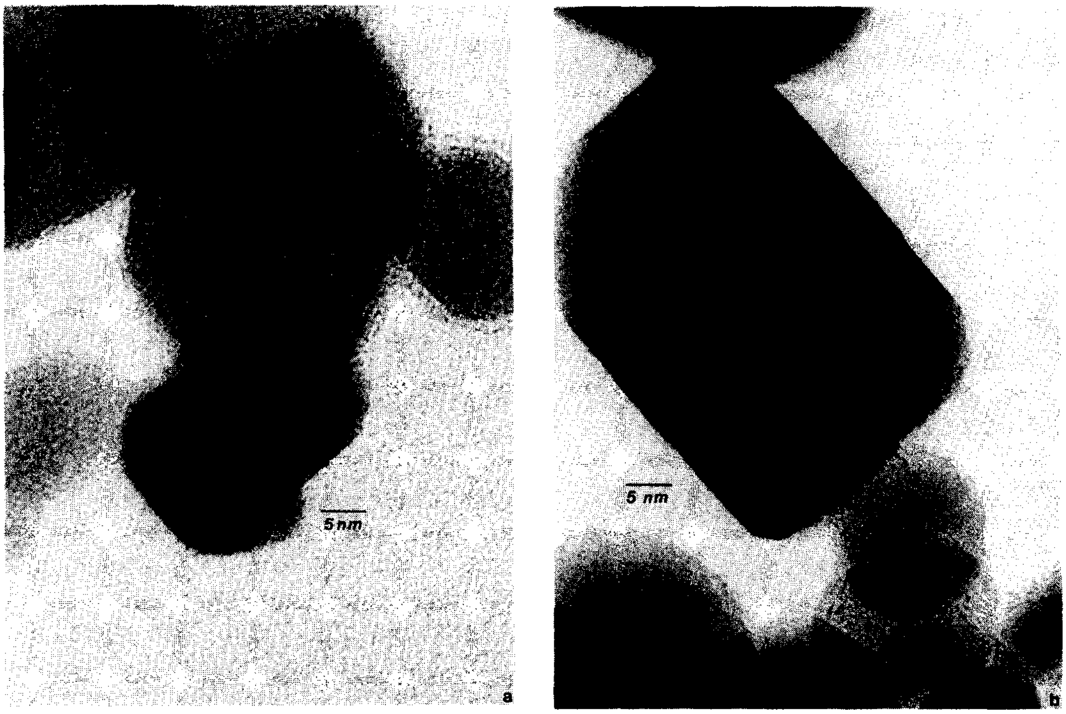

Fig. 1. Electron micrographs of α-Cr_2O_3 (as prepared).

further purified prior to application by passing the gases through Oxisorb and cold traps.

Infrared Spectroscopy

IR carbonyl spectra were recorded in the frequency range from 2400 to 1900 cm^{-1} on a Perkin–Elmer spectrophotometer type 580 B at a resolution of 5.2 cm^{-1}. The samples were pressed (at 10 tons cm^{-2}) into infrared-transparent, self-supporting wafers (typically having 20 to 30 mg cm^{-2}); the wafers were mounted on the sample holder of an *in situ* IR cell, the principles of which were described previously (*17*). The cell was modified so as to permit spectroscopy in the temperature range 80 to 300 K (*18*). Spectra were recorded at 80 K under varying pressures of CO (0.5–40 Torr; 1 Torr = 133.3 N m^{-2}) or under a constant CO pressure of 40 Torr and variable temperatures (80–300 K). The stability of surface species formed on adsorption was further tested by desorption (evacuation at 10^{-5} Torr) experiments.

Pretreatment Procedures

The α-Cr_2O_3 was pretreated *in situ* in the heating zone of the IR cell in three different ways, designated I, II, and III. The Roman numerals will be used in the text to denote the treatment which a sample under consideration has experienced.

Treatment I. This consisted simply in evacuation of the sample at 10^{-5} Torr at 670 K for 60 min, followed by cooling of the sample to the adsorption temperature under dynamic vacuum.

Treatment II. This consisted in reduction in flowing H_2 (50 cm^3 min^{-1}) at 770 K for 60 min to remove all excess oxygen. The sample was then evacuated (10^{-5} Torr) at 770 K for 30 min to remove adsorbed water and to produce a partially dehydroxylated surface; finally, the sample was cooled to the adsorption temperature under dynamic vacuum.

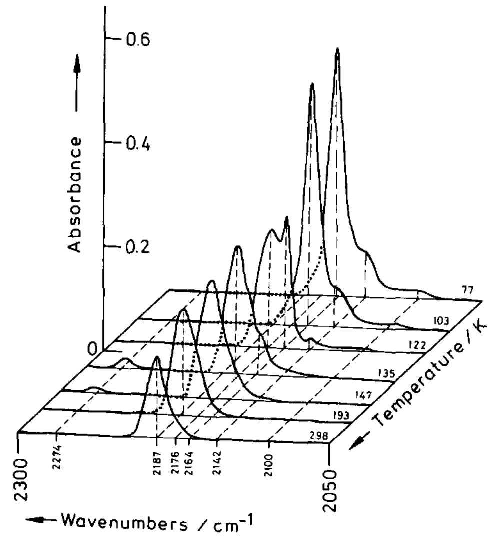

FIG. 2. Temperature dependence of carbonyl IR spectra of CO (40 Torr) adsorbed on α-Cr_2O_3(II).

Treatment III. This consisted in heating the sample in flowing O_2 (50 cm^3 min^{-1}) at 570 K for 30 min so as to produce an "oxidized" sample containing excess oxygen. This treatment was followed by evacuation (10^{-5} Torr) at 570 K for 60 min and cooling to the adsorption temperature under a dynamic vacuum.

RESULTS

The carbonyl IR spectra of CO adsorbed on the thermoevacuated α-Cr_2O_3(I) in the temperature range 77–250 K were complex, the most prominent feature being located at 2164 cm^{-1}. This band was asymmetric toward higher frequencies and showed distinct shoulders at intermediate temperatures. In addition a shoulder also occurred at 2142 cm^{-1}. The principal band at 2164 cm^{-1} probably contained contributions from H-bonded CO in the low-temperature regime (*16*). Physically adsorbed CO typically absorbs near the gas-phase frequency (2143 cm^{-1}) and should therefore contribute to the shoulder at 2142 cm^{-1} at the lowest temperatures of 77–100 K. In the presence of 40 Torr CO, however, this band vanishes only around 270–280 K, indicating an additional CO surface complex. At room temperature in the presence of CO, the spectrum consists of a composite band centered at 2166 cm^{-1} with a distinct shoulder at 2180 cm^{-1}. The corresponding surface complexes decompose slowly on evacuation with the band positions shifting slightly to higher frequencies.

Figure 2 shows the temperature dependence of the carbonyl spectra of CO adsorbed (at 40 Torr) on the H_2-reduced specimen α-Cr_2O_3(II). These spectra show two major bands at 2164 cm^{-1} and between 2176 and 2187 cm^{-1}. Much weaker bands are observed at temperatures below 130 K at 2142 and 2100 cm^{-1}. At 77 and 103 K the dominant feature in the spectra is the band at 2164 cm^{-1}, the intensity of which decreases only slightly when the temperature is increased from 77 to 103 K. This drop in intensity may be due to desorption of H-bonded CO. A subsequent temperature increase to 120 K leads to an abrupt decrease in intensity of this band and a new intense band develops at 2176 cm^{-1}. The position of this band shifts to higher frequencies as the temperature is further increased (coverage decreased) while its intensity slowly decreases. The band at 2164 cm^{-1} has almost completely vanished at 147 K. When room temperature is reached, only one asymmetric band at 2187 cm^{-1} is observed. The position of this high-frequency band, which first appears at 2176 cm^{-1} in the spectra at 120 K, is clearly temperature-dependent, and hence coverage-dependent.

It is interesting to note that the positions of the two bands observed at room temperature on α-Cr_2O_3(I), namely those at 2180 and 2166 cm^{-1}, are very close to the positions of the two strongest bands on α-Cr_2O_3(II) although their temperature behavior appears to be different. The high-frequency band was also observed by Scarano *et al.* (*11*, *12*) between 2170 and 2185 cm^{-1} at room temperature, the position of the band shifting to higher frequency with decreasing coverage. The same au-

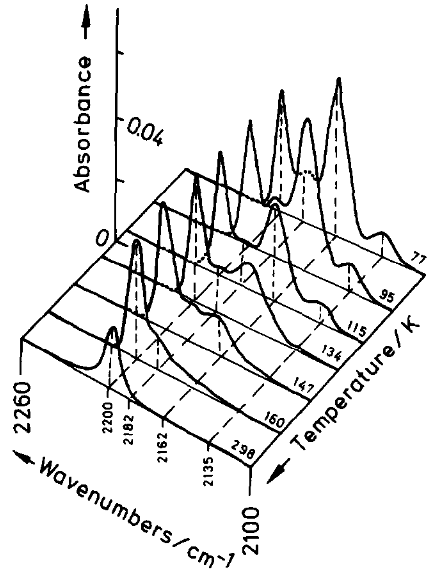

FIG. 3. Temperature dependence of carbonyl IR spectra of CO (40 Torr) adsorbed on α-Cr_2O_3(III).

thors reported the appearance of a shoulder at ~2162 cm^{-1} at low temperatures, which, however, never appeared as the dominant band in the spectra. Also, Scarano *et al.* (*11, 12*) did not observe the abrupt formation of the high-frequency band as shown in Fig. 2.

The spectra observed on CO adsorption on α-Cr_2O_3(III) containing excess oxygen are displayed in Fig. 3. At 77 K four weak bands are clearly resolved, namely at 2135, 2162, 2182, and 2200 cm^{-1}. The positions of these bands do not depend on temperature or coverage; their intensities, however, respond to temperature increase very distinctly, thus indicating significantly different thermal stabilities for the corresponding surface complexes. The band at 2135 cm^{-1} is entirely eroded at 147 K, while the band at 2162 cm^{-1} still persists at this temperature. The band at 2182 cm^{-1} is still more stable and is observed as a shoulder at 160 K. Clearly, the surface complex characterized by the higher carbonyl frequency is the more thermally stable. The position of the band at 2182 cm^{-1} closely coincides with the frequency range of the high-frequency band on α-Cr_2O_3(II). However, the band position on α-Cr_2O_3(III) is not coverage-dependent and, moreover, the corresponding species is significantly less stable than that giving rise to the high-frequency band on α-Cr_2O_3(II). These observations clearly suggest that the surface complexes are different on the two differently pretreated chromia surfaces.

The thermal stability of the band at 2200 cm^{-1} on α-Cr_2O_3(III) is exceptional. The intensity of this band (Fig. 3) remains constant in the temperature range from 77 to 160 K and drops to approximately 50% of its initial value at 300 K.

DISCUSSION

Two major questions must be addressed. (i) What is the reason for the abrupt appearance of the high-frequency band on α-Cr_2O_3(II) at approximately 120 K ? and (ii) Can the observed carbonyl frequencies be correlated with oxidation states and coordination numbers of the Cr^{x+} site?

Sample α-Cr_2O_3(II) was reduced in flowing hydrogen at 770 K to remove excess oxygen. Scarano *et al.* (*11, 12*) pretreated their sample in H_2 at 970 K, but in a static system. They assigned the high-frequency band (2170–2185 cm^{-1}) to CO coordinated to Cr^{3+}. The coverage dependence was explained as being due to dynamic and static adsorbate–adsorbate interactions, the importance of which was experimentally demonstrated by isotope dilution (^{12}CO in ^{13}CO). For these adsorbate–adsorbate interactions to occur, it is necessary that the CO oscillators vibrate with identical intrinsic frequencies (i.e., identical coordination sites) and that the oscillators are parallel and located in close proximity. In their model considerations, Scarano *et al.* (*11, 12*) have therefore suggested a surface which is flat on an atomic scale (see Scheme II in Ref. (*12*)). This plane was thought to be derived from the neutral hexagonal (0001) face, which consists of alternately occupied and unoccupied rows of oxygen ions in the outermost atomic layer.

Removal of these parallel rows of oxygen ions together with an equivalent amount of Cr^{3+} ions to maintain electrical neutrality leads to the required atomically flat surface, in which Cr^{3+}_{3c} ions are exposed in trigonal positions in the outermost layer. Hence, the proposed adsorption complex is a $Cr^{3+}_{3c} \leftarrow CO$ complex. It must, however, be mentioned that the proposed surface model with Cr^{3+} in low coordination being exposed is certainly not an energetically favorable situtìon, although it might be forced under the rather severe reduction conditions applied by Scarano *et al.* (*11, 12*). In any case, these authors observed the development of the high-frequency band spontaneously on admission of CO at 77 K.

In contrast, as described above, the band developed abruptly on α-Cr_2O_3(II) in our experiments when a temperature of approximately 120 K was reached. It seems that simultaneously the band intensity at 2164 cm^{-1} dropped abruptly, thus suggesting a possible interconversion of the two corresponding surface carbonyl complexes. The close correspondence of the band positions and the similar coverage-dependence suggests that we are indeed observing the same surface complexes as Scarano *et al.* (*11, 12*). They assigned the 2162 cm^{-1} band to CO coordinated on Cr^{3+}_{5c} ions, which are located on the prismatic $(10\bar{1}0)$ faces. The spectra in Fig. 2 show that the band at 2164 cm^{-1} is by far the most prominent at temperatures below 120 K, before the high-frequency band becomes built up. Assuming that the assignment of Scarano *et al.* (*11, 12*) is correct, then we must conclude that α-Cr_2O_3(II) preferentially exposes cus Cr^{3+}_{5c} ions. The abrupt formation of the high-frequency species can then only be explained by either contamination of coordinatively more unsaturated sites (Cr^{3+}_{3c} or Cr^{3+}_{4c}) and displacement adsorption at 120 K, or by a CO-induced reorganization of at least patches of the surface large enough to allow for the intermolecular interactions. We are not in a position at present to make a clear decision between these alternatives nor can we discuss a possible surface reorganization in any more detail. We believe, however, that a CO-induced change of the coordination of surface cations to oxygen ions cannot in principle be ruled out.

At this point we can conclude that the carbonyl stretching band at 2164 cm^{-1} is to be assigned to a CO molecule which is coordinated to a Cr^{3+}_{5c} ion, while the high-frequency band (2170–2187 cm^{-1}) should be attributed to a $Cr^{3+}_{3c} \leftarrow CO$ surface complex, according to Scarano *et al.* (*11, 12*). However, the possibility of a Cr^{3+}_{4c} center being the coordination site should not yet be entirely ruled out (see below).

Oxygen treatments at 570 K should produce Cr^{x+} ions in oxidation states higher than +3 (*1, 4, 5*). Chromium chromate species have been suggested to exist on the chromia surface after oxidative treatment (*5*), in which the Cr^{6+}/Cr^{3+} pairs can undergo *d–d* electron exchange interactions (*19, 20*). The spectra shown in Fig. 3 for α-Cr_2O_3(III) seem to be consistent with the creation of Cr^{x+} ions with $x > 3$. Particularly the band at 2200 cm^{-1} must be attributed to a coordination site in high oxidation state. The high frequency and the high stability of the respective surface CO complex can only be explained on this basis. We suggest tentatively Cr^{5+}_{5c} ions. Additional support for this assignment will be given below. The position of the band observed at 2182 cm^{-1} is close to that of the high-frequency band of α-Cr_2O_3(II); however, the stability of the corresponding surface complex appears to be lower than that of the proposed $Cr^{3+}_{3c} \leftarrow CO$ (or $Cr^{3+}_{4c} \leftarrow CO$) complex (compare Figs. 2 and 3). On the other hand, it is more stable than the $Cr^{3+}_{5c} \leftarrow CO$ complex with the characteristic frequency at 2164 cm^{-1}. Therefore, it is possible to infer a Cr^{4+} site in a high coordination state, e.g., Cr^{4+}_{5c}. Hence, a surface complex $Cr^{4+}_{5c} \leftarrow CO$ is expected to be present on the α-Cr_2O_3(III) surface. The band at 2162 cm^{-1} is attributed to $Cr^{3+}_{5c} \leftarrow CO$ as described above.

In addition to the bands discussed above, absorptions (although relatively weak) were observed near or below the gas-phase frequency of CO (2143 cm^{-1}). α-Cr_2O_3(I) and α-Cr_2O_3(II) developed a band at 2142 cm^{-1} which can also be seen in the low-temperature spectra of Scarano *et al.* (*12*). These authors, however, did not discuss this band in any detail. It can only be speculated that the band corresponds to a CO ligand which is coordinated to a low-valent Cr^{2+} ion with d^4 electron configuration so that d-π^* back-donation contributes to the coordination bond. The existence of Cr^{2+}, at least on the H_2-reduced α-Cr_2O_3(II), is possible (*1*, *21*). This same sample also exhibits a weak band at 2100 cm^{-1} below ~130 K. Speculatively, we ascribe this band to a CO molecule bridging two adjacent cation sites. Finally, a band at 2135 cm^{-1} appears at temperatures below 135 K on α-Cr_2O_3(III). Chromium oxidation states lower than 3+ are certainly not to be expected on this sample containing excess oxygen. Zecchina *et al.* (*9*) had also observed a band near 2130 cm^{-1} on α-Cr_2O_3 after reduction in CO at 670 K. They were unable to assign this band but they excluded Cr^{2+} ions as possible coordination sites. In the present case the only speculative interpretation may then again be a bridging CO involving chromium ions in higher oxidation states.

In the following, an attempt will be made to support the assignments given above for the principal bands which were observed at frequencies higher than the gas-phase frequency of CO. Positive frequency shifts relative to the gas-phase frequency are typically observed when CO is coordinated to high-valent cations via a σ-donor bond involving the 5σ lone pair electrons on the C atom. This bonding type is the only possible one for cations with d^0 electron configuration. If d electrons are available, d-π^* back-bonding contributions to the coordination bond may be nonnegligible and would lead to an additional frequency shift of opposite sign. At least for d^0 cations, the bonding can be discussed based on a purely electrostatic model. As a consequence, an increasingly positive frequency shift of the C–O stretching frequency is expected with increasingly positive charge on the cation center. Implicitly, this principle has been applied in the previous discussion in this paper (vide supra).

Hush and Williams (*22*) have shown theoretically that the C–O stretching frequency should increase monotonically with the electric field strength of the (d^0) cation center. Several examples of such correlations have in fact been reported (*15*, *23–27*). In calculations of the electric field strength, the effect of cation neighbors must be taken into account. This was considered by Angell and Schaffer (*23*) and by Larsson and co-workers (*25*). Harrison and Thornton (*24*), on the other hand, in their attempts to correlate C–O stretching frequencies with the electric field strength exerted by cations which were anchored onto a SnO_2 surface, calculated the electric field strength F as

$$F = eZR^{-2} \tag{1}$$

where eZ is the formal charge of the cation and R is equal to the sum of the effective ionic radius and the van der Waals' radius of the C atom (0.15 nm). Obviously, Eq. (1) entirely neglects all contributions to the electric field strength from neighboring surface atoms. Harrison and Thornton (*24*) have proposed to include these contributions by modifying Eq. (1) by an additive term:

$$F = eZR^{-2} + K, \tag{2}$$

where K is constant for cations in comparable environments.

In earlier papers (*15*, *27*), we have suggested an alternative empirical approach to account for the coordination of the central ion in the oxide surface by calculating the strength of the electrostatic bond

$$s = \frac{Z}{N}, \tag{3}$$

which is defined by Pauling (*28*) as the ratio of the cation charge Z and its coordination

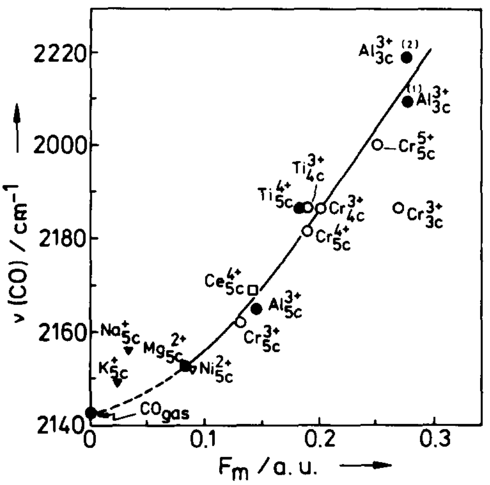

FIG. 4. Correlation between ν(CO) and electric field strength F_m (arbitrary units): Al^{3+}_{3c}(1) refers to Al_2O_3, Al^{3+}_{3c}(2) to SiO_2–Al_2O_3; (●, ▼) cations having d^0 electron configuration; (○, ▽) cations having d^n ($n \neq 0$) electron configuration; (□) tentative assignment.

number N. A modified electric field strength F_m is then defined as

$$F_m = sR_m^{-2}, \qquad (4)$$

where R_m is calculated as outlined above by using effective ionic radii of the central cation in the considered coordination, as compiled by Shannon (*29*). The electric field strength calculated in this way is very sensitive to the cation coordination, since the coordination number not only influences the strength of the electrostatic bond s but also the R_m value which enters as the square in Eq. (4).

For correlations to be established with C–O stretching frequencies, mechanical coupling effects and effects of adsorbate–adsorbate interactions should be eliminated. Mechanical coupling effects (between M–CO and MC–O stretching vibrations) can be estimated following the procedure described by Okawa *et al.* (*30*). The accuracy of these estimates is limited since the frequencies of the metal–carbon stretching mode are not known. Our estimates resulted in shifts of less than 5 cm^{-1} maximum. The experimentally observed frequencies have therefore not been corrected for mechanical coupling effects for the present purpose.

Adsorbate–adsorbate interaction effects can be eliminated by considering only frequencies extrapolated to zero coverage where neither dynamic nor static interactions perturb the C–O stretching frequency. This latter condition was not strictly observed in our previous correlations (*15*). Therefore, we present here a refined correlation in Fig. 4, in which only C–O frequencies for CO adsorbed on MgO, Al_2O_3, SiO_2–Al_2O_3, and TiO_2 surfaces which correspond to vanishing coverage are used. The frequency values measured in our laboratory coincided very closely (to within ±2 cm^{-1}) with values reported by Zecchina *et al.* (*31*) and Della Gatta *et al.* (*32*) for Al_2O_3, by Morterra *et al.* (*33*) for TiO_2, and by Escalona Platero *et al.* (*34*) for MgO.

In calculating the s-values, the effective cation coordination number N in the considered cus state of the cation was taken into account. The effective ionic radii were taken from the compilations of Shannon (*29*). Some approximations are necessary here, since effective ionic radii are not reported for all possible coordinations of surface cus cations. Hence, as a first approximation the reported ionic radii for tetrahedral coordination are applied for 3*c*- and 4*c*-cations, while the effective ionic radii in octahedral coordination are used for 5*c*-cations.

Considering only the data points in Fig. 4 for Mg^{2+}_{5c}, Al^{3+}_{5c}, Al^{3+}_{3c} (in Al_2O_3 and SiO_2–Al_2O_3), and Ti^{4+}_{5c} (which have exclusively d^0 electron configuration), and including the gas-phase frequency (2143 cm^{-1}) at $F_m = 0$, a nonlinear correlation seems to result. The theoretically predicted correlation is also nonlinear, as shown by Hush and Williams (*22*). An additional experimental point is included in this correlation, which we tentatively assigned to Ce^{4+}_{5c}. Admittedly, the number of data presently available to support this type of correlation is rather limited. Nevertheless, we believe that this empirical correlation is promising and should provide a means of determining oxidation states and coordination numbers of cus surface cations from experimentally determined C–O stretching frequencies.

We will test this approach using the data obtained in the present paper for the adsorption of CO on α-Cr_2O_3. The corresponding points are included in Fig. 4. It turns out that Cr^{5+}_{5c}, Cr^{4+}_{5c}, and Cr^{3+}_{5c} according to the assignments given above fit the correlation line surprisingly well. F_m values were calculated for each oxidation state for 3*c*-, 4*c*-, and 5*c*-coordination states. The data points for all other coordinations but the 5-coordinate state fall unrealistically far off the correlation curve. However, in the case of Cr^{x+} centers, d-π^* back-bonding contributions may influence the stretching frequency. The *d*-electron density for Cr^{5+} (d^1) and Cr^{4+} (d^2) is low, so that to the best of our knowledge the σ-donor bond should be the dominating factor with these highly charged metal centers. Cr^{3+} has d^3 electron configuration. In the 5-coordinated state, however, the cation may be sufficiently shielded by the oxygen ligands so that d-π^* overlap with the CO ligand is minimal. In fact, Scarano *et al.* (*12*) concluded from their study of intermolecular interactions that d-π^* back-bonding was negligible in the $Cr^{3+}_{5c} \leftarrow CO$ complex.

The case of the high-frequency band at 2187 cm^{-1} which is observed on α-Cr_2O_3(II) is intriguing. If the assignment of Scarano *et al.* (*12*) is considered, i.e., $Cr^{3+}_{3c} \leftarrow CO$, the corresponding point for Cr^{3+}_{3c} deviates considerably from the correlation line, the frequency being lower by approximately 25 cm^{-1} than that expected. This, however, can be accounted for by significant d-π^* contributions to the coordination bond as observed by Scarano *et al.* (*12*) by their isotope dilution experiments. On the other hand, assuming 4-coordination for the Cr^{3+} cation and negligible d-π^* back-donation, the Cr^{3+}_{4c} falls neatly on the correlation curve (see Fig. 4). The present approach would certainly not permit a decision between these two alternatives. The experimental evidence provided by Scarano *et al.* (*12*) must undoubtedly lead to preference of the first alternative (i.e., $Cr^{3+}_{3c} \leftarrow CO$), although it must still be noted that the crystallographic plane suggested by these authors is energetically unfavorable.

Finally, a comment regarding the data for TiO_2 needs to be made. The carbonyl stretching frequency for CO adsorbed on partially dehydroxylated TiO_2 (anatase) was consistently reported to be 2178–2184 cm^{-1} (*15, 26, 33, 35*). In a study of TiO_2 supported on SiO_2 (*35*), we observed 2180–2188 cm^{-1} on thermoevacuated samples and 2178–2183 cm^{-1} on samples reduced in flowing H_2 at 773 K. During the course of the present work, we have included TiO_2 (rutile) and observed again a band at 2182 cm^{-1} (extrapolated at zero coverage) on thermoevacuated as well as on H_2-reduced samples. We therefore tend to believe that the coordination site for CO on TiO_2 surfaces is in fact a Ti^{3+} cation center on thermoevacuated (oxygen loss leads to TiO_{2-x}) and H_2-reduced materials. This assumption, however, can only be brought into conformity with the correlation of Fig. 4 if the Ti^{3+} center is 4-coordinated. An alternative explanation might be the formation of $Ti^{4+}_{5c} \leftarrow CO$ complexes on H_2-reduced surfaces which can hardly be differentiated on the basis of their carbonyl frequencies as shown in Fig. 4.

Also included in Fig. 4 are data for CO adsorption at 77 K on NaCl (*36*), KCl (*37*), and NiO (*38*). The data points for $Na^+ \leftarrow CO$ and $K^+ \leftarrow CO$ deviate from the correlation toward higher frequencies. This is probably due to the fact that the cations are coordinated, by Cl^- anions rather than by oxygen ligands. The value for CO adsorbed on NiO (100) faces on which 5-coordinated Ni^{2+} (d^8) ions are exposed, is close to the correlation line. This is surprising in view of the highly occupied *d* orbitals of Ni^{2+} which have the right energy and symmetry to overlap the σ and π^* orbitals of coordinated CO molecules (*38*). Further studies are required to understand this result and the role of *d* electrons in determining the frequency of CO molecules on transition metal cationic sites.

CONCLUSIONS

In the present study we have demonstrated, in agreement with previous results of other authors (*1, 11, 12*), that H_2-treated α-Cr_2O_3 exposes preferentially Cr^{3+} cations in different coordinations and possibly some Cr^{2+} ions. Samples containing excess oxygen possess cus Cr^{4+} and Cr^{5+} in addition to Cr^{3+} ions in the surface. The various oxidation states can be detected by IR spectroscopy of adsorbed CO. A correlation between the C–O stretching frequency and a modified electric field strength also provides the possibility of assigning the coordination state of the cus cations. Although this empirical correlation is still based on a limited number of experimental data, we believe that it is a useful and simple approach toward the characterization of cus cation sites, provided d-π^* back-donation in the coordination bond can be neglected. It must be admitted, however, that the possible influence of surface (or site) relaxation and of metal–oxygen bond covalency has not been taken into account. Also, the effect of the CO induced heterogeneity can be eliminated by extrapolation of the C–O stretching frequency to zero coverage. This procedure, however, may suffer from intrinsic heterogeneities due to variable distribution of O^{2-} and OH^- ligands for cations having identical oxidation states and coordination numbers. Nevertheless, in view of the results presented here we believe that this empirical approach can be further developed successfully as a simple method for the characterization of cus cation sites on oxide and possibly other (sulfide) surfaces.

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