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Infrared Study of the Nature and Localization of Some Forms of Oxygen Adsorbed on the α-Chromia Surface

The concentration of excess oxygen on the surface of α-chromia strongly depends on the pretreatment conditions. Moreover, quite different values are determined by various methods (*1–3*), probably because of the different adsorption forms. For this reason it was of interest to attempt to determine the characteristics of each form separately. Here we discuss the nature and localization of oxygen adsorbed on Cr_2O_3 and producing IR bands in the region 970–1020 cm^{-1}.

Chromia was obtained by thermal decomposition of ammonium dichromate followed by calcination in air at 500°C (*4*). The electron microphotographs, taken with a JEM-100-B apparatus, revealed a polyhedral shape of the particles. The BET surface area of the sample was 44 m^2/g and showed only a small change during the experiments. For the IR studies, pellets of the appropriate thickness were prepared. All IR experiments were performed with a UR-20 spectrometer in the region 700 to 4000 cm^{-1}. A vacuum apparatus ensuring a residual pressure below 10^{-4} Torr (1 Torr = 133.3 N m^{-2}) was used. A calibrated gas burette connected to the IR cell was utilized for introducing definite amounts of gas in the cell. Prior to the experiments, the samples were subjected to repeated heat treatment at 400°C under vacuum and under oxygen (100 Torr) to remove eventual organic impurities and adsorbed water.

The IR spectrum of Cr_2O_3 evacuated at 500°C for 2 h (Fig. 1,**1**) shows low-intensity bands with maxima at 890, 920, 975, 1045, 1145, and 1235 cm ^{1} which are characteristic of an unoxidized chromia surface (*3–5*). The absence of any bands at 1200–1700 cm^{-1}, where the stretching vibrations of CO_3^{2-} groups and the H–O–H deformation modes are observed (*6*), indicates that no measurable amounts of carbonates and adsorbed water are present on the surface. At 3000–3800 cm^{-1}, the region of O–H stretching modes, no bands were observed either; i.e., the surface was completely dehydroxylated. The sample thus treated was subjected to 1 h oxidation (P_{O_2} = 100 Torr) at 500°C, then cooled to room temperature in the same atmosphere and evacuated. Three intense bands with maxima at 980, 995, and 1015 cm^{-1} appeared in the IR spectrum, while the background bands in the lower-frequency region changed negligibly (Fig. 1,**2**). All three bands characterize metal–oxygen stretching modes (*3–5*). Portions of ammonia were successively admitted to the oxidized sample. This was accompanied by the appearance and increase in intensity of two bands with maxima at 1220 and 1610 cm^{-1} characterizing δ_s and δ_{as} of coordinatively bonded ammonia, respectively. The increase in the amount of adsorbed ammonia led to a gradual decrease in the intensity of the band at 1015 cm^{-1} (Fig. 1,**3**). At a maximum ammonia saturation of the surface this band completely disappeared (Fig. 1,**4**). The coefficient of extinction of coordinatively bonded ammonia, calculated using the dependence of the absorption at 1220 cm^{-1} on the amount of adsorbed ammonia, was 0.11 cm^2 μmol^{-1}.

Figure 1 (**5**) shows the spectrum of an unoxidized sample (its state as in Fig. 1,**1**) after ammonia adsorption. The adsorption in this case leads to the appearance of four bands in the region 1000–1700 cm^{-1}, at 1610, 1215, 1150, and 1110 cm^{-1}. The three

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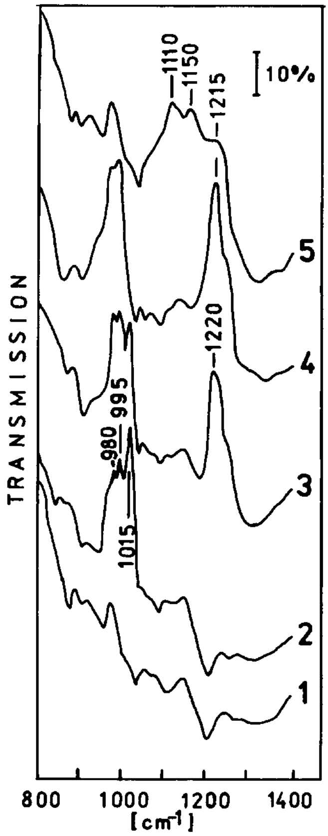


FIG. 1. IR spectra of Cr_2O_3: (**1**) background evacuated at 500°C; (**2**) after oxidation at 500°C followed by evacuation at room temperature; (**3**) after introduction of 4.25 μmol NH_3; (**4**) saturation with NH_3; (**5**) NH_3 adsorbed on a sample treated as described under step "1".

latter bands characterize the symmetric deformation vibrations of three kinds of surface M–NH_3 complexes, whereas the band at 1610 cm^{-1} corresponds to the asymmetric deformation modes of the three complexes and is insensitive to the Lewis site acidity.

The nature of oxygen, giving bands in the region 970–1020 cm^{-1} when adsorbed on α-chromia, has been discussed previously (*1–5, 8, 9*). It is established by isotopic exchange that oxygen adsorption is dissociative (*8*) and the order of the Cr–O bond is close to 2 (*5*). Indeed, the double metal–oxygen bond is in principle observed between 900 and 1100 cm^{-1} (*9*). Comparison of the $V^{4+}{=}O$ and $V^{5+}{=}O$ stretching modes (*6*) indicates that the more electropositive the metal ion, the higher the corresponding frequency of vibration. In brief, the three bands under consideration are due to oxygen connected by a double bond to chromium ions possessing different electropositivities.

The most advanced and popular model of the α-chromia surface was proposed by Zecchina *et al.* (*5*). According to them, the excess oxygen (they also considered the bands at 880–900 cm^{-1}) is located on the (001) chromia plane and its varying spectral behavior is due to different degrees of surface dehydroxylation. The bands in the region 970–1020 cm^{-1} cannot be explained in such a way since they were observed on a completely dehydroxylated surface. Furthermore, the (0001) plane [001 in Ref. (*5*)] cannot be the only one exposed on the chromia surface. For crystals of the corundum type, such as α-chromia, the (0001), $(11\bar{2}0)$, $(10\bar{1}0)$, $(11\bar{2}1)$, $(22\bar{4}1)$, $(22\bar{4}3)$, $(20\bar{2}1)$, $(10\bar{1}1)$, $(10\bar{1}2)$, $(10\bar{1}4)$, and $(14\ 14\ \overline{28}\ 3)$ planes are characteristic of the surface (*10*). The adsorbed oxygen should occupy oxygen vacancies, i.e., the places of bulk oxygen if the lattice is not limited. Figure 2 shows schemes of some chromia planes (the structures presented being also characteristic of planes that are not given here) and some possible sites for oxygen adsorption. Obviously, on the basis of steric considerations, excess oxygen on (0001) and $(10\bar{1}0)$ planes will be connected with two chromium ions simultaneously. As a result, the order of the Cr–O bond will be close to one and the corresponding stretching frequencies will be below 970 cm^{-1}. Moreover, by analogy with the MgO and anatase surfaces (*11*) and on the basis of a number of results showing the relatively low oxygen coverage on Cr_2O_3, it can be concluded that the five-coordinated chromium ions are inert toward adsorption of some reagents, especially oxygen. Therefore, the considered bands are due to oxygen connected to the four-coordinated

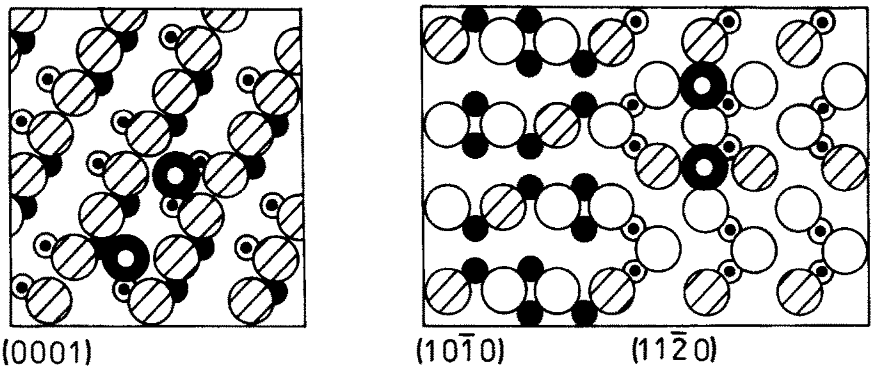


FIG. 2. Scheme of some planes of stoichiometric Cr_2O_3. ●, Five-coordinated Cr^{3+}; ⊙, four-coordinated Cr^{3+}; ○, three-coordinated O^{2-}; ⊘, two-coordinated O^{2-}; ◉, to be adsorbed oxygen.

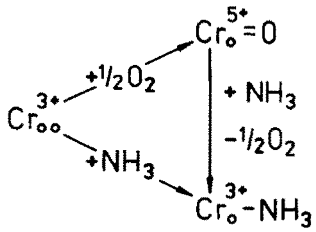
chromium ions situated on some of the side crystal faces.

The electrophilic properties of metal ions with equal coordination numbers may strongly differ depending on the coordination state of the ligands (*12*). The surroundings of a metal ion can be expressed as $M^{n+}(X_1 - X_2 \ldots X_m)$. The number of figures in parentheses shows the coordination number of the metal ion; each figure denotes the number of vacancies of the corresponding ligand. The higher the coordination saturation of the ligands (the smaller the sum of the figures in parentheses), the smaller the compensation of the central metal ion charge and the higher its electrophility. Thus, the four-coordinated Cr^{3+} on the chromia surface can be classified as follows:

α Cr^{3+} (2–0–0–0)
(on the (0001) basal plane)
β Cr^{3+} (1–1–0–0)
γ Cr^{3+} (2–1–0–0) } on some side planes
δ Cr^{3+} (2–1–1–0)

In the three latter forms each chromium ion may be connected with one additional oxygen atom. Following this scheme, bands at 1015, 995, and 980 cm^{-1} can be attributed to oxygen adsorbed on β, γ, and δ sites, respectively. Let us consider these three sites. The β sites, being the most acidic ones, will form the most stable complexes with ammonia. On the contrary, after oxidation, the corresponding Cr^{5+} ions, having a larger amount of uncompensed charge, will manifest the highest reducibility. For this reason, ammonia replaces oxygen from β sites only. Such a replacement does not contradict the thermal stability of ammonia and oxygen which are adsorbed on α-chromia (*4*). Interaction of NH_3 with reduced and oxidized β sites may be expressed as shown in Scheme 1, where o represents a coordination vacancy.

Using Scheme 1, we indirectly calculated the extinction coefficient of the band at 1015 cm^{-1}. Its value was 0.13 cm^2 μmol^{-1}. The similarity in structure of the three kinds of $Cr^{5+}{=}O$ groups, their stretching frequencies, and the spectral half-widths of the corresponding bands allowed us to accept this value for the extinction coefficient of the bands at 995 and 980 cm^{-1}. Then, the concentration of β sites will be 2.8 sites/



SCHEME 1

nm^2, while the total concentration of β, γ, and δ sites will amount to ca. 5 sites/nm^2. This is within the framework of the theoretically expected concentration of four-coordinated Cr^{3+} situated on the side crystal planes of α-chromia.

The proposed determination of the nature and localization of adsorbed oxygen on chromia is in agreement with the experimental results obtained after ammonia adsorption on an unoxidized sample. The three adsorption forms observed correspond to the three sites for oxygen adsorption. The band at 1220 cm^{-1} may also be due to ammonia adsorbed on α sites whose acidity is very close to that of the β sites. Finally, it should be noted that the other kinds of oxygen adsorbed on Cr_2O_3 are likely to be located on sites on edges (not considered here) and on sites connected with hydroxy groups. Perhaps the bands at 890 and 910 cm^{-1} are due to "chromate-like" structures on the (0001) plane whose Cr–O bonds have an order between 1 and 2.

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