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The Chemistry of Silica-Supported Cr Ions: A Characterization of the Reduced and Oxidized Forms of Chromia/Silica Catalyst by Calorimetry and Ultraviolet–Visible Spectroscopy

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CrO_3/SiO_2 samples with low Cr loading (0.5% Cr by weight) have been prepared by impregnation. Formation of the oxidized surface phase, reduction, thermal deactivation, and reoxidation have been studied. During the initial thermal treatment of the samples, two processes occur. These are anchorage of CrO_3 onto the surface, yielding surface chromates and dichromates, stable toward temperature, and second, degradation of nonanchored CrO_3 to lower valence states, easily reoxidized at 823 K. Reduction with CO at 623 K yields a 98% population of Cr^{II}. Four species of such ions (with different electronic transitions) are present at the surface: two are reactive (Cr_A and Cr_B) and two less reactive (Cr_{C1} and Cr_{C2}). Thermal deactivation converts Cr_A into Cr_C and does not affect Cr_B. A fraction of Cr_C (at least some 30%) is unavoidably present at the surface. In the most active samples Cr_A is about 45% and Cr_B about 25%. Reoxidation of Cr_A and Cr_B occurs with comparable reaction heats (480 and 425 kJ, respectively) via a nonactivated process. Cr_C oxidation is strongly activated and occurs under O_2 pressure.

INTRODUCTION

Because of its widespread industrial usage as the Phillips catalyst for ethylene polymerization, the CrO_3/SiO_2 system has been subjected in the past to an extensive investigation. A substantial contribution to the understanding of its properties came a few years ago from Krauss and coworkers (*1–4*): one of our two laboratories contributed in the same period to such an effort with a series of papers (*5, 6*). Several papers by other authors have since appeared, the most recent ones being those by Groeneveld *et al.* (*7, 8*).

A number of points remain which are either not fully understood or still debated. As to the catalyst before any reaction (both in the oxidized and in the reduced form), we single out the following points:

(a) Different surface structures (chromate or dichromate) have been proposed for the oxidized phase (*3, 5, 7, 9*);

(b) little work has been devoted to the mechanism of anchorage of CrO_3 to the surface: the actual range of temperature in which it occurs is not known precisely (*7, 9*);

(c) although the substantial presence of Cr^{II} in properly reduced samples is now accepted, the occurrence of reactive Cr^{III} is still under discussion (*5, 10*);

(d) Cr^{II} ions with different coordinative situations are known (*5, 6*) to occur on the surface: there is, however, a lack of detail about their actual coordination state.

As to the reoxidation of reduced samples, only data about uptakes are available (*2, 5*), together with a rough estimate of the reaction heat (*2*).

In an attempt to gain further information on some of the above points, we have carried out a study of the oxidized and reduced forms of CrO_3/SiO_2 by means of two rather different techniques, namely, microcalorimetry and uv–vis spectroscopy, the former allowing mainly *quantitative* information on the energetics of surface pro-

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cesses (and to some extent on their kinetics), the latter yielding basically *qualitative* evidence on the state of the catalyst. The coupling of calorimetric and spectroscopic (ir) techniques has already proved useful (*11*).

The system dealt with in this paper is a simplified version of the industrial catalyst, in that: (i) a lower loading is adopted, (ii) nonporous silica is used as support, (iii) in order to reach highest activity, the sample first undergoes a severe dehydration, then an activation in O_2, and is eventually reduced in CO.

In order to study the heterogeneity among Cr^{II} ions, we have investigated systematically the role of thermal deactivation of the catalyst (*5*, *6*), which affects selectively the ions in lower coordination.

EXPERIMENTAL

SAMPLE PREPARATION

Catalyst samples have been prepared (*5*) by impregnation of silica (Aerosil Degussa 2491, nitrogen BET surface area 330 $m^2\ g^{-1}$) with a titrated aqueous solution of CrO_3 (Carlo Erba RP). A chromium percentage close to 0.5% (0.543) in weight was chosen in order to have a catalyst with an appreciable concentration of Cr ions at the surface but still in the range of proportionality between catalytic activity and chromium content (*5*). On the basis that the silica surface area is unaffected by the presence of the load, the chosen percentage corresponds to a nominal surface concentration of 0.31 μmole m^{-2} (1.90×10^{17} Cr ions m^{-2}).

ACTIVATION PROCEDURE

To eliminate water from the surface, freshly prepared samples were outgassed under high vacuum by slowly raising the temperature up to 1023 K in about 6 hr and then maintaining this temperature for about 1 hr. During the thermal treatment, the color of the samples turned gradually from yellow-brown to pale gray. The temperature was then lowered to 823 K and the samples were contacted with 40 Torr (1 Torr = 133 N m^{-2}) of oxygen for 30 min. The samples, after this last treatment, are bright yellow and will hereafter be indicated as S_{ox} (standard oxidized).

The reduced form of the catalyst (pale blue) was obtained from these samples by contact at 623 K with a CO pressure of 40 Torr for 30 min and subsequent evacuation at 473 K. Carbon dioxide formed during the reduction process was condensed away by a liquid N_2 trap. Such samples, which promote very actively the polymerization of ethylene, are hereafter indicated as S_{red} (standard reduced).

DEACTIVATION PROCEDURE

Heating at 973 K under high vacuum of the reduced active samples for a period of 4 hr depresses enormously the activity toward polymerization and, to some extent, toward the chemisorption of gases (*5*, *6*). Such samples (pale blue) are hereafter indicated as D_{red} (deactivated reduced).

EXPERIMENTAL TECHNIQUES

(*a*) *Calorimetry*

Reaction heats and related uptakes were measured by a gas-volumetric apparatus connected to a Tian-Calvet twin microcalorimeter (*12*). Both activation and deactivation of the catalyst have been performed in the calorimetric cell connected to a separate high-vacuum system, before the insertion of the cell into the calorimeter and the attachment to the volumetric frame. Particular care was devoted during this operation to avoiding any contamination.

The catalyst was then exposed to very small doses of oxygen, up to saturation. During the reaction of each dose, the pressure over the adsorbent was monitored, along with the development of the calorimetric peak.

The calorimeter was kept permanently at 310 K.

(*b*) *Diffuse Reflectance Spectroscopy*

A Beckman DK2 double-beam spectrophotometer was used. As the sample and the reference are placed on different exit ports, two identical conventional Spectrosil cells were used, 1 mm thick, modified so as to be attached to a vacuum system.

The reference was low-surface-area dehydroxylated α-Al_2O_3 outgassed at 1073 K and sealed under vacuum.

The sample cell was mounted on a movable frame so that both thermal treatments and spectroscopic measurements could be made without disconnecting the cell from the vacuum system.

The instrument yields R_∞ (reflectance) vs λ (wavelength) graphs. Spectra are shown here as $F(R_\infty)$ vs $\tilde{\nu}$ (wavenumber) plots, $F(R_\infty)$ being the Schuster–Kubelka–Munk function (*13*), as this function furnishes the ratio between adsorption and scattering coefficient at any wavelength.

RESULTS

Activation

Freshly prepared CrO_3/SiO_2 samples after impregnation and drying in air at room temperature (RT) show the spectrum A in Fig. 1. Other spectra in the figure show the changes upon outgassing at RT (B) and at increasing temperatures up to 1023 K (C, 423 K; D from 623 K upward). Spectrum E is obtained after oxidation at 823 K, and represents the spectrum of the standard oxidized catalyst (S_{ox}).

Outgassing at room temperature causes a marked decrease in the reflectance: the whole B spectrum cannot be reported in the figure, as $F(R_\infty)$ values become exceedingly large and unreliable in the region 20,000–40,000 cm^{-1}, the reflectance being below 10%. However, in the original R_∞ vs λ spectrum the band maxima seem to remain unchanged.

Heating under vacuum, on the contrary, decreases the overall intensity of the spectra (C, D), which can therefore be thoroughly examined and compared with spectrum A.

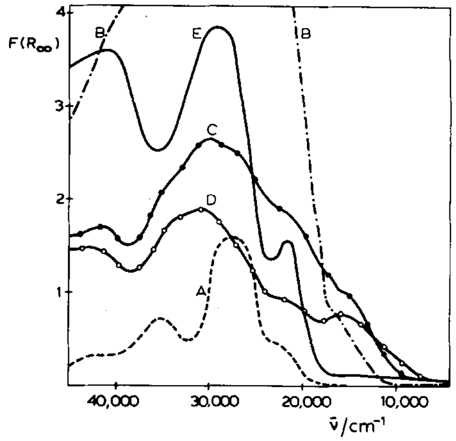


FIG. 1. uv–vis–nir spectra of the sample during the activation process (Kubelka–Munk function vs wavenumber). Curve A: freshly prepared samples in air; after 1 hr outgassing at B, room temperature; C, 423 K; D, 623 K and higher temperatures up to 1023 K; E, after oxidation at 823 K (S_{ox}).

The thermal treatment at 423 K also causes a definite change in the spectrum shape. The spectrum C shows components at 23,000, 27,000, and 42,000 cm^{-1} already present in the starting spectrum A; a new component at 29,000 cm^{-1} is seen, together with the appearance of absorption in the region below 20,000 cm^{-1}, completely absent in the starting material.

Heating at 623 K (spectrum D) does not cause the appearance of new components: an overall decrease in intensity is observed, apart from a small increase in the region below 12,000 cm^{-1}. From 623 to 1023 K no further changes are detected. This spectrum is unaffected by admission of CO, N_2, and O_2 at RT. On the contrary, the successive oxidation at 823 K, leading to S_{ox} (spectrum E), gives rise to a marked variation in the spectrum. Bands below 20,000 cm^{-1} disappear and three well-defined absorptions at 21,000, 29,000, and 42,000 cm^{-1} are present. To test its stability, the S_{ox} sample was heated under vacuum for 1 hr at increasing temperatures: no changes were observed in the spectrum up to 823 K.

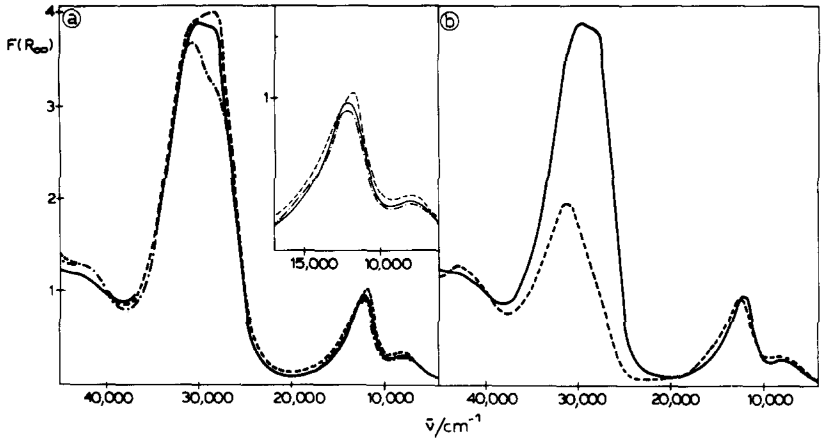


FIG. 2. uv–vis–nir spectra of reduced samples (Kubelka–Munk function vs wavenumber). (a) Spectra from various standard reduced samples. The inset shows a magnification of the *d–d* region. (b) Comparison between a standard reduced sample (solid curve) and the corresponding reduced deactivated sample (broken curve).

Reduction

The reduction of S_{ox} samples to S_{red} leads to spectra of the type shown in Fig. 2a: the three spectra reported were obtained by reduction of different samples from the same batch. Some differences among them are seen, indicating some fluctuations in the final state of the samples.

Absorption occurs both in the *d–d* region, at 8000 and 12,200 cm^{-1}, and in the charge transfer (CT) region at 29,000 and 43,000 cm^{-1}. The band at 8000 cm^{-1} is very weak; the 12,200-cm^{-1} band shows slightly different shapes (inset), suggesting the presence of components.

The more intense absorption in the CT region is complex, and at least two components at ~28,000 and ~30,000 cm^{-1} can be observed.

The spectra of various S_{red} samples (Fig. 2a) vary both in the overall intensity and in the relative intensity of the different bands. A possible reason for the changes in the overall intensity is the variable packing of the powder in the reflectance cell, as a result of which different amounts of sample are exposed to the beam. Other reasons are discussed later. The differences in relative intensities are particularly evident in the charge transfer transitions: the ratio between the absorptions at ~28,000 and ~30,000 cm^{-1} can even be inverted, indicating detectable variations in the relative population of different Cr ions.

The deactivation process leads to samples exhibiting spectra like the dashed curve in Fig. 2b. A large variation occurs upon deactivation in the charge transfer region: the component at ~28,000 cm^{-1} is drastically decreased, the one at ~30,000 cm^{-1} is found at 31,000 cm^{-1}, whereas the band at 43,000 cm^{-1} increases somewhat.

In the *d–d* region, only a slight displacement (~400 cm^{-1}) toward higher frequencies of the two bands is seen, together with the appearance of a very weak shoulder at ~15,000 cm^{-1}.

Reoxidation

Upon exposure to oxygen, both S_{red} and D_{red} samples readily react even at room temperature. The sample oxidation is accompanied by a luminescent effect (*9*, *14*), which cannot be easily detected with our spectrometer. We have observed, however, that the effect is much more limited in the case of D_{red} samples.

Because of the incomplete reproducibility of reduced samples (Fig. 2a), calorimetric measurements have been run on four different S_{red} samples.

In three cases, very small (0.1–3 μmole) doses of oxygen have been used, to detect the possible occurrence of successive oxidation steps as coverage increases. The plot (not reported) of integral heats of adsorption (Q_{int}) vs adsorbed amounts for the three cases shows that all points fall on the same straight line: variations are only observed in the total adsorptive capacity of different samples. In one case, larger doses of oxygen (~10 μmole) were used, to check whether possible systematic errors in the volumetric measurements had accumulated in the small-dose runs. Figure 3a shows this last experiment, together with one small-dose run: the two sets of points locate the same straight line, so suggesting the absence of appreciable systematic errors. A difference in the total amount adsorbed can be seen. Figure 3b illustrates one small-dose run on a D_{red} sample. In both Figs. 3a and b, plots are definitely linear: this suggests that the reaction heats are constant throughout the coverage range. The differential heats of adsorption on S_{red} and D_{red} are roughly the same (460 and 425 kJ, respectively): the amounts of O_2 adsorbed are, on the contrary, drastically different (Table 1).

TABLE 1

Extent of Reoxidation Expressed as the Ratio between O_2 Adsorbed Molecules and Cr Ions

T (K)	S_{red}	D_{red}
310	0.70 ± 0.12	0.25 ± 0.07
823	0.98 ± 0.01	0.97 ± 0.02

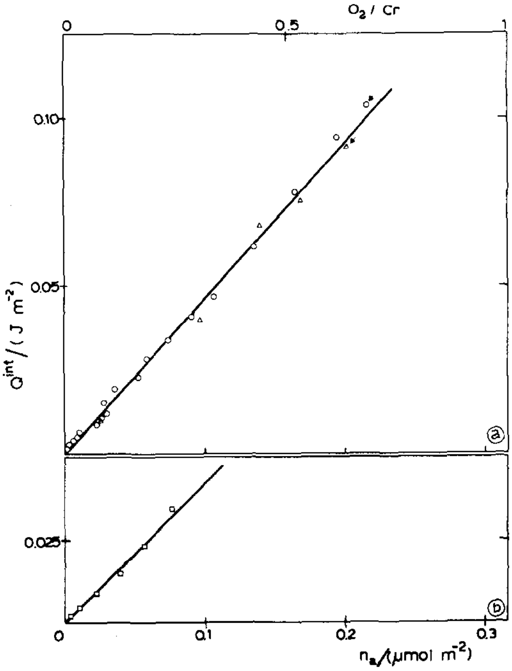


FIG. 3. Reoxidation of reduced samples at 310 K. Non-activated process: integral heats vs adsorbed amounts. (a) Standard reduced sample: (○) small-dose run, (△) larger dose run. (b) Reduced deactivated samples.

The lower row in Table 1 reports, for comparison, the data, obtained in a different volumetric system (*5*), concerning the reoxidation at high temperature.

Two main considerations arise from Table 1. First, not all the chromium is active toward O_2 adsorption at RT, even on S_{red}; second, deactivation roughly concerns two-thirds of Cr ions active on S_{red}.

In the whole range of Fig. 3, the reaction process is fast; no oxygen pressure is detectable after chemisorption of each dose and the shape of the heat emission peaks (Fig. 4, peak 1) is characteristic of instantaneous processes.

The final points in Figs. 3a and b (arrows) correspond to an abrupt and marked change in thermokinetics and to the appearance of a pseudoequilibrium pressure of about 0.1 Torr. Successive admission of oxygen causes slow and feeble heat emissions (peak 2 in Fig. 4) due to a very activated process, during which additional oxygen is adsorbed under pressure. The corresponding uptakes are so small that volumetric data are unreliable: the entity of this phenomenon can, however, be estimated by a Q_{int} vs p plot.

These plots are reported in Fig. 5 both for adsorption and for desorption runs. On both S_{red} and D_{red} the vertical portion of the

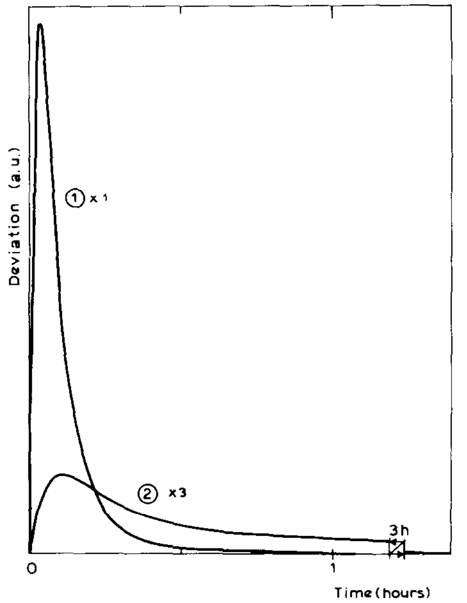


FIG. 4. Calorimetric peaks. Peak 1, typical thermokinetics of nonactivated process (Fig. 3); peak 2, typical thermokinetics of activated process at coverages higher than the final ones of Fig. 3.

curves corresponds to the data in Figs. 3a and b (small doses).

The arrow shows the onset of slow phenomenon under study (final points in Figs. 3a, b).

In spite of its pressure dependence, the process under consideration is completely irreversible: upon desorption (full points) no desorption heats can be measured.

The amount of heat released in the slow process is nearly the same in the two cases and turns out to be 3% of the total in the case of S_{red}, and about 14% in that of D_{red}. We infer from thermokinetics that the slow process is more activated in the case of D_{red}, in agreement with the more marked pressure dependence of the curve in Fig. 5 in this case.

In Fig. 5 data have been reported just up to 1.3 Torr. Indeed, for higher pressures, very small heats are recorded, indicating the continuation of the process.

Figure 6 illustrates the spectra on the reoxidation of S_{red} (6a) and D_{red} (6b). In both cases spectrum A is that of starting reduced material, spectrum B was taken immediately after the exposure of the sample to 40 Torr of oxygen at RT, spectrum C is that after 12-hr contact, and spectrum D illustrates the reoxidation of the samples at 823 K under the same pressure of oxygen for 10 min. In spite of the difference in pressure (40 Torr as against 0.1 Torr), spectra B are probably to be compared with the final situations achieved in Figs. 3a and b (arrows), if account is taken of the slowness of the activated process. Differences between spectra B and C should point out the occurrence of the activated process, which is exhausted in a short time at 823 K (spectra D).

Curves D for both S_{red} and D_{red} are identical and coincided with the spectrum of S_{ox}, so showing that for both samples the reoxidation is complete in this condition.

As far as curves B and C are concerned, we examine first the region below 20,000 cm^{-1}. In curves B the bands around 8000 and 12,600 cm^{-1}, characteristic of the reduced samples, are markedly decreased but not depleted, while components at ~15,000 and ~10,000 cm^{-1} are seen. In the case of D_{red} the decrease of the original pair (at 12,600 and 8,000 cm^{-1}) is more limited and the intensity of the 15,000- and 10,000-cm^{-1} pair is higher. We examine next the region above 25,000 cm^{-1}. Curves B show the expected absorptions of S_{ox} at 29,000 and 41,000 cm^{-1}. In the case of S_{red} reoxidation, their intensity is nearly the same as in S_{ox}, whereas it is somewhat lower in the D_{red} case. In this region curves B and C nearly coincide. Finally, we draw attention to the behavior of the 21,800-cm^{-1} band: completely absent in spectra A, it appears in spectra B with highest intensity; a 12-hr contact causes a small decrement of this band on S_{red}, not observed on D_{red}; a further decrement is caused by reoxidation at 823 K.

DISCUSSION

Surface Phase Formation

The formation of a definite surface phase

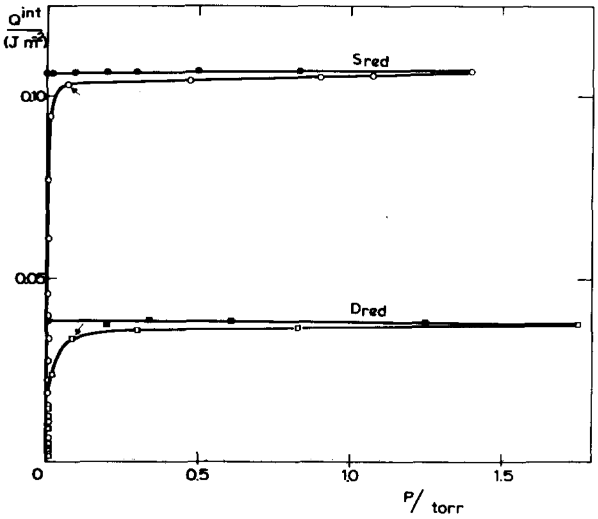


FIG. 5. Reoxidation of reduced samples at 310 K: integral heats vs pressure. (○) Standard reduced sample (S_{red}); (□) reduced deactivated sample (D_{red}). Open symbols, adsorption; solid symbols, desorption.

during the activation process has already been documented (*1, 5, 7, 9*), together with some degradation of Cr^{VI} at the surface to lower valence states (*9*). The anchorage of Cr^{VI} onto the surface is assumed to involve esterification of suitable silanols, yielding surface chromates or dichromates. Whereas according to Hogan (*9*) this process takes place below 393 K, Groeneveld *et al.* (*7*) claim that it occurs at much higher temperatures.

Our data support this latter view. The

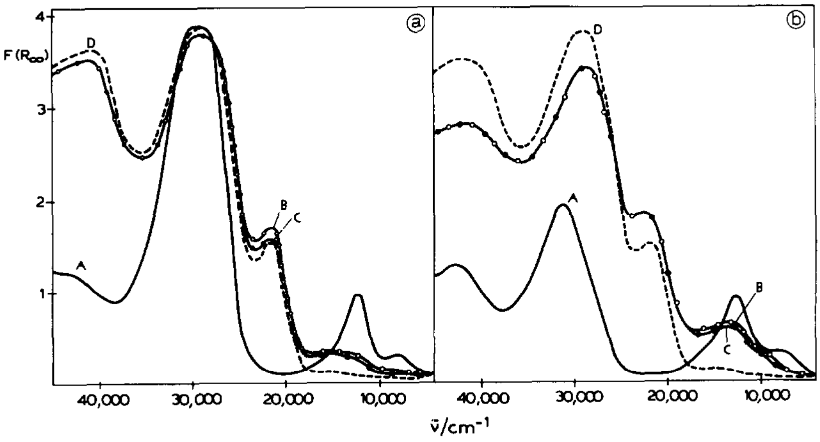


FIG. 6. uv–vis–nir spectra after reoxidation of standard reduced (a) and reduced deactivated (b) samples (Kubelka–Munk function vs wavenumber). Curves A (——), starting material; curves B (○—○), immediately after exposure to 40 Torr of oxygen at room temperature; curves C (●—●), after 12-hr contact; curves D (----), exposure to 40 Torr of oxygen at 823 K for 10 min.

spectrum in Fig. 1 of the starting material, both before (A) and after (B) RT outgassing, is quite different from spectrum E, which is representative of the surface oxidized phase, thus showing that Cr^{VI} anchorage has not yet occurred.

Spectrum C (423 K outgassing) shows a component at 29,000 cm^{-1} (monitoring the presence of the surface phase) and a band at 27,000 cm^{-1} characteristic of the Cr^{VI} not yet anchored (spectrum A): the esterification reaction has started, but it is far from being complete. The absorptions in the *d–d* region moreover indicate the occurrence of Cr in valence states lower than six, i.e., degradation of Cr^{VI} takes place besides the anchorage process.

Both processes are exhausted at 623 K (spectrum D), as no further changes are seen at higher temperatures. This is confirmed by the absence in spectrum D of the 27,000-cm^{-1} band and the occurrence of Cr^{II} as an ultimate product of the degradation of Cr^{VI} (crossing of curves C and B, absorption below 12,000 cm^{-1}).

This latter phenomenon accounts for the observed decreases in the overall intensities. Taking into account that, once anchored, the surface Cr^{VI} species are stable (as shown by the thermal stability of S_{ox}), we infer that lower valence states of Cr arise from the degradation of Cr^{VI} not yet anchored. Unlike similar experiments run in flow systems (*7, 9*), this process is certainly magnified in our measurements because of the absence of any O_2 in the gas phase.

It is difficult to draw information about the low-valence Cr ions from spectrum D because of its complexity. They seem, however, to be stabilized by the interaction with the matrix. This is demonstrated first by the invariance of the spectrum above 623 K. A second piece of evidence is as follows. From a thermodynamic point of view, nonanchored CrO_3 is expected to yield α-chromia particles: in the following discussion we show that this process occurs to a very limited extent only. A possible explanation is that the degradation of Cr^{VI} is accompanied by a shielding of Cr ions in the matrix as shown by the insensitivity of the sample toward reactive gases.

It is sufficient to oxidize the sample at 823 K to complete the formation of the surface oxidized phase. The sample is, however, previously outgassed up to 1023 K to eliminate from the surface a large fraction of silanols, which, on the one hand, could cause during oxidation at 873 K the formation of α-chromia (*9, 15*) and, on the other hand, lead to "low-quality" reduced samples (*2*).

The question arises whether the S_{ox} spectrum has to be assigned to surface chromates or dichromates. If reference is made to the electronic spectra of potassium chromate and dichromate either in solution or in crystals (as done by Groeneveld *et al.* (*7*) and by some of us in a preceding paper (*5*)), the presence of a band around 22,000 cm^{-1} would suggest the presence of dichromates.

The nature (not easily describable) of the surface species is probably equally distant from that of anions in solution and anions in the bulk. We may envisage two effects caused by the anchorage of chromates or dichromates onto the surface, namely, the reduction in the symmetry of the Cr^{VI} moiety and the formation of highly covalent bonds with surface silicon. Both these effects may induce, in the case of chromates, the intensification of a band in the range 21,000–23,000 cm^{-1}, as shown by the spectra of solid chromates other than potassium chromate (*16*) and the monosubstituted chromates in solution (*17*).

A better reference could come, in principle, from the electronic spectra of organic esters of chromic (and dichromic) acid. Unfortunately, the literature on this topic is sparse: only the more prominent bands are reported (*18*) in the case of organic chromates (one in the range 25,000–27,800 cm^{-1}; the other at 34,700–35,700 cm^{-1}). No data are available for organic dichromates. We thus feel that sounder evidence about the probable presence of surface dichromates comes from other experiments (*5*) and that the contemporary presence of chromates cannot be ruled out.

The Reduced Samples and Their Deactivation

In order to discuss the electronic spectra of both S_{red} and D_{red}, the average oxidation number of Cr in reduced samples has first to be assessed. This can be done from the data in Table 1 (lower row) by assuming that, after oxidation, all Cr ions are in the hexavalent state (*5*). Two results emerge. In S_{red} and D_{red}, Cr has the same average oxidation number, i.e., no variation occurs during deactivation. Second, with the O_2/Cr ratio being very close to unity, the vast majority of Cr is in the divalent state.

Small discrepancies from the ideal value of two nevertheless occur systematically. These can be interpreted as due either to the presence at the surface of reactive Cr^{III}, which requires only three-fourths of an O_2 molecule to be fully oxidized, or to some Cr^{III} not reactive (clustered in α-chromia particles), which is not reoxidized at all. In the former case some 10% of Cr would be in the trivalent state, while in the latter case a fraction of about 2% would be enough to account for the observed O_2/Cr ratios.

Although the presence of reactive Cr^{III} has been documented on samples at higher loading (about 2%) (*5, 7*), we favor, with Krauss *et al.*, the latter hypothesis as far as our samples are concerned.

A fraction of about 10% of reactive Cr^{III} would reveal itself in the spectrum, especially after chemisorption of molecules assuring an octahedral coordination: this is never so (*15, 19*). We therefore interpret the spectra in Fig. 2 as entirely ascribable to Cr^{II}. No absorption due to α-chromia particles (17,000 and 22,000 cm^{-1}) is seen in the spectrum, in agreement with its extremely low amount.

We discuss the *d–d* region first, starting from the S_{red} spectrum. In principle, the location of *d–d* bands should allow the determination of the symmetry of the surface Cr^{II} by comparison with known bulk compounds. Unfortunately all known coordination states of Cr^{II} (for reference see (*5*)) yield a couple of bands in the region 14,000–5000 cm^{-1}, including the here unrealistic octahedral one so that no clear inference about the coordination and symmetry state of Cr ions can be made on this basis. We are thus forced to refrain from discussing the uv–vis bands of the samples by means of symmetry notations and will therefore proceed in the following on a purely phenomenological basis.

As shown in preceding papers (*6*), the deactivation process probably consists in the increase in coordination of some exposed divalent Cr ions, by the interaction with neighboring surface (or near to the surface) groups like hydroxyls or oxygen atoms in siloxane bridges. Accordingly, a variation is expected upon deactivation. This basically appears as a limited blue shift of the band around 12,200 cm^{-1}. As we know that not all the Cr at the surface undergoes deactivation (*5, 6*), a probable explanation of the shift is the transformation of a low-energy component (say, that at 11,500 cm^{-1}, evident in spectrum A in Fig. 2a) into a higher frequency one (about 15,000 cm^{-1}, partially visible as a weak shoulder in Fig. 2b).

As discussed in the following paragraph, the deactivated ions are not readily reoxidized at RT (unlike the exposed ones) so that their contribution to the *d–d* region of D_{red} can be estimated from the spectrum in Fig. 6b. Taking into account that the adjacent intense band at 21,800 cm^{-1} causes an upward displacement of the curve in the *d–d* region, it is seen that Cr ions not reacting with O_2 at RT are represented by a band at 15,000 cm^{-1} (as guessed) and by another one at 12,600 cm^{-1} (i.e., nearly coinciding with the band maximum before reaction) of nearly equal intensity. Two different species of deactivated Cr are thus present on the sample. Both of them are expected to show two *d–d* transitions, and in fact a peak is observed at 10,000 cm^{-1}, perhaps the partner of the 15,000-cm^{-1} band.

The variations induced in the spectrum by deactivation may be compared to some extent with the shifts caused by the adsorption of oxygen donor ligands such as water, alcohols, silanols, and siloxanes (*4*). Two cases occur. Weak ligands form 1 : 1 or 2 : 1 complexes, with band maxima at 12,500 and 17,000 cm^{-1}, respectively. Stronger ligands cause much higher shifts at low ligand to Cr ratios: a band around 15,000–16,000 cm^{-1}, however, is formed when Cr^{II} ions probably reach an octahedral configuration (4 : 1 complexes in the opinion of Krauss *et al.*). The species of deactivated Cr^{II} showing no (or very limited) shift seems thus to reach its final coordination state by the coordination of one or two very weak ligands. As to the other species (15,000-cm^{-1} band), it possibly arises from the coordination of one or two slightly stronger ligands. The alternative explanation (coordination of up to four strong ligands) would involve an octahedral site for the deactivated Cr^{II}, quite improbable in the silica structure. Oxygen atoms at the surface are likely to behave as very weak donors: heterogeneity among them, however, may arise because of the presence of variously strained siloxane bridges: moreover surface hydroxyls could play a role in the coordination.

In the CT region, unusually low-energy absorptions occur, which are related to exposed Cr^{II} ions. The component at 28,000 cm^{-1} is suppressed by deactivation together with activity toward polymerization of ethylene. The component initially at ~30,000 cm^{-1} is found after deactivation at 31,000 cm^{-1}. It is difficult to state whether its intensity is unchanged, but certainly an increase at the expense of the lower frequency component has to be ruled out. Cr^{II} ions causing this absorption are therefore in a stable configuration and do not act as intermediates in the deactivation process. This agrees with what is found by CO or NO adsorption on deactivated samples (*6*).

As to the nature of these low-energy CT bands, little can be said on the basis of the hitherto poorly developed theory of electronic transfer in complexes. However, such transitions seem to require the presence of definite molecular orbitals, with covalent character, extending over more than two atoms, e.g., structures like O–Cr–O or Cr–O–Cr. The former may arise from the reduction of surface chromates, the latter of dichromates. A third possibility is the occurrence of Cr–Cr bonds, as in chromous acetate, in which $\sigma \rightarrow \sigma^*$ transitions at low energies are found. Obviously a choice among the envisaged structures is not possible on the basis of these spectroscopic data alone.

The band at 43,000 cm^{-1} is not found in pure silica, and has thus to be related to the presence of supported Cr. We are unable, however, to propose an assignment; its increase upon deactivation would suggest that deactivated Cr ions are the source of this absorption, but the extent of the increase is far too small to support this idea. The deactivated Cr^{II} ions will in any case absorb above 40,000 cm^{-1}, i.e., at definitely higher energies than the exposed ones: we infer from this a definite loss of covalency of the Cr–O bonds upon deactivation.

In conclusion, up to four different species of Cr^{II} are singled out, two exposed and two deactivated. A first one (henceforth labeled Cr_A), in a very low coordinative state and certainly involved in the polymerization centers, is characterized by transitions at ~11,500 and 28,000 cm^{-1}. A second species (Cr_B), although in a low-coordinative state, does not undergo deactivation (i.e., it is in a stable configuration): the corresponding bands fall at ~12,200 and 31,000 cm^{-1}. The two other species seem to arise from the surface rearrangement of Cr_A, and are characterized by absorption at 12,600, 15,000, and >40,000 cm^{-1}.

The difference in the spectra of S_{red} seem, on this basis, to arise from random fluctuations in the relative populations of the different species of Cr^{II}, the most active samples being those with the highest content of Cr_A (most intense bands at 11,500 and 28,000 cm^{-1}).

Reoxidation

Calorimetric measurements point out the occurrence of two distinct reoxidation processes, one very fast, i.e., little (or non-) activated, the other very slow and definitely activated, the transition between them being quite abrupt. At RT the former is far more important, as shown both by the heats released in each process and by the variations in the spectra in Fig. 6 due to 12-hr contact. The values of the uptakes in Table 1 (upper row) show that the extent of the fast RT reoxidation is drastically decreased by deactivation: this means that, as is reasonable, only the exposed ions are involved in the first process. Making the simplifying hypothesis that Cr_A is present on D_{red} in negligible quantity, one can compute that exposed ions are partitioned on S_{red} into 45% of the total as Cr_A, 25% as Cr_B, and the rest as Cr_C.

On both D_{red} and S_{red}, the differential heat of adsorption is constant all along the coverage, even at the lowest coverages examined (less than 1% of the total adsorbed amount). This clearly indicates that no stepwise oxidation occurs, i.e., formation of intermediate valence states. The process can be simply thought of as the breaking of an oxygen molecule onto a Cr ion giving rise to a surface chromate or dichromate. No (or little) activation energy is required for such a process, in particular if account is taken that π-bonding of the O_2 molecule (peroxidic-like structure) probably acts as the intermediate for the reaction (*14, 20*). A possible reaction scheme is thus:

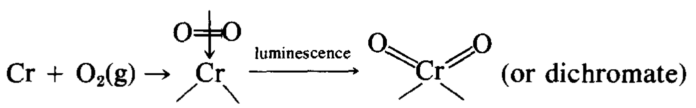


Figure 7a illustrates a possible potential energy well scheme for such a reaction. The absicissa is the distance from Cr to the centre of gravity of an O_2 molecule. One curve refers to chromates (or dichromates) and is displaced upwards by the dissociation energy of O_2, with respect to the other curve (referring to peroxidic-like species). This latter curve is displaced along the z axis because most probably the Cr–O_2 distance is larger in this case. Although largely arbitrary, the figure accounts for the absence (or negligible presence) of activation energy.

The differential heats of reaction on S_{red} and D_{red} are very close to each other. This means that Cr_A and Cr_B show a roughly equal reaction heat toward O_2. The difference between the two values is probably meaningful: from the relative population of Cr_A and Cr_B, we reckon that the standard energies of reaction would be -480 and -425 kJ on Cr_A and Cr_B, respectively, i.e., a difference of about 10% only. Two different explanations may be advanced. The reoxidation of Cr_A and Cr_B may lead to different surface species (e.g., Cr_A yielding chromates and Cr_B dichromates preferentially): a close comparison of the standard energies of reaction would be in this case not too meaningful. If, on the other hand, both kinds of Cr give rise on the average to the same oxidized species, such a difference would simply monitor the difference in surface stabilization energy of the two Cr ions, obviously larger for Cr_B. As curves B in Figs. 6a and b do not differ in shape, we favor the latter hypothesis. It should be noticed that the intensity in curves B of the bands due to oxidized species is puzzling. Whereas the erosion in the d–d region is in good agreement with the extent of reoxida-

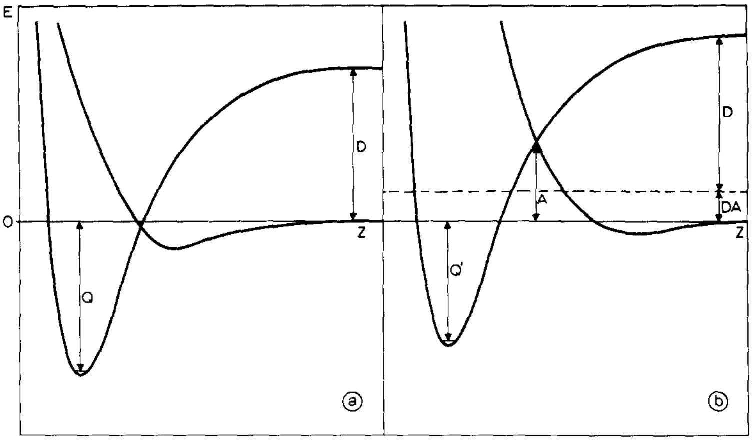
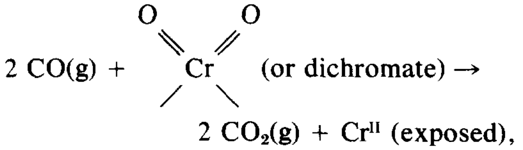


FIG. 7. Potential energy well schemes. (a) Nonactivated process; (b) activated process. E, potential energy; Z, Cr–O_2 distance; Q, heat of reaction; A, activation energy; D, dissociation energy of O_2; DA, deactivation energy of Cr^{II}.

tion, the higher energy bands appear much more intense than expected. This could be due to the fact that the Kubelka–Munk function does not parallel the concentration of the absorbing species at very high values of the function itself (*13*). Another phenomenon, however, seems to take place. Consider the 21,800-cm^{-1} band which, both in Figs. 6a and b, is in curves B even more intense than in the final curves D. The oscillator strength of the surface oxidized species seems thus to decrease upon increase of the extent of reoxidation. In our opinion, this fact may be explained assuming electronic interactions between surface oxidized species, whose effect would be similar to those already discussed. The covalent character of Si–O bonds is likely to facilitate the transmission of an electronic effect. The adopted loading corresponds to some 12% coverage of the surface (*5*). Most probably the distribution of oxidized species over the surface is far from being random, so that the probability of finding two adjacent electronically interacting chromate (or dichromate) groups could be substantial.

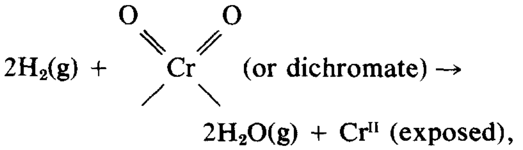
The value of the standard energy of reoxidation is very high (−460 kJ), in agreement with it having the nature of a real chemical reaction, of the same order of magnitude of the standard enthalpy of the reaction $CrO(s) + O_2(g) \rightarrow CrO_3(s)$ (~300 kJ). It also compares well with the heat of adsorption of O_2 on vanadium supported on silica (~400 kJ $mole^{-1}$) (*21*). The previous determination by Krauss *et al.* (~590 kJ $mole^{-1}$) appears to be overestimated by at least 30% (*22*).

An accurate value of the standard energy of reoxidation of exposed Cr^{II} ions also allows some information to be gained about the reduction process. The standard energy of reduction by CO at 310 K,



$$2\,CO(g) + \overset{O\quad O}{\underset{/\quad\backslash}{Cr}}\ \text{(or dichromate)} \rightarrow 2\,CO_2(g) + Cr^{II}\ \text{(exposed)},$$

is easily computed from the standard formation energies of CO and CO_2 and the above datum. It turns out to be −106 kJ: the same quantity in the case of reduction with H_2,



$$2H_2(g) + \overset{O\quad O}{\underset{/\quad\backslash}{Cr}}\ \text{(or dichromate)} \rightarrow 2H_2O(g) + Cr^{II}\ \text{(exposed)},$$

is only −24 kJ. The exothermicity of such processes agrees with the finding by

Groeneveld *et al.* (*7*) and accounts for the spontaneity of both reductions, the standard entropy of reaction probably being small in both cases (two gaseous molecules appear both as reactants and as products). This means that the reduction process does not take place at 310 K for kinetic reasons only.

The reoxidation of nonexposed Cr is activated, i.e., is strongly dependent on time, pressure, and temperature. At 310 K the process is very slow (as shown by both the thermokinetics and the changes induced in the spectra by 12-hr contact) but fast at 823 K. The RT activated reoxidation does not discriminate between the two types of nonexposed Cr (C_1 and C_2). The role of the O_2 pressure can be understood by supposing that the above-mentioned peroxidic-like precursor now approaches the nature of O_2 just very weakly adsorbed onto not readily accessible Cr ions. Figure 7b illustrates the potential energy well scheme appropriate for this case. The coordinates are the same as in Fig. 7a. Because the final situation achieved is the same, the curve referring to the oxidized surface phase is unchanged, but for a displacement along the ordinate, which takes into account the variation in energy brought about by the deactivation of Cr_A ions. Because this process is spontaneous, and probably involves little entropic changes, we think that it has to be exothermic (upward shift). The other curve is displaced to the right with respect to the analogous curve on Fig. 7a, to take account of the changed type of interaction: for the same reason the well depth is smaller. Both these features and the presence of the deactivation energy cooperate in the onset of a marked activation energy.

This picture, however, is oversimplified. Were the activation energy the same for all deactivated Cr ions, the heat evolution would parallel the change of the oxygen pressure, and in particular would stop only when no pressure is detectable in the gas phase. Pseudoequilibrium pressures are, on the contrary, observed. This seems to suggest the presence of a range of activation energies, i.e., heterogeneity within C_1 and C_2 species, in agreement with other data on the chemisorption properties of deactivated samples (*23*).

Finally, we may compare the present results with those published by Krauss *et al.* on the variation of the heat evolved per Cr^{II} mole upon RT oxidation as a function of the reduction temperature (*2*). In their opinion, the decrease observed for increasing temperatures is due to a change in the "quality" of the Cr^{II} ions, all of which are supposed active toward oxygen. We have shown, however, that, when active, different species of Cr^{II} have nearly the same activity. We thus feel that this effect is due to an increasing extent of deactivation (caused by higher reduction temperatures), which transforms active Cr^{II} into a completely nonactive species.

CONCLUSIONS

As to the fate of loaded CrO_3 during thermal treatment, two processes are operative. The esterification of CrO_3 with surface silanols occurs over a rather wide temperature range (423–623 K): once anchored to the surface, the resulting species are stable. Nonanchored CrO_3 is, on the contrary, subjected to a degradation process leading not to α-chromia-like particles, as expected on a thermodynamic basis, but to surface-stabilized low-valence states of Cr (among which is Cr^{II}), which are fully reoxidized at 823 K. The final situation achieved may be described in terms of surface chromates or dichromates. Their occurrence cannot be established on a purely spectroscopic basis: both kinds of species probably occur on the surface.

After reduction, about 98% of the Cr is in the divalent state. Up to four different species of Cr^{II} have been singled out: two exposed (Cr_A and Cr_B) and two nonexposed (Cr_{C_1} and Cr_{C_2}), with different electronic spectra. On the former two, oxygen adsorption is non- (or very little) activated and occurs with comparable reaction heats. The reoxidation of the latter species is strongly activated and takes place under O_2 pressure. Thermal deactivation of the sample converts Cr_A into Cr_C, whereas Cr_B seems to be unaffected. Even on the most active samples, a fraction of Cr_C is always present (~30%): fluctuations in the final state of the catalyst are due to different extents of the transformation $Cr_A \rightarrow Cr_C$. The Cr_A population is some 45% of the total: a fraction of it is involved in the centers for ethylene polymerization.

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