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Carbon Monoxide Oxidation over Chromium Sesquioxide. I. Nature of Oxygen Adsorbed on Cr_2O_3

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The nature of oxygen species adsorbed on Cr_2O_3 surface in the temperature range 131—163 °C was studied in detail by application of the transient response method with simultaneous measurements of the electrical conductivity of the catalyst as a p-type semiconductor. The distribution of oxidation power of the adsorbed oxygen species was also measured. The mode of the distribution curve of oxidation power indicates that the oxygen can be classified into two groups which differ in oxidation power as well as in the catalytic activity for the oxidation of CO. From the comparison between the results of the transient response and the oxidation power measurements, it is concluded that the rapidly and slowly adsorbed oxygen groups observed by the transient response method correspond to those of oxygen species of higher and lower oxidation power, respectively. Kinetic analysis of the conductivity response curve caused by the adsorption of oxygen leads to the conclusion that the dissociative adsorption of oxygen associated with electron transfer from the catalyst takes place simultaneously on two different kinds of adsorption sites at substantially different rates.

The adsorption of oxygen on Cr_2O_3 has been studied by a number of investigators[1,2] with special reference to the nature of adsorbed oxygen. It is widely accepted that the adsorption of oxygen on the surface is dissociative, even at room temperature. However, infrared studies[3,4] of the adsorbed oxygen on Cr_2O_3 revealed that there exist several different adsorption bands due to the different vibrations of bonds between the surface cation and oxygen, produced as a results of the dissociative chemisorption. The existence of the variety of surface oxygen may result in a complexity of reactions in which the surface oxygen takes part.

In order to provide necessary information on the role of adsorbed oxygen participating in the CO oxidation over Cr_2O_3, this paper deals with the nature of surface oxygen species and their activity for this reaction. The transient response method was used together with measurement of the distribution of oxidation power of the surface oxygen species.

Experimental

The chromium sesquioxide was prepared by decomposing chromium trioxide in an air flow at 450 °C for 5 h. The X-ray diffraction analysis of the sample indicated that the sample was in the form of α-Cr_2O_3. The sample used as the catalyst was in 24—32 mesh granule and was found to have a BET surface area of 21 m^2/g. The catalyst is a p-type semiconductor under the whole range of experimental conditions, showing an increase in electrical conductivity with increasing amount of adsorbed oxygen.

The experiments were carried out with either oxidized or reduced catalysts. The oxidized catalyst was prepared by pretreatment in a stream of O_2(20%)–N_2 mixture at 131 °C for more than 24 h and the reduced catalyst was prepared by reduction with a CO(6%)–nitrogen stream at the same temperature until no carbon dioxide in the effluent stream was detected. The electrical conductivity of the oxidized catalyst thus prepared was constant and no change in the conductivity could be observed with prolonged oxidation. The conductivity thus attained was 3.2×10^{-6} ohm^{-1} cm^{-1}. For the reduced catalyst, the electrical conductivity was found to be negligibly small as compared to that of the oxidized catalyst.

Commercial CO, CO_2, and N_2 were carefully purified through a dry ice–methanol trap to remove water vapor. A Pyrex glass tube reactor containing 55.2 g catalyst was immersed in an oil bath. The temperature of the catalyst bed was kept uniform within ±0.1 °C at desired temperatures.

A flow system was employed in all the experiments and the total flow rate of the gas stream was always kept constant at 160±2 ml/min. In applying the transient response method, the concentration of one or two components in the inlet gas stream was changed stepwise by using nitrogen as a balancing gas. The reaction conditions were always chosen in such a way that the total conversion of carbon monoxide did not exceed ten percent in all the runs.

The gases were analyzed by gas chromatography and the conductivity of the catalyst bed was measured with a d.c. bridge. The amount of surface oxygen species was analyzed with a potassium iodode solution as a reducing agent and the distribution of oxidation power was determined by measurements at various pH's. More detailed descriptions of the transient response method,[5,6] conductivity measurement[5] and the analysis of surface oxygen species[7-9] can be found elsewhere.

Results and Discussion

Nature and Amount of Surface Oxygen Species. The nature of oxygen species adsorbed on the metal oxides varies a great deal with respect to the oxidation power and catalytic activity as in the case of NiO,[8] MnO_2,[5,7] and Pb_3O_4.[10] In order to determine the catalytically active oxygen species on Cr_2O_3 surfaces for carbon monoxide oxidation, the distribution of oxidation power of the surface oxygen species was measured with a potassium iodide solution at various pH for the catalysts exposed to various gas stream. The results are shown in Fig. 1. The amount of oxygen species on the oxidized surface shows a bimodal distribution with respect to the oxidation power similar to those adsorbed on MnO_2[5] and Pb_3O_4[10] (curve I, Fig. 1). One group of oxygen species has an oxidation power (O.P) higher than 9.0 and another with one lower than 9.0. We designate the surface oxygen species in the two groups $O_s{}^h$ and $O_s{}^l$, respectively.

When the oxidized surface was exposed to a stream of CO(6%)–N_2 mixture for 30 min at 163 °C, the

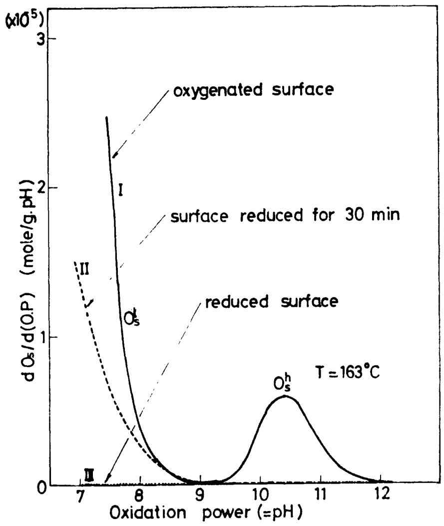

Fig. 1. Variation of the distribution of oxidation power by the reduction with CO.

newly measured distribution curve showed complete disappearance of $O_s{}^h$ accompanying an appreciable decrease of $O_s{}^l$ (curve II, Fig. 1). The partly reduced catalyst showed no variation in the amount of $O_s{}^l$ when it was kept standing in pure nitrogen stream for different periods of time, indicating that no transformation between $O_s{}^l$ and $O_s{}^h$ took place.

When the oxidized surface was completely reduced for 24 h by the same gas mixture until no carbon dioxide was detected in the effluent gas stream, no more oxygen species were detected by the KI method on this reduced surface (curve III, Fig. 1).

Based on these results it may reasonably be concluded that both $O_s{}^h$ and $O_s{}^l$ are active for the reaction with carbon monoxide and the rate of the reaction is high with $O_s{}^h$ and low with $O_s{}^l$.

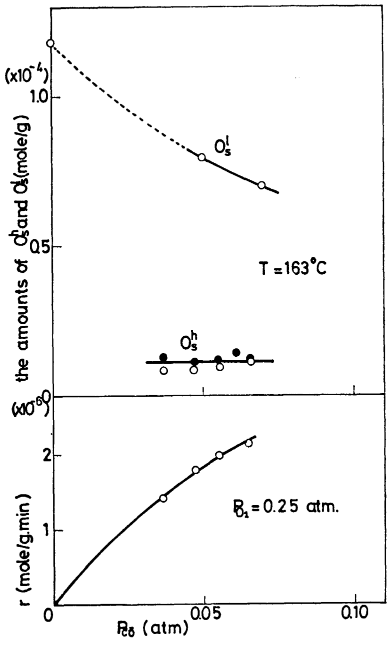

Fig. 2. The amounts of O_s^h and O_s^l and the rate of CO_2 formation on Cr_2O_3 as a function of P_{CO}.

The total amount of the surface oxygen species was determined with hydrazine solution,[7] which is a stronger reducing reagent than potassium iodide solution, and the amount was found to be 1.3×10^{-4} mol/g.

After the steady states of the reaction were attained at 163 °C with the feed streams of various partial pressure of carbon monoxide, the amounts of $O_s{}^h$ and $O_s{}^l$ existing on the surface were analyzed. The results are shown in Fig. 2 together with the reaction rate at each steady state. In this case, the amount of $O_s{}^l$ was determined as the difference between the total amount determined by the hydrazine method and the amount of $O_s{}^h$ determined by the potassium iodide method. The amount of $O_s{}^h$ remains constant irrespective of the partial pressure of carbon monoxide in the feed, with which the reaction rate varies considerably (Fig. 2). The open and solid circles for $O_s{}^h$ curve represent the repeated runs, indicating the satisfactorily good reproducibility of the data. The amount of $O_s{}^l$, on the other hand, decreases with increasing partial pressure of carbon monoxide in the feed stream. The results suggest that the rate of the reproduction of $O_s{}^h$ from gaseous oxygen is sufficiently rapid as compared with the rate at which $O_s{}^h$ is removed by the reaction with carbon monoxide, while the rate of the reproduction of $O_s{}^l$ is not great enough and eventually the amount of $O_s{}^l$ decreases with increasing partial pressure of carbon monoxide, where the reaction rate are higher. The deviation of the reaction rates from the first-order dependence in carbon monoxide can be explained by the diminution of $O_s{}^l$.

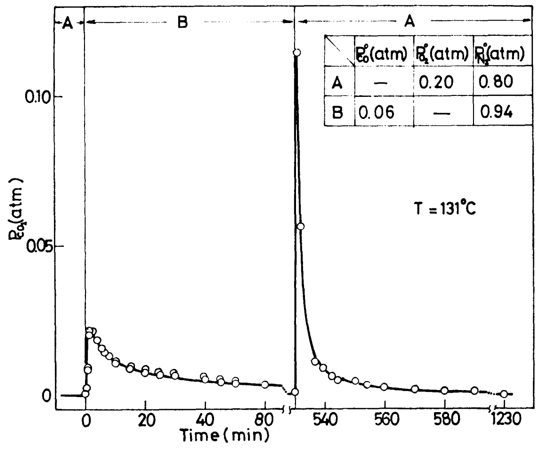

Fig. 3. CO–CO_2 response.

Amount of Surface Oxygen Determined by the Transient Response Method. After the catalyst was completely oxidized in the stream of O_2(20%)–N_2 mixture, the feed was suddenly replaced by the stream of CO(6%)–N_2 mixture and the CO(inc., 0)–CO_2 response was followed for 530 min until no more desorption of carbon dioxide was observed. The results are shown in Fig. 3. Since no oxygen is present in the gas phase after changing the feed composition, the graphical integration of the CO(inc., 0)–CO_2 response curve gives the amount of carbon dioxide produced by the reaction between surface oxygen species and carbon monoxide and then released from the surface. It is estimated to be 2.5×10^{-4} mol/g.

In the subsequent run, the feed stream of CO(6%)-N_2 mixture was replaced by the stream of O_2(20%)-N_2 mixture and additional outflow of carbon dioxide was observed (Fig. 3, righthand-side). This addional release of carbon dioxide can be attributed to the desorption of irreversibly adsorbed carbon dioxide due to the competitive adsorption of oxygen on the same adsorption site. The behavior of adsorbed carbon dioxide will be discussed in detail in a subsequent paper (part II).[11] The amount of the irreversibly adsorbed carbon dioxide is estimated to be 5.2×10^{-5} mol/g. Hence the total amount of carbon dioxide produced by the reaction between surface oxygen species and carbon monoxide should be 3×10^{-4} mol/g, corresponding to 1.5×10^{-4} mol/g of surface oxygen species. The value is in good agreement with that estimated by the hydrazine method.

On the assumption that the cation layer in the undistorted (001) plane of α-chromia is associated with the surface, the number of surface chromium ions was calculated by McIver and Tobin[12] to be 9.8×10^{14} atom/cm^2. The oxygen adsorption on Cr_2O_3 surface might be dissociative. The amount of oxygen species adsorbed on the surface by the response method corresponds to 8.6×10^{14} atom/cm^2 by using BET surface area of 21 m^2/g. The value is very close to that of surface chromium ions, indicating that each of the dissociatively adsorbed oxygen is bonded to a chromium ion and the surface chromium ions are almost entirely covered with adsorbed oxygen atoms. The fact that the total amount of adsorbed oxygen does not change even when the oxidized surface is exposed to a stream of pure nitrogen at 131 °C for 60 min indicates that the adsorption of oxygen to the surface is fairly strong.

Adsorption of Oxygen on the Reduced Surface. After the reduced catalyst had been kept in a stream of pure nitrogen, the stream was replaced by a stream of O_2(20%)-N_2 mixture and the responce in the oxygen concentration in the effluent stream and the electrical conductivity of the catalyst were followed simultaneously. The results of the response in the conductivity (open circle) are shown in Fig. 4. Owing to the adsorption of oxygen the electrical conductivity of the catalyst increases very rapidly at the initial stage but becomes very slow in the following period of time. Since the catalyst is a p-type semiconductor, the increase in conductivity indicates the shift of electron from the catalyst to the adsorbed oxygen probably bringing about the formation of oxygen anions.

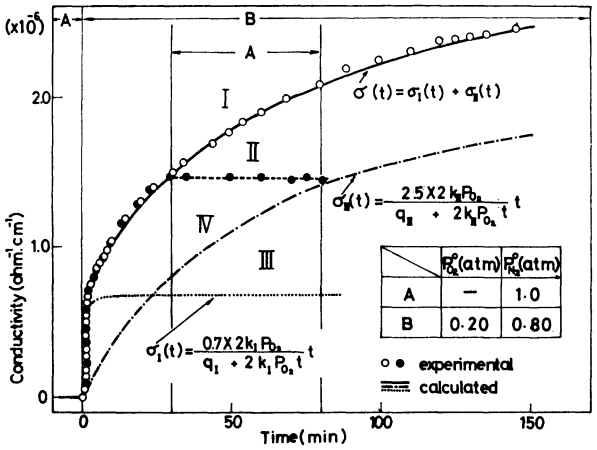

Fig. 4. O_2 (inc., 0)-σ response.

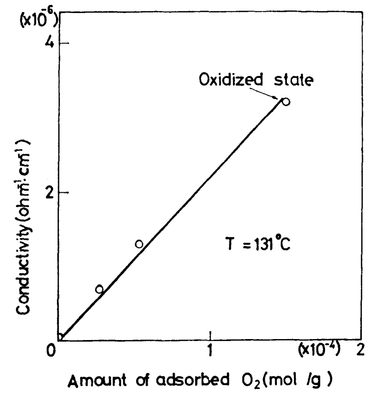

Fig. 5. Linear relationship between the amount of adsorbed O_2 and the conductivity.

From the response in the oxygen concentration in the effluent stream, we can estimate the amount of adsorbed oxygen at each instant. When the conductivity of the catalyst is plotted against the amount of adsorbed oxygen at each instance, a linear relationship is obtained (Fig. 5). The linearity differs slightly from that obtained by Weller and Voltz,[13] who found that the conductivity was proportional to the 1.2 power of the amount of adsorbed oxygen. Although they stated that the precision of this relationship was not high because of the absolute changes in conductivity observed, the difference in the method of pretreatment of the sample might have caused the disagreement.

The observed response data show at first very rapid and then gradual increases in conductivity. This characteristic behavior of the response curve strongly suggests that the change is due to two different steps. Possible cases are; 1) the successive two-step electron transfer at different rates to the adsorbed oxygen from the catalyst, 2) adsorption of oxygen followed by bulk diffusion into the body of oxide associated with successive electron transfer as suggested by Burwell *et al.*,[2] and 3) the parallel adsorption of oxygen onto two different kinds of active sites at different adsorption rates associated with electron transfer. If 1) or 2) were the case, a gradual increase in the conductivity should be observed when the O_2(20%)-N_2 stream is replaced by a pure nitrogen stream during the course of response measurement. However, the experimental results (solid circles) showed no such changes in conductivity, remaining constant (Fig. 4). Thus the most probable case should be 3). The constancy of the conductivity of the catalyst, which was kept in the pure nitrogen stream, indicates the irreversibility of the oxygen adsorption on both types of active site.

Let us thereby assume the following two parallel elementary steps for the adsorption of oxygen.

$$O_2(g) + S_I \xrightarrow{k_I} O_s^- \cdot S_I \qquad \text{(very fast)} \qquad (1)$$

$$O_2(g) + S_{II} \xrightarrow{k_{II}} O_s^- \cdot S_{II} \qquad \text{(slow)} \qquad (2)$$

where S_I and S_{II} denote the different sites for the adsorption of oxygen with different activities, and O_s^- denotes the negatively charged oxygen spcies. One can roughly estimate the total amounts of $O_s^-\cdot S_I$ and $O_s^-\cdot S_{II}$ by using conductivity data (Fig. 4) and the linear relationship (Fig. 5). Let us suppose that the initial rapid increase in conductivity up to 0.7×10^{-6} ohm^{-1} cm^{-1} is mainly due to the rapid adsorption on site S_I and the gradual increase thereafter results from the slow adsorption on sites S_{II}. Since the conductivity of the catalyst reaches a maximum, 3.2×10^{-6} ohm^{-1} cm^{-1}, with the saturated amount of adsorbed oxygen (Fig. 5), the saturated amounts of $O_s^-\cdot S_I$ and $O_s^-\cdot S_{II}$ are estimated to be 3.3×10^{-5} mol/g and 1.17×10^{-4} mol/g, respectively.

Assuming the dissociative adsorption of oxygen, the rates of adsorption on S_I and S_{II} are given, respectively, by

$$\frac{d\theta_I}{dt} = \frac{2k_I}{q_I}(1-\theta_I)^2 P_{O_2} \tag{3}$$

$$\frac{d\theta_{II}}{dt} = \frac{2k_{II}}{q_{II}}(1-\theta_{II})^2 P_{O_2} \tag{4}$$

where q_I and q_{II} are the saturated amounts of $O_s^-\cdot S_I$ and $O_s^-\cdot S_{II}$, respectively, and θ_I and θ_{II} are the coverage fractions of respective sites.

The rates of oxygen adsorption on sites S_I and S_{II}, respectively, can be easily estimated from the graphical differentiation of the response curve in two portions, from zero to 0.7×10^{-6} ohm^{-1} cm^{-1} and from that to 3.2×10^{-6} ohm^{-1} cm^{-1}. For this purpose, the response curves of P_{O_2} and σ at initial stage are shown in Fig. 6. $d\theta_I/dt$ and $d\theta_{II}/dt$ thus obtained at each instance are plotted against $(1-\theta_I)^2$ and $(1-\theta_{II})^2$, respectively, and linear relationships are obtained (Fig. 7), where $(1-\theta_I)^2$ and $(1-\theta_{II})^2$ are denoted by θ_V^2, indicating Eqs. 3 and 4 fit the data satisfactorily. From the slopes of both straight lines, two adsorption rate constants, k_I and k_{II}, are calculated, respectively, as

$$k_I = 1.75\times10^{-4} \text{ mol/g atm min}$$

$$k_{II} = 4.8\times10^{-6} \text{ mol/g atm min}$$

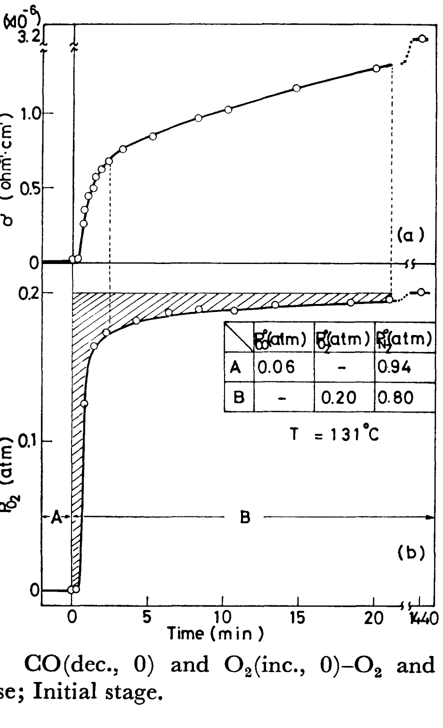

Fig. 6. CO(dec., 0) and O_2(inc., 0)–O_2 and σ response; Initial stage.

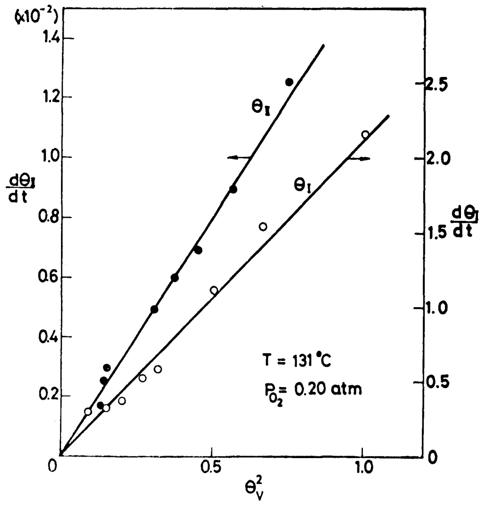

Fig. 7. Plots of $d\theta_I/dt$ and $d\theta_{II}/dt$ vs. θ_V^2.

Equations 3 and 4 can be easily integrated with the initial conditions, $\theta_I=0$, $\theta_{II}=0$ at $t=0$, to give

$$\theta_I(t) = \frac{at}{1+at} \tag{5}$$

$$\theta_{II}(t) = \frac{bt}{1+bt} \tag{6}$$

where $a=2k_I P_{O_2}/q_I$ and $b=2k_{II}P_{O_2}/q_{II}$. These equations give the time variation of fractional coverage of sites S_I and S_{II}, and can easily be transformed into the time variation of conductivity owing to the oxygen adsorption on both sites.

$$\sigma_I(t) = \frac{0.7at}{1+at} \tag{7}$$

$$\sigma_{II}(t) = \frac{2.5at}{1+at} \tag{8}$$

σ_I and σ_{II} are the conductivity contribution due to the adsorption of oxygen on sites S_I and S_{II}, respectively. With the values of $q_I=3.3\times10^{-5}$, $q_{II}=1.17\times10^{-4}$ mol/g and $P_{O_2}=0.2$ atm, Eqs. 7 and 8 are calculated as illustrated by curves III and IV in Fig. 4, respectively. Superposition of curves III and IV gives the calculated curve I, indicating an excellent agreement with the observed data. We might conclude that oxygen is adsorbed dissociatively on two different kinds of adsorption sites with simultaneous charge transfer from the catalyst.

The results showing that O_s^h is much more quickly reproduced than O_s^l from gaseous oxygen suggest that O_s^h and O_s^l correspond to $O_s^-\cdot S_I$ and $O_s^-\cdot S_{II}$, respectively. q_I (the amount of $O_s^-\cdot S_I$) and q_{II} (the amount of $O_s^-\cdot S_{II}$) correspond fairly well to the amount of oxygen species which produce irreversibly adsorbed CO_2 and reversibly adsorbed CO_2, respectively. The carbon dioxide formed on S_I seems to be adsorbed irreversibly and that formed on S_{II} reversibly.

Davydov, Shchekochikhin and Keier[14] demonstrated that the reaction of CO takes place primarily with oxygen combined with Cr ions exhibiting the lowest degree of coordinative saturation with respect to oxygen. The surface compounds produced in the process, however, form slightly stronger bonds with the surface than the suface compounds combined with the Cr ions exhibiting the higher degree of coordinative saturation with respect to oxygen. The correspondence mentioned above seems to be reasonable.

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