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Application of Transient Response Method to the Study of Heterogeneous Catalysis

I. Nature of Catalytically Active Oxygen on Manganese Dioxide for the Oxidation of Carbon Monoxide at Low Temperatures

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The nature and the behavior of the surface oxygen species on manganese dioxide were studied in detail by means of the transient response method. The surface oxygen on manganese dioxide during the oxidation of carbon monoxide at −15°C was classified into two parts, O_s^h and O_s^l, and O_s^h was found to be responsible for the catalytic activity of this oxide. The amount of O_s^h determined by the transient response method was in good agreement with that obtained by the analysis with the KI method which was used in our previous work. It was concluded that the O_s^h is in the forms of O_2^- or O^- and is rapidly regenerated with the gaseous oxygen during the catalytic oxidation of carbon monoxide. This regeneration seems to take place instantaneously upon the release of electrons as the sequence of the reactions between the ionized oxygen species and the gaseous carbon monoxide followed by the desorption of carbon dioxide formed. The O_s^l, probably in the form of oxygen molecules, can transform into O_s^h, but the rate is very slow.

INTRODUCTION

The flow method under a steady state has frequently been used for kinetic studies of heterogeneous catalytic reactions. Because of the complexity of the reaction sequences on the catalyst, the information obtained merely from the analysis of reaction components under a steady state is too limited to elucidate the mechanism of the reaction. In order to obtain as much information as possible about the events on the catalyst surface, an attempt was made to introduce a transient response method to the steady state flow method. Since it is based on the ordinary flow method, a minor perturbation introduced can differentiate the rate of events on the catalyst under any reaction conditions being as they are. In the present study, the catalytic oxidation of carbon monoxide on manganese dioxide was studied by this method.

Boreskov, Popovsky and Sazonov (*1*) and Boreskov (*2*) have pointed out that the catalytic activity of various metal oxides for complete oxidation reaction and homomolecular oxygen exchange reaction are related to the bond energy of active oxygen on the surface of the oxides. According to their investigation, the oxygen on the surface is bound with various strengths and the catalytic activity can be attributed to the weakly bound oxygen. Kasatkina and Zuev (*3*) and Kasatkina and Amerikov (*4*) also pointed out from the isotopic oxygen exchange reaction on manganese dioxide at 25–400°C that the oxygen on the surface can be classified into two parts; one is weakly bound and the other is strongly bound to the surface, and the former part of the oxygen is catalytically active for carbon monoxide oxidation reaction.

Uchijima, Takahashi and Yoneda (*5*) developed an analytical method for the classification of surface oxygen species with respect to the oxidation power and suggested that the particular surface oxygen is effective for the particular oxidation reaction.

According to our previous study (*6*) conducted with manganese dioxide catalysts by using this analytical method it was concluded that the oxygen on the surface can be classified into two parts with respect to the oxidation power. The oxygen of higher oxidation power was designated as O_s^h and that of lower oxidation power as O_s^l. It was concluded that a part of O_s^h is effective for the oxidation of carbon monoxide and that it was related to the weakly bound oxygen as characterized by Boreskov and Kasatkina. A further study on the nature of this active oxygen on the surface is the main theme of the present investigation.

TRANSIENT RESPONSE METHOD

There are several different methods which can be applied to follow a nonsteady state of a reaction system. In the present study, a transient response to a step change in the concentration of reaction components was followed. A differential flow type reactor with an appropriate amount of catalyst is used and the system is kept under a steady state with a constant flow rate at a given temperature. By using a four-way valve attached to the inlet of the reactor the stream of the reaction gas mixture is switched over from one to the other in which only one component is slightly different in its concentration. The concentration jump is restricted slightly so that no appreciable temperature change would take place. The response of the exit gas concentration and/or electrical conductivity of the catalyst is followed by gas chromatographic analysis and a conductivity measurement device. The characteristic behavior of the response curve can provide information on the amount and the state of adsorbed species, and on the rates of several elementary steps including the charge transfer to and from the catalyst.

EXPERIMENTAL METHODS

A commercial manganese dioxide (0.7 wt % Fe, 0.00096 wt % SO_4^{2-}) was used as the catalyst which was prepared by electrolysis of manganese sulfate solution. The catalyst in 60–80 mesh granule was dried in a flowing gas mixture of oxygen (20%) and nitrogen (80%) at 110°C for 24 hr. The BET surface area with nitrogen was 31 m^2/g. The Hall effect measured in air at room temperature showed that this catalyst was a *n*-type semiconductor.

Carbon monoxide (CO, 99.73%; O_2, 0.04%; N_2, 0.18%; H_2, 0.03%; and CO_2, 0.02%), nitrogen (N_2, 99.99%; O_2, 0.00045%; balance Ar), helium (He, 99.999%; O_2, 0.0009%; N_2, 0.00013%; balance Ar) and oxygen (O_2, 99.8%; N_2, 0.0047%; CH_4, 0.0025%; CO_2, 0.0005%; balance Ar) from commercial cylinders were purified by potassium hydroxide and silica gel with a dry ice–methanol trap to remove water vapor and carbon dioxide. Carbon dioxide from a commercial cylinder was also purified through a dry ice–methanol trap to remove water vapor.

The catalyst (39.8 g) was packed in the reactor consisting of a copper tube (0.55 cm i.d. and 83 cm length) immersed in a methanol bath. The thermocouples were inserted into both ends of the catalyst bed and the temperature was controlled in a range from −5 to −26°C with an accuracy of ±0.05°C. The temperature difference between the inlet and the outlet of the bed was always less than 0.1°C. The thermocouple and the copper tube were previously confirmed to be catalytically inactive under reaction conditions.

The total flow rate of the gas was kept constant at 180 ± 1 ml (NTP)/min, and the mean residence time calculated at this flow rate was 4 sec. The transient response to the step change in the composition of He–N_2 mixture was completed within 10 sec. The intraparticle diffusion resistance of the catalyst was found to be negligible by examining the rate data for catalysts of different sizes, 60–80 and 80–100 mesh, at 50°C. The external mass transport effect was also found to be negligible at the same temperature by examining the rate data at a constant W/F with various flow rates and catalyst amounts. The concentrations of carbon monoxide, carbon dioxide and oxygen were varied by changing the concentration of nitrogen or helium as the diluent. Whenever the gas stream was switched from one to another, special care was taken so as not to affect the total flow rate and the change in the total flow rate upon changing the gas stream was controlled within 1%. The reaction conditions were chosen in such a way that the total conversion did not exceed 5%.

The conductivity of the catalyst was measured by using either a d.c. bridge or an a.c. bridge of various frequencies up to 30 kHz. Since the results obtained by both methods showed similar behavior, the d.c. measurements were commonly used. A schematic drawing of the conductivity cell is shown in Fig. 1. The catalyst (0.5 g) was mounted between two platinium perforated disks and the upper platinium disks were pressed firmly by a stainless steel spring. An additional amount of catalyst (8.5 g) was placed in the same cell to facilitate the measurement of reaction rates and the amount of adsorbed species. The platinium disks and the stainless steel spring were previously confirmed to be catalytically inactive under the reaction conditions.

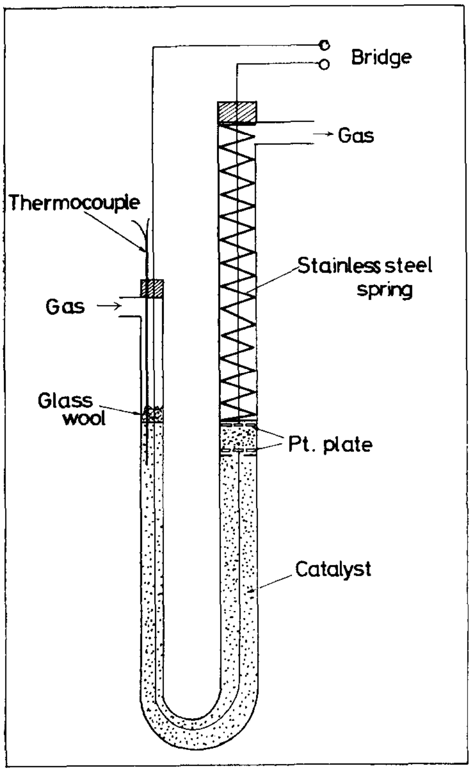

Fig. 1. Schematic drawing of the electrical conductivity cell.

The surface oxygen species were analyzed by the KI method which was described in the previous paper (*6*).

Experimental Results and Discussion

The response of the component B in the outlet gas mixture to a step change in the concentration of A in the inlet gas stream is designated as the A–B response. When A is increased, A(inc.)–B, and when decreased, A(dec.)–B, and when A is increased from nil, A(inc., 0)–B, and when decreased down to nil, A(dec., 0)–B.

1. *Distribution of Oxidation Power of the Surface Oxygen Species During the Carbon Monoxide Oxidation at a Low Temperature*

The distribution of oxidation power of the surface oxygen species during the carbon monoxide oxidation at 50°C was presented in Ref. (*6*). In the present study, the same measurements were made with the catalyst used at −15°C. To obtain more reliable data, the analysis of surface oxygen by the KI method was made at nine different pH values covering the range from 7.1 to 12.2. The results are shown in Fig. 2. As shown in Fig. 2, the same mode of distribution with respect to the oxidation power exists also at this lower temperature. Hence we may again classify the surface oxygen into two parts, one which has a higher oxidation power than pH 9 and the other which has a lower oxidation power than pH 9. We designate again the surface oxygen species in both parts as O_s^h and O_s^l, respectively.

2. *Reaction Between the Surface Oxygen Species and the Gaseous Carbon Monoxide*

The catalyst which was used for the reaction under a steady state was reduced with a carbon monoxide–helium mixture until the production of carbon dioxide became too small to be detected and it was then treated with oxygen–helium mixtures of various concentrations for 24 hr. After this mixture was replaced with a pure helium stream for 30 min, the stream was

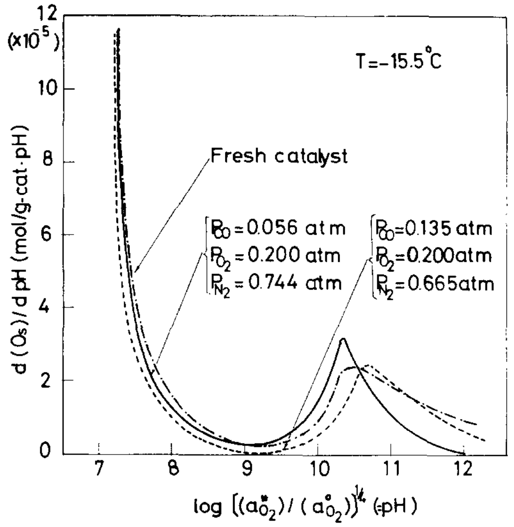

FIG. 2. Distribution of oxidation power of the surface oxygen in various atmospheres.

switched over to a helium stream containing carbon monoxide. The CO(inc., 0)–CO_2 response was followed and presented as curve (1) in Fig. 3. As shown in the figure, the response data followed the same curve regardless of the difference in the partial pressures of oxygen in the oxidizing gas stream as tabulated in Fig. 3. The same response was observed even after oxidation for 30 min. Since there is no oxygen in the gas phase, the carbon dioxide produced results from the reaction between gaseous carbon monoxide and active surface oxygen. The formation of carbon dioxide, therefore, should be initially rapid and then decrease monotonously due to the monotonous decrease in the amount of active surface oxygen. The response curve obtained here, however, did not show such a behavior and rather showed a maximum. The slow formation of carbon dioxide at the initial stage of the response will be ascribed to the slow desorption of carbon dioxide formed on the catalyst surface.

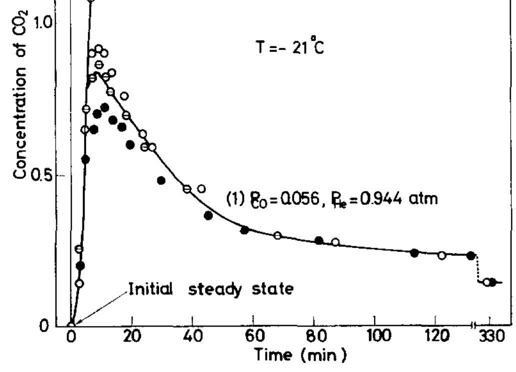

FIG. 3. The CO(inc., 0)-CO_2 response.

When the pure helium stream was switched to the helium stream containing both carbon monoxide and oxygen, the response was as presented by curve (2) in Fig. 3. If the regeneration of active surface oxygen is slow compared with the reaction between gaseous carbon monoxide and active surface oxygen, as suggested by Klier and Kuchynka (*7*), this curve will show a maximum and will reach a new steady state of lower value. This response curve, however, did not exhibit the maximum but monotonously reached a new steady state of a much higher value. It may reasonably be concluded from these results that the regeneration of active surface oxygen is fairly rapid compared with the reaction between gaseous carbon monoxide and active surface oxygen.

As shown in Fig. 3, the curve (1) obtained as CO(inc., 0)–CO_2 response in the system without oxygen shows a pseudo-steady state for a considerable period of time and does not show a decrease down to zero. This can be ascribed to the following two causes. As was stated in the previous section, there are two types of oxygen on the surface, O_s^l and O_s^h, and only O_s^h is active for the oxidation of carbon monoxide and the amount of O_s^l is very large compared with that of O_s^h. Hence, if O_s^l gradually transforms into O_s^h while O_s^h is being consumed by the reaction with gaseous carbon monoxide, the formation of carbon dioxide will last for a long period of time with a rate equivalent to that of this transformation. Winter (*8*) suggested such a slow transformation of surface oxygen species. Another cause is the presence of oxygen in the gas phase as an impurity in carbon monoxide and helium supplied from the cylinders. The fraction of oxygen contained in the mixture of both gases was 2.7×10^{-5} and this corresponds to 5.4×10^{-5} in the concentration of carbon dioxide formed. This value is almost the same as that observed after 24 hr. One can evaluate the amount of active oxygen initially existing on the surface by the graphical integration of curve (1) up till 330 min with a substraction of the secondary contribution of oxygen mentioned above. The amount of active oxygen initially existing on the surface thus determined was $0.8\text{–}1.3 \times 10^{-5}$ mol/g ($1.6\text{–}2.5 \times 10^{13}$ molecule/cm^2) depending on the activity of the catalysts. This value is in good agreement with that obtained by Klier and Kuchynka (*7*), namely $4\text{–}6 \times 10^{12}$ molecule/cm^2 at 20°C and $1\text{–}1.4 \times 10^{13}$ molecule/cm^2 at 100°C.

The amount of surface oxygen on the catalysts was also analyzed by the KI method and the results were presented in Fig. 4. The surface oxygen was analyzed with a fresh catalyst which was previously reduced by carbon monoxide–helium mixture until no carbon dioxide could be detected.

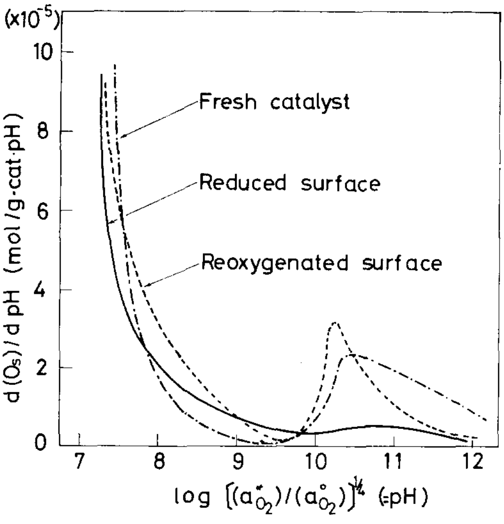

FIG. 4. Variation of the distribution curves of oxidation power of the surface oxygen due to various treatments.

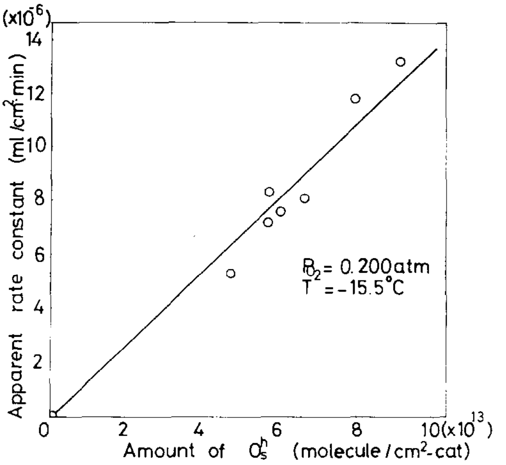

FIG. 5. Linear relationship between the apparent rate constant and the amount of O_s^h.

The distribution curve obtained with this reduced catalyst shows the disappearance of O_s^h as compared against that of the fresh catalyst. Reoxidation of this reduced catalyst with oxygen (20%)–helium mixture for 30 min shows a complete regeneration of this vanished oxygen. The amounts of oxygen of lower oxidation power were almost the same as that in the catalysts. This result clearly indicates that the oxygen of higher oxidation power is responsible for the reaction with gaseous carbon monoxide. Since the rate of carbon monoxide oxidation on manganese dioxide is of the first order with respect to carbon monoxide, this rate constant was plotted against the amount of this active oxygen, O_s^h, with catalysts of various activities. The results showed a good proportionality as shown in Fig. 5 and this provides further evidence for above conclusion. The amount of this active oxygen, O_s^h, determined by the KI method as shown in Fig. 5 is in good agreement with that obtained by the response method.

3. Form of Catalytically Active Oxygen

A number of investigators using either ESR (*8, 9*) or the conductivity measurement (*10–12*) proposed that the surface oxygen species on various metal oxides are ionized. Thus, it is a point of interest to know whether O_s^h on MnO_2 is neutral or ionized. In order to investigate this problem it will be worthwhile to examine the KI method in detail. In the KI methods, the reduction of the surface oxygen was assumed to take place as a coupling of the following two simultaneous reactions,

$$\tfrac{1}{2}O_2 + 2H^+ + 2e \rightleftharpoons H_2O, \qquad (1)$$

$$I_3^- + 2e \rightleftharpoons 3I^-. \qquad (2)$$

According to our measurements on the equilibrium potential of reactions (2) on MnO_2 electrode, it was found that the equilibrium of I_3^-/I^- system passed into that of IO_3^-/I^- system at pH values higher than 11.25 as shown in Fig. 6.

$$IO_3^- + 6H^+ + 6e \rightleftharpoons I^- + 3H_2O. \qquad (3)$$

The equilibrium potentials of these reactions are given as follows:

$$E_1 = E_1^0 + \frac{RT}{2F}\ln\frac{(a_{O_2})^{1/2}(a_{H^+})^2}{(a_{H_2O})}, \qquad (1')$$

$$E_2 = E_2^0 + \frac{RT}{2F}\ln\frac{(a_{I_3^-})}{(a_{I^-})^3}, \qquad (2')$$

$$E_3 = E_3^0 + \frac{RT}{6F}\ln\frac{(a_{IO_3^-})(a_{H^+})^6}{(a_{I^-})(a_{H_2O})^3}. \qquad (3')$$

The pH dependencies of E_1, E_2 and E_3 are 59.1, 0 and 59.1 mV/pH, respectively. At pH values lower than 11.25, the reaction (1) will be coupled with reaction (2) and the electromotive force E_r for the reduction of the surface oxygen by I^- ion will therefore be given as $E_r = E_1 - E_2$. Since this E_r is dependent on pH, the distribution on the oxidation power of oxygen species can be obtained by the measurement at different pH values. At pH values higher than 11.25, however, if reaction (1) is coupled with reaction (3), E_r, which is given by $E_1 - E_3$, should be constant being independent of pH due to the same pH dependencies of E_1 and E_3. Therefore, the amount of surface oxygen measured in this higher pH region should be constant being independent of pH. As shown in Figs. 2 and 4 this was not the case and the distribution of the surface oxygen was dependent upon pH even in this higher pH region. This suggests that the reaction coupled with reaction (3) is not reaction (1) but either or both of the following reactions.

$$O_2^- + 4H^+ + 3e \rightleftharpoons 2H_2O, \qquad (4)$$

$$O^- + 2H^+ + e \rightleftharpoons H_2O. \qquad (5)$$

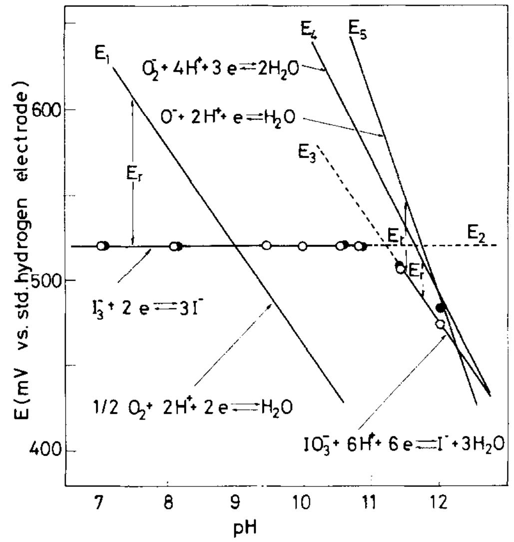

FIG. 6. Diagram of the oxidation–reduction potential as a function of pH: (○) experimental data; (●) $I_3^-/I^- = 0.0126$.

$E_1 = E_1^0 + (RT/2F)\ln[(a_{O_2})^{1/2}(a_{H^+})^2/(a_{H_2O})]$

$E_2 = E_2^0 + (RT/2F)\ln[(a_{I_3^-})/(a_{I^-})^3]$

$E_3 = E_3^0 + (RT/3F)\ln[(a_{IO_3^-})(a_{H^+})^6/(a_{I^-})(a_{H_2O})^3]$

$E_4 = E_4^0 + (RT/3F)\ln[(a_{O_2^-})(a_{H^+})^4/(a_{H_2O})^2]$

$E_5 = E_5^0 + (RT/F)\ln[(a_{O^-})(a_{H^+})^2/(a_{H_2O})]$

The equilibrium potentials of these reactions are given as follows:

$$E_4 = E_4^0 + \frac{RT}{3F}\ln\frac{(a_{O_2^-})(a_{H^+})^4}{(a_{H_2O})}, \qquad (4')$$

$$E_5 = E_5^0 + \frac{RT}{F}\ln\frac{(a_{O^-})(a_{H^+})^2}{(a_{H_2O})}. \qquad (5')$$

Since E_4 and E_5 have the pH dependency of 78.8 and 118.2 mV/pH, respectively, the value of E_r of the coupled system of reaction (3) with either of reaction (4) or reaction (5) will also be dependent on pH and, hence, the distribution of the oxidation power of surface oxygen can be measured as shown in Figs. 3 and 5. Based on these discussions, therefore, we may reasonably assume that the catalytically active oxygen O_s^h measured in a higher pH region would be either or both of the two types of oxygen ions, i.e., O_2^- and O^-.

In this regard, the following transient response provides another valuable information. After a steady state of the reaction is

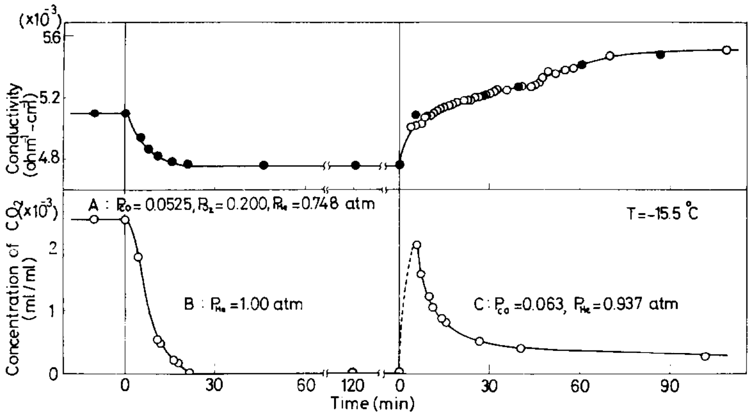

FIG. 7. The CO–CO_2 and the CO-conductivity response.

reached, the stream of reaction gas mixture was switched over to a stream of pure helium and the change in both the electrical conductivity of the catalyst and the concentration of CO_2 produced were followed simultaneously. The results were shown in Fig. 7. The electrical conductivity decreased gradually until it reached a new steady state after 20 min. The concentration of released CO_2 also decreased gradually until ultimately no appreciable amount was detected after 25 min.

In our separate experiments, which will be published elsewhere, it was found that no conductivity change was observed when carbon dioxide was reversibly adsorbed or desorbed during the reaction of carbon monoxide oxidation. Hence, although the variations in the electrical conductivity and also in the concentration of carbon dioxide last for almost the same period of time, the change in the electrical conductivity cannot be attributed to the desorption of carbon dioxide. Carbon monoxide, which is usually considered to be adsorbed as an electron doner, was also found not be adsorbed on the surface by the separate experiments and, therefore, it cannot be held responsible for the decrease in electrical conductivity. Since this catalyst is a *n*-type semiconductor, another possibility which can be allowed would be the picking up of an electron from the catalyst by oxygen on the surface, presumably an oxygen molecule, which was previously adsorbed on the surface, because there was no oxygen in the gas phase. This reminds us that there is an abundance of less active oxygen, $O_s{}^l$, on the surface and this oxygen can be slowly transformed into active oxygen. Therefore, the less active oxygen $O_s{}^l$ are probably the oxygen molecules and pick up electrons slowly to form active oxygen O_2^- or O^-.

After this catalyst was kept in a stream of pure helium for several hours, the gas was again switched over to a mixture of carbon monoxide and helium. The electrical conductivity again increased due to the release of electrons as the sequence of the reaction between the gaseous carbon monoxide and negatively charged surface oxygen species followed by the desorption of electrically neutral carbon dioxide from the surface. This observed behavior of the electrical conductivity of the catalyst provides further evidence pointing of the fact that the catalytically active oxygen species on the surface are negatively charged.

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