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Distribution of Oxidation Power of Surface Oxygen Species on Manganese Dioxide during the Oxidation of Carbon Monoxide

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The oxidation power of surface oxygen species on manganese dioxides and their catalytic activities were measured simultaneously. The results showed that the distribution of oxidation powers varies depending upon the ambient gas atmospheres and that the catalytic activity for the oxidation of carbon monoxide is closely related to the oxygen species of higher oxidation powers. Discontinuous changes were observed both in the oxidation power distribution and in the catalytic activity at a certain partial pressure of carbon monoxide and it was attributed to the change of crystallographic structure of the surface layer of the catalyst. The mode of the variation of the distribution of oxidation power suggests the existence of two different kinds of oxygen: One is dependent in its amount on the partial pressure of carbon monoxide and the other is not. Based upon these results, a new reaction mechanism was proposed.

INTRODUCTION

The catalytic oxidation of carbon monoxide on manganese dioxide has been extensively studied by a number of investigators [*1–3*]. As is well known, manganese dioxide is not a stable oxide such as other transition metal oxides, NiO etc. [*4*], and the valency of Mn ions as well as the surface state of manganese dioxide varies readily with the surrounding gas atmosphere and the temperature. This characteristic feature of manganese dioxide affects the catalytic activity thereof. Since the catalytic activities of transition metal oxides are mainly controlled by the surface active oxygen on the solids [*5, 6*], it would be worthwhile to investigate the variation of oxidation power of surface oxygen species during the course of oxidation reaction of carbon monoxide.

In this study, the catalytic activity and the variation of oxidation power of surface oxygen species on manganese dioxide were measured simultaneously to determine the amount and the role of the surface active oxygen in the catalytic oxidation of carbon monoxide. The strength of the bond between the surface oxygen and the manganese dioxide surface was also studied by a desorption method.

EXPERIMENTAL

A commercial manganese dioxide for dry cells prepared by electrolysis of manganese sulfate solution was used as the catalyst. Examination by X-ray diffraction analysis revealed an amorphous state of the sample. The BET surface area was found to be 30.8 m^2/g. The catalyst in 60–80 mesh particle size was dried by heating in a flowing gas mixture of 20 vol % oxygen and 80 vol % nitrogen at 110°C for 24 hr. Carbon monoxide (99.73 vol % CO, 0.04 vol % O_2, 0.18 vol % N_2, 0.03 vol % H_2 and 0.02 vol % CO_2), nitrogen and oxygen from commercial cylinders were purified by potassium hydroxide and silica gel plus a Dry Ice–Methanol trap to remove carbon dioxide and water vapor.

The reactor consists of a quartz tube of 4.5 mm i.d. containing 0.55-g catalyst. This was immersed in an electrically heated fluidized bed, and hence the temperature of the catalyst bed was kept uniform within ±0.1°C at the desired temperature.

The activity of the catalyst was measured in a flow system under atmospheric pressure, with the total flow rate of the reaction gas mixture of 176 cm^3/min at 50°C. The concentrations of carbon monoxide and oxygen were varied by changing the concentration of nitrogen as a diluent. Reaction conditions were chosen in such a way that the total conversion of carbon monoxide did not exceed 0.05 for all measurements.

When a fresh catalyst was used, the initial activity was very high, however it decreased gradually down to about one-fifth of the initial activity. Approximately 7–10 hr were needed before a fresh catalyst reached its steady state activity under a given reaction condition. After measuring the reaction rate at a steady state, the catalyst was rapidly cooled down to 17°C in the flow of the same reaction gas mixture and was then removed from the reactor and introduced quickly into a vessel under a nitrogen flow. The catalyst sample in the vessel was then subjected to analysis of the surface oxygen either by the KI method [*5*] or the hydrazine method [*7*].

When the KI method was used for the analysis of the surface oxygen, a phosphate buffer solution with 3 wt % of KI was introduced into the vessel and allowed to react with the catalyst under vigorous shaking. The reaction mixture was then filtered by suction through a glass filter set in the vessel. All these procedures were carefully carried out under a nitrogen flow. A given amount of 1 *N* hydrochloric acid was added to the filtrate, and the iodine formed was titrated with a standard sodium thiosulfate solution using starch as an indicator. It was confirmed that the value of pH of phosphate buffer solution after reacting with the catalyst did not alter for 24 hr.

In the case of the hydrazine method, a measured amount of 0.1 *N* hydrazine sulfate solution (pH 8.4–8.6) was introduced into the reaction vessel, and after left standing for the reaction, the mixture was filtered. Several drops of 0.01 *N* sulfuric acid solution and 0.3 g of sodium bicarbonate as a buffer were then added to the filtrate and the pH of the solution was adjusted to 7.0–7.2. The residual hydrazine was then titrated back by the 0.1 *N* iodine solution.

The amount of surface oxygen determined by the KI method varies with the time of reaction between the catalyst and the iodine solution. When the pH of the solution is close to neutral, several hours were required to obtain a constant amount of the surface oxygen, but for higher values of pH, the time required became shorter. From these results, 2.5 hr was adopted for the reaction time. For the same reason, 25 min was adopted in the case of the hydrazine method.

It was ascertained by a test with formaldoxime that no Mn^{2+} ion was formed in the filtrates of both methods. Experimental details of both the KI and the hydrazine methods are given in the literatures [*5*, *7*, *8*].

EXPERIMENTAL RESULTS AND DISCUSSIONS

1. Catalytic Activity of Manganese Dioxide

The rate of catalytic oxidation of carbon monoxide on an electrolytic manganese dioxide is proportional to the first order with respect to the partial pressure of carbon monoxide. The results of typical runs at 50°C were shown in Fig. 1(a). As may be seen from the figure, there is an abrupt change in the rate when the carbon monoxide partial pressure exceeds 65 mm Hg. This anomalous behavior was observed over fairly wide ranges of temperature and the partial pressure of oxygen and even with the natural manganese dioxide ores.

Two separate regions 1 and 2, respectively, were designated as shown in Fig. 1(a).

2. Variation of Oxidation Power of Surface Oxygen Species

The amounts of the surface oxygen on the catalysts used for the catalytic oxidation of carbon monoxide over a range of different partial pressures of carbon monoxide were determined by the KI method at four different pH's. The results were shown in Fig. 1(b). In both regions 1 and 2, the amounts of the surface oxygen determined

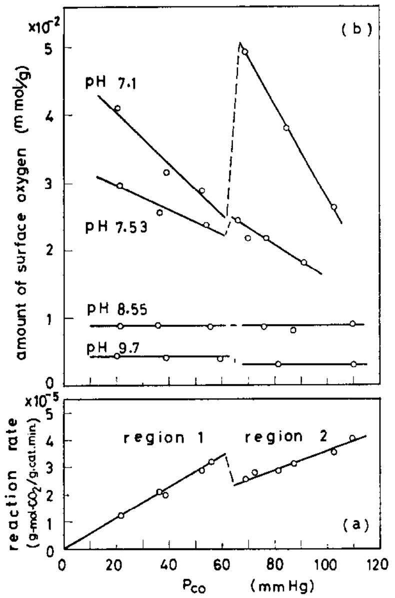

FIG. 1. The amount of surface oxygen determined by the KI method and the rate of CO_2 formation on MnO_2 as a function of p_{CO}; $p_{O_2} = 152$ mm Hg; $T = 50°C$.

at pH's of 7.1 and 7.53 decrease linearly with the increasing partial pressure of carbon monoxide but there are discontinuous changes in the amount of the surface oxygen at $p_{CO} = 65$ mm Hg as was observed in the reaction rate. The amounts of the surface oxygen determined at pH's of 8.55 and 9.7, however, remain constant in both regions 1 and 2 regardless of the partial pressures of carbon monoxide. At pH = 8.55, the amounts of the surface oxygen determined in both regions are almost the same, but at pH = 9.7, the amounts of the surface oxygen in both regions are different and again show a stepwise change at $p_{CO} = 65$ mm Hg.

In the case of the KI method, the reduction of the surface oxygen takes place as the coupling of the following two simultaneous reactions,

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

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

the redox potentials of which are expressed as

$$E_1 = E_1^0 + \frac{RT}{2F}\ln\frac{(a_{O_2})^{1/2}(a_{H^+})^2}{(a_{H_2O})} \qquad (3)$$

$$E_2 = E_2^0 + \frac{RT}{2F}\ln\frac{(a_{I_3})}{(a_{I^-})^3}, \qquad (4)$$

respectively. The electromotive force E_r of the reduction of the surface oxygen by I^- ion will therefore be given as

$$\begin{aligned} E_r &= E_1 - E_2 \\ &= (E_1^0 - E_2^0) + \frac{RT}{F}\Big[\ln(a_{O_2})^{1/4} \\ &\qquad + \ln(a_{H^+}) - \ln\frac{(a_{I_3^-})^{1/2}}{(a_{I^-})^{3/2}}\Big], \end{aligned} \qquad (5)$$

where a_{H_2O} is taken to be a unity.

Since the surface oxygen species are believed to have activities or oxidation powers broadly varied over a certain range, the oxygen which has a positive value of E_r at given conditions will be reduced by the coupled reaction of (1) and (2). If the limiting activity is designated as $a^*_{O_2}$, this is to be determined as the activity which gives $E_r = 0$ at given conditions of a_{H^+}, a_{I_3} and a_{I^-}. Rearranging Eq. (5), one may express $a^*_{O_2}$ by the following equation:

$$\begin{aligned} -\ln(a^*_{O_2})^{1/4} &= \frac{F}{RT}(E_1^0 - E_2^0) \\ &\qquad + \ln(a_{H^+}) - \ln\frac{(a_{I_3})^{1/2}}{(a_{I^-})^{3/2}}. \end{aligned} \qquad (6)$$

In the practical measurements made here, the conditions were so chosen that the value of $(a_{I_3^-})^{1/2}/(a_{I^-})^{3/2}$ could be kept as constant as possible. Hence, Eq. (5) may be reduced to

$$\log\left[\frac{(a^*_{O_2})}{(a^0_{O_2})}\right]^{1/4} = (\mathrm{pH}), \qquad (7)$$

where

$$\begin{aligned} -\log(a^0_{O_2})^{1/4} &= \frac{1}{2.303}\cdot\frac{F}{RT}(E_1^0 - E_2^0) \\ &\qquad - \log\frac{(a_{I_3})^{1/2}}{(a_{I^-})^{3/2}}. \end{aligned}$$

$(a^*_{O_2})/(a^0_{O_2})$ may be called the relative oxidation power of the surface oxygen which is critically reduced by I^- ions of a given concentration at a corresponding pH. The amount of the surface oxygen $(O)_s$ determined at a given pH, therefore, is the amount of surface oxygen species which have higher activities than $a^*_{O_2}$. The amounts

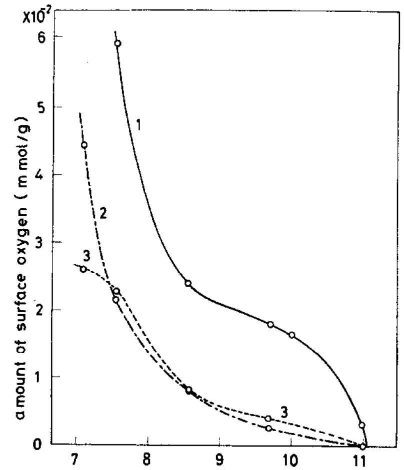

FIG. 2. The amount of surface oxygen of the manganese dioxide as a function of $\log[(a^*_{O_2})/(a^0_{O_2})]^{1/4}$. Curve 1, fresh catalyst; curve 2, region 2(p_{CO} = 75, p_{CO_2} = 152 mm Hg); curve 3, region 1(p_{CO} = 55 mm Hg, p_{O_2} = 152 mm Hg); T = 50°C.

of surface oxygen on a fresh catalyst and also on the catalysts in regions 1 and 2 were determined at various pH's and were plotted in Fig. 2 as the function of

$$\log\left[\frac{(a^*_{O_2})}{(a^0_{O_2})}\right]^{1/4}.$$

By graphical differentiation of the curves in Fig. 2, the characteristic distribution of oxidation power of each catalyst can be obtained as shown in Fig. 3. They suggest that there are two different types of oxygen, one appears in the region of higher oxidation power and the other in the region of lower oxidation power. They are denoted as O_s^h and O_s^l, respectively. The mode of these distribution curves also remind us that there were two types of oxygen, one is dependent in its amount on the partial pressure of carbon monoxide and the other is independent of the partial pressure of carbon monoxide. It may be noticed from these results that the amount of the surface oxygen O_s^l is dependent on the partial pressure of carbon monoxide, while the amount of the surface oxygen O_s^h is independent of the partial pressure of carbon monoxide. Since the effects of carbon monoxide partial pressure are different for O_s^l and O_s^h, these oxygens should be quite different in their nature.

The distribution curves were determined at different partial pressures of carbon monoxide covering region 1 and region 2, and the results are shown in Fig. 4 and Fig. 5, respectively. It may be seen from these results that the distribution of oxidation power of a catalyst varies remarkably depending on the partial pressure of carbon monoxide during the reaction and also that there is a discontinuous change in the distribution at 65 mm Hg of carbon monoxide partial pressure.

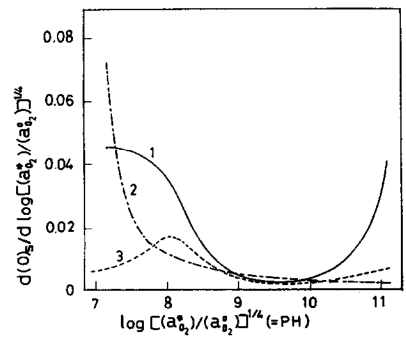

FIG. 3. Distribution curves of the oxidation power for the surface oxygen of the MnO_2. Curve 1, fresh catalyst; curve 2, region 2 (p_{CO} = 75 mm Hg, p_{O_2} = 152 mm Hg); curve 3, region 1 (p_{CO} = 55 mm Hg, p_{O_2} = 152 mm Hg); T = 50°C.

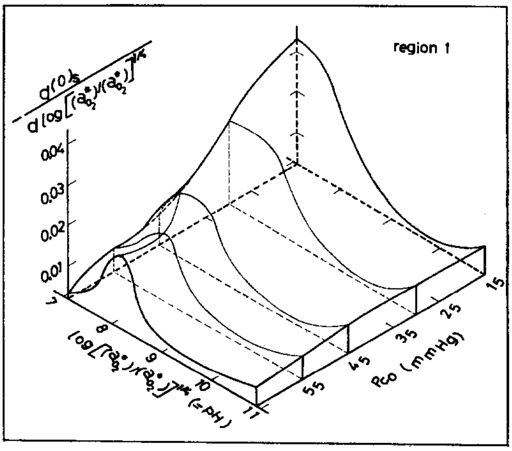

FIG. 4. Distribution surface of the oxidation power for the surface oxygen; region 1; p_{O_2} = 152 mm Hg; T = 50°C.

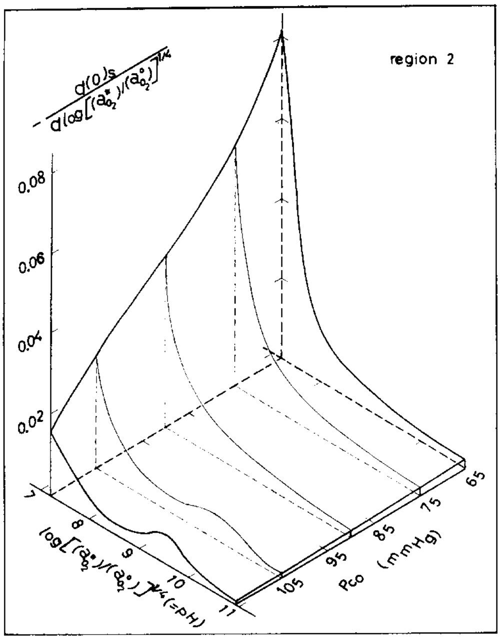

FIG. 5. Distribution surface of the oxidation power for the surface oxygen of the MnO_2; region 2; p_{O_2} = 152 mm Hg; T = 50°C.

3. *Catalytically Active Oxygen*

From the results shown above, the variation of oxidation power of the surface oxygen may be observed but direct information cannot be obtained as to which regional oxygen is effective for the oxidation of carbon monoxide.

As is well known, water vapor strongly retards the catalytic oxidation of carbon monoxide on manganese dioxide. During the course of this study, when water vapor was introduced into the reaction gas stream, a temperature rise of the catalyst bed was observed, accompanied by a marked decrease of catalytic activity. This suggests that the heat of adsorption of water is large [*1*] and the observed inhibiting effect of the water vapor therefore results from the strong adsorption of water on active sites [*9*] at which the active oxygen should be adsorbed. Poisoning with water, therefore, may be a useful tool to determine which regional oxygen is effective for this reaction.

After establishing the steady state activity, pulses of water vapor were injected repeatedly into the reaction gas stream until the activity of the catalyst was entirely nulified. The amount of the surface oxygen of this poisoned catalyst was then analyzed by the KI method at different pH's. The results obtained with poisoned catalysts for regions 1 and 2 are given in Fig. 6 and Fig. 7, respectively, with the same type of results obtained with a nonpoisoned catalyst. Comparing these two curves, one may notice with the poisoned catalyst that among the regional oxygen $O_s{}^h$ the oxygen having higher relative oxidation power than

$$\log[(a^*_{O_2})/(a^0_{O_2})]^{1/4} = 10.5$$

disappeared. From these results, one may conclude that among $O_s{}^h$ the regional surface oxygen which has a relative oxidation power

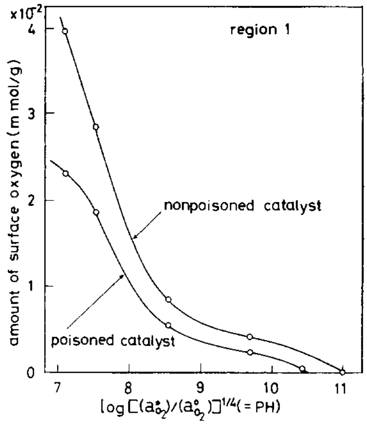

FIG. 6. The amount of surface oxygen as a function of $\log[(a^*_{O_2})/(a^0_{O_2})]^{1/4}$ for the manganese dioxides poisoned and nonpoisoned by H_2O; region 1, p_{CO} = 23.6 mm Hg, p_{O_2} = 152 mm Hg; T = 50°C.

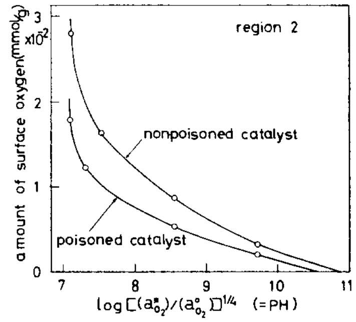

FIG. 7. The amount of surface oxygen as a function of $\log[(a^*_{O_2})/(a^0_{O_2})]^{1/4}$ for the manganese dioxides poisoned and nonpoisoned by H_2O; region 2, p_{CO} = 102 mm Hg, p_{O_2} = 152 mm Hg; T = 50°C.

higher than $\log[(a^{*}_{O_2})/(a^{0}_{O_2})]^{1/4} = 10.5$ is kinetically effective for the oxidation of carbon monoxide. We denote this oxygen as O_s^{h*}.

The amount of this active oxygen O_s^{h*} determined was calculated as 9.4×10^{12} atom/cm^2 for the catalyst in region 1 and 4.8×10^{12} atoms/cm^2 for the catalyst in region 2. The ratio of the amount of active oxygen O_s^{h*} in region 2 to region 1 is 0.51 and is very close to the ratio of the apparent rate constants for both regions, 0.63. As was mentioned in the preceding section, the initial activity of a fresh catalyst decreased gradually until a steady state activity was reached. The amount of active oxygen on the catalyst at a steady state is about one-fifth of that of the fresh catalyst as shown previously in Fig. 2. This is exactly the same as seen in the ratio of the activities of a fresh catalyst and the catalyst at a steady state. The proportionality between the amounts of O_s^{h*} and the values of rate constants will support the conclusion described above. Since the amount of this active oxygen is not dependent on the partial pressure of carbon monoxide, the regeneration of this active oxygen during the reaction should be very rapid as compared to the rate of its removal with carbon monoxide.

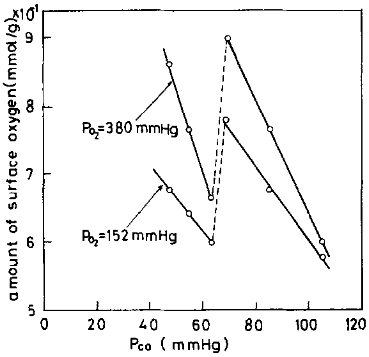

FIG. 8. The amount of surface oxygen of the MnO_2 determined by the hydrazine method as a function of the p_{CO} and the constant p_{CO_2}, 152 and 380 mm Hg; $T = 60°C$.

4. Some Aspects on the Behavior of Surface Oxygen during the Reaction

The amount of surface oxygen on the catalyst during reaction was determined by the hydrazine method and the results are given in Fig. 8. Comparing Fig. 8 with Fig. 1(b), it may be noted that the amount of surface oxygen measured by the hydrazine method varies in the same manner as was observed in the results obtained by the KI method, although the amount of oxygen determined by the hydrazine method is 15–25 times higher than that obtained by the KI method (pH 7.1). The amount of surface oxygen on the catalyst used at $p_{CO} = 64$ mm Hg, and $p_{O_2} = 152$ mm Hg, as shown in Fig. 8, is equal to 2.34×10^{15} atom/cm^2. The amount of the surface oxygen on the fresh catalyst determined by the hydrazine method was found to be 2.92×10^{15} atom/cm^2. If we consider that the fresh catalyst has an orthorhombic structure such as seen in groutite, α-MnO(OH), the total amount of surface oxygen would be 1.49×10^{15} atom/cm^2 [*13*]. This estimated amount of surface oxygen is one-half of surface oxygen on the fresh catalyst determined by the hydrazine method as shown previously. Therefore, the amount of the surface oxygen determined by the hydrazine method will reasonably be assumed to represent the amount of oxygen in the surface layer. With this in mind, it may be said that the catalyst used at $p_{CO} = 64$ mm Hg and $p_{O_2} = 152$ mm Hg, as shown in Fig. 8, has lost about 20% of the surface layer oxygen initially held on the fresh catalyst. Since the fresh catalyst was analyzed to have a composition of $MnO_{1.84}$, the composition of the surface layer of the catalyst mentioned above corresponds to $MnO_{1.47}$. Although this discussion is limited to the composition of the surface layer, the results of the calculation would suggest that there is a possibility of a transition of the crystallographic structure of the catalyst surface from MnO_2 to Mn_2O_3 upon increasing the p_{CO} from region 1 to region 2. Mathieu [*4*] pointed out from his X-ray study that manganese oxide of a higher oxidation state was readily and reversibly reduced with carbon monoxide to Mn_2O_3. It was also pointed out by Saito [*14*] that the absorption of O_2 on Mn_2O_3 resulted in the transformation of the crystallographic structure from Mn_2O_3 to MnO_2 and that the catalytic activity for the oxidation of carbon monoxide on Mn_2O_3 was lower than that on MnO_2. From these points of view, the abrupt change of the amount of the surface oxygen as well as the reaction rate at $p_{O_2} = 65$ mm Hg, as shown in Figs. 1 and 8, may reasonably be attributed to the structural change of the catalyst surface, namely, the surface structure is MnO_2 in region 1 and Mn_2O_3 in region 2. As was previously discussed by Klier [*12*], the lower the oxidation state, the stronger the oxygen is bound to the surface. This may be the reason why the amount of surface oxygen suddenly increases at the transition from region 1 to region 2.

Let us assume that the overall oxidation process of carbon monoxide can be represented by the following steps:

$$\mathrm{S}^* \cdot \mathrm{O_s}^{\mathrm{h}*} + \mathrm{CO} \xrightarrow{k_1} \mathrm{S}^* + \mathrm{CO_2}, \tag{8}$$

$$\mathrm{S}^* + \tfrac{1}{2}\mathrm{O_2} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \mathrm{S}^* \cdot \mathrm{O_s}^{\mathrm{h}*}, \tag{9}$$

$$\mathrm{S} \cdot \mathrm{O_s}^{\mathrm{l}} + \mathrm{CO} \xrightarrow{k_4} \mathrm{S} + \mathrm{CO_2}, \tag{10}$$

$$\mathrm{S} + \tfrac{1}{2}\mathrm{O_2} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \mathrm{S} \cdot \mathrm{O_s}^{\mathrm{l}}, \tag{11}$$

where S^* and S are the sites which hold O_s^{h*} and O_s^{l}, respectively. By applying the steady state method, the amounts of $S^* \cdot O_s^{h*}$ and $S \cdot O_s^{l}$ may be estimated as follows:

$$\mathrm{S}^* \cdot \mathrm{O_s}^{\mathrm{h}*} = \frac{k_2(\mathrm{S}^*)_0 \cdot p_{\mathrm{O_2}}^{1/2}}{k_3 + k_2 p_{\mathrm{O_2}}^{1/2} + k_1 p_{\mathrm{CO}}} \tag{12}$$

and

$$\mathrm{S} \cdot \mathrm{O_s}^{\mathrm{l}} = \frac{k_5(\mathrm{S})_0 \cdot p_{\mathrm{O_2}}^{1/2}}{k_6 + k_5 p_{\mathrm{O_2}}^{1/2} + k_4 p_{\mathrm{CO}}}, \tag{13}$$

where $(S^*)_0$ and $(S)_0$ are the total amounts of S^* and S on the surface, respectively.

If k_2 and k_3 are very large compared to k_1, Eq. (12) reduces to

$$\mathrm{S}^* \cdot \mathrm{O_s}^{\mathrm{h}*} = \frac{k_2(\mathrm{S}^*)_0 \cdot p_{\mathrm{O_2}}^{1/2}}{k_3 + k_2 p_{\mathrm{O_2}}^{1/2}}. \tag{14}$$

When the partial pressure of oxygen is constant, Eq. (14) gives the constant value of the amount of $S^* \cdot O_s^{h*}$ without depending on the partial pressure of carbon monoxide. If $k_4 p_{CO}/(k_6 + k_5 p_{O_2}^{1/2}) < 1$, Eq. (13) reduces to

$$\mathrm{S} \cdot \mathrm{O_s}^{\mathrm{l}} = \mathrm{a}(\mathrm{S})_0 k_5 p_{\mathrm{O_2}}^{1/2}(1 - \mathrm{a})(k_4 p_{\mathrm{CO}}), \tag{15}$$

where $\mathrm{a} = 1/(k_6 + k_5 p_{O_2}^{1/2})$. With a constant value of p_{O_2}, Eq. (15) gives the amount of $S \cdot O_s^{l}$ as a linear function of the p_{CO}. The mode of the variation of the amount of surface oxygen which were shown in Figs. 1 and 8, therefore, can be well explained with the reaction scheme assumed above. As was discussed in previous section, O_s^{l} is not kinetically effective for the oxidation of CO. Therefore the reaction (10) should be very slow compared to the reaction (8). From the results of the separate investigations carried out by using the relaxation method, which will be presented elsewhere, the variation of the amount of O_s^{l} was found to be very slow compared to the oxidation rate of carbon monoxide. Therefore, it suggests that the reaction (10) plays a role only in controlling the amount of the surface oxygen O_s^{l} and is not kinetically effective for the oxidation of CO. The amount of surface active oxygen O_s^{h*} in the region 1 and 2 were found to be about 1/300 and 1/600 of the total surface oxygen measured on the surface of the fresh catalyst.

5. *Desorption of the Surface Oxygen*

Kasatkina and his co-workers [*10, 11*] suggested that there were two different surface oxygens on MnO_2 with respect to their bond energy, one which was weakly adsorbed and effective for the oxidation of CO and the other which was strongly adsorbed and effective for the exchange reaction of oxygen at high temperatures. We concluded in the preceding section that the oxygen having a higher oxidation power than $\log[(a^*_{O_2})/(a^0_{O_2})]^{1/4} = 10.5$ is effective for the oxidation of CO at 50°C. It will be worthwhile to examine, therefore, the strength of the bond of this active oxygen onto the surface.

A fresh catalyst was placed in a quartz tube and the air was completely replaced by flowing nitrogen. The tube was then dipped into a fluidized bed which was controlled at a desired temperature in the range 20–190°C with the nitrogen flowing. After being held at given temperatures for 2 hr, the catalyst was rapidly cooled down to about 17°C in the flowing nitrogen and then sub-

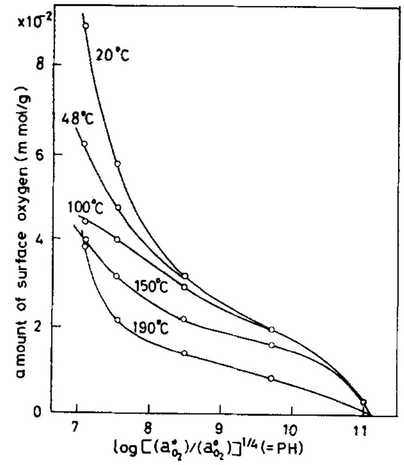

FIG. 9. The amount of surface oxygen of the fresh manganese dioxide as a function of $\log[(a^*_{O_2})/(a^0_{O_2})]^{1/4}$ and the temperature to desorb the surface oxygen.

jected to analysis of the surface oxygen by the KI method. All procedures were carried out without exposure to air. The variation of the amount of surface oxygen due to the desorption at various temperatures are shown in Fig. 9. As may be seen from the figure, the oxygen having a relative oxidation power higher than $\log[(a^*_{O_2})/(a^0_{O_2})]^{1/4} = 7.1$ was removed to half of its amount below 100°C and most of the other half of this oxygen was not desorbed and still remained at 190°C, while on the other hand, 70% of the active oxygen O_s^{h*} having a relative oxidation power higher than $\log[(a^*_{O_2})/(a^0_{O_2})]^{1/4} = 10.5$ was removed in a temperature range 100–190°C. Since most of the oxygen having a relative oxidation power higher than $\log[(a^*_{O_2})/(a^0_{O_2})]^{1/4} = 7.1$ consists of O_s^1 as shown previously, it may be said from these results that there are at least two different kinds of oxygen with respect to O_s^1, one which is a very loosely bound oxygen and the other which is a fairly strongly bound oxygen. O_s^{h*} would be the one which is moderately bound to the surface which lies between these two kinds of O_s^1. Since the word moderate is relative in a sense, the active oxygen which was found to be moderately bound to the surface in our experiments may correspond to the weakly bound oxygen which was suggested by Kasatkina and his co-workers.

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