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The Catalysis of Carbon Monoxide Oxidation with Oxygen on Molybdenum Trioxide

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The mechanism of the catalytic oxidation of CO with O_2 on MoO_3 was studied kinetically over a wide pressure range in a closed circulation and static system, by measuring the electric conductivity of the catalyst during the reaction and by using the tracer technique with isotopic oxygen $^{18}O_2$. The rate-determining step is the reaction between the active oxygen of the catalyst and CO from the gas phase. During the reaction, oxygen molecule is chemisorbed dissociatively and irreversibly on such sites which are composed of two adjacent defects of active oxygen. From the measurements of the electric conductivity, the catalyst was found to be in a slightly reduced state during the catalysis of CO oxidation. The deficient amount of active oxygen in the steady state of the catalysis was determined by reducing the oxidized catalyst by CO of low pressure until the conductivity became the same value as that in the steady state of the catalysis. The deficient ratio of active oxygen, $1\text{-}\theta$, was calculated from the CO_2 produced. The following relation was obtained between the rate constant of reduction of MoO_3 by CO, k_{CO}, and that of the oxidation of the reduced MoO_3 by O_2, k_{O_2}, in the steady state of the reaction in a mixed gas with a composition of $CO/O_2 = 2/1$:

$$k_{CO} \cdot P_{CO} \cdot \theta = 2\ k_{O_2} \cdot P_{O_2} \cdot (1\text{-}\theta)^2.$$

INTRODUCTION

Kinetical studies of carbon monoxide oxidation on supported MoO_3 have been reported by several authors (*1–3*). Recently, Rabette and Olivier studied the catalytic oxidation of CO with O_2 on molybdenum oxide which was obtained from the vacuum decomposition of 12-molybdosilicic acid $H_4SiMo_{12}O_{40}$ in the temperature range 380–522°C in a closed recirculation system and proposed that the active oxido-reduction sites are the mobile oxygen atoms of the φA phase (*1*). Kazusaka and Lunsford studied the catalytic oxidation of CO with N_2O on the partially reduced MoO_3 supported on silica gel in the temperature range 0–120°C and proposed the reaction process between molecular complexes of N_2O and CO rather than the reduction and oxidation process of MoO_3 on the basis of kinetic results and EPR spectroscopy measurements (*2*).

The discrepancy between these two authors in the reaction mechanism is of interest in connection with the inconsistent conditions of the pretreatments of their catalysts. Watanabe *et al.* reported interesting results regarding this point (*3*). They studied CO oxidation with N_2O on MoO_3 supported on α-TiO_2. They described that the reaction proceeds on the reduced surface at 0°C in the same manner as that on the reduced MoO_3 supported on silica gel, although, on the oxidized surface, it proceeds very slowly even at 300°C.

Studies of CO oxidation on pure MoO_3, however, have only rarely been found in the literature (*4, 5*). Trifiro and Pasquon reported that MoO_3 is inactive for CO oxidation with O_2 at a temperature below 350°C, where it is active for the oxidation of propylene, ammonia, and methanol (*4*). Nozaki and Ohki reported the catalytic activity of pure MoO_3 for CO oxidation with O_2 in the flow system at a temperature above about 500°C, although they did not mention any details of the kinetics and mechanism of this catalysis (*5*).

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A detailed study on the reaction mechanism of CO oxidation with O_2 on pure MoO_3 has not been reported up to now. Our purpose, in the present paper, is to elucidate the kinetics and mechanism of CO oxidation with O_2 on pure MoO_3 in detail, using the usual kinetic method which was combined with measurements of the electric conductivity of the catalyst during the reaction.

This procedure was so effective in following the variation of the surface state of the catalyst during the reaction and in investigating the interaction between the catalysts surface and each of the reactant gases that detailed information could be obtained about the mechanism of this reaction as well as the surface state of the catalyst in the steady state of the reaction (*6*). The tracer technique with isotopic oxygen ^{18}O was also used to study the oxidation process of the catalyst surface by oxygen in the steady state of the catalysis.

EXPERIMENTAL

A proanalytical grade reagent of molybdenum trioxide obtained from the East Merck Company was used as the catalyst. It had a surface area of 0.4 m^2/g, as determined by the BET method using nitrogen as the adsorbate at $-196°C$. It was found to have a rhombic crystal form by X-ray powder analysis.

Carbon monoxide and oxygen from commercial cylinders were purified by fractional distillation using liquid nitrogen. The isotopic oxygen $^{18}O_2$ (99.1% ^{18}O) obtained from the British Oxygen Company was used without further purification.

The apparatus used in this experiment is shown schematically in Fig. 1. A reactor tube of fused quartz (Q.R.), in which a pair of electrodes of gold (G.E.) were mounted, was heated by a electric furnace (E.F.). The temperature of the catalyst bed was maintained constant with an accuracy of ±1°C. The stop cocks, A-E, were metallic cocks, with Viton used as the sealing material to avoid contamination with grease vapor. The stop cocks, F-M, were grease cocks. The trap T_1 was cooled continuously by liquid nitrogen or a dry ice–ethanol mixture to protect the catalyst from grease and mercury vapor, while the trap T_2 was cooled in order to collect the reaction product (CO_2).

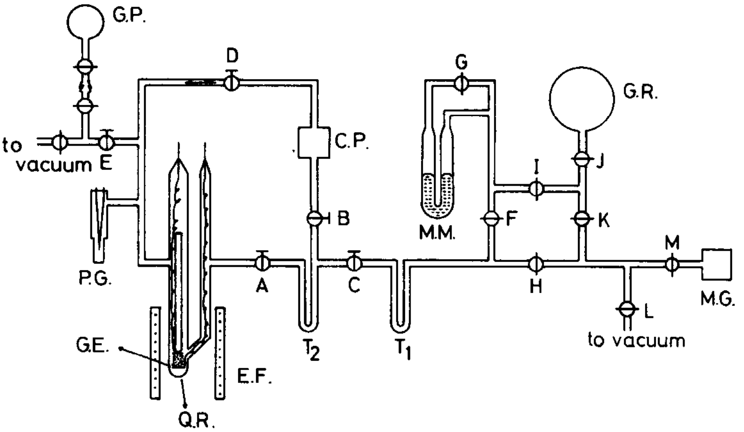

FIG. 1. Schematic representation of the vacuum unit for the measurements on the reaction kinetics, the electric conductivity of the catalyst, and the isotopic studies: A–E, metal stop cocks; F–M, grease stop cocks; Q.R., quartz tube reactor; E.F., electric furnace; G.E., golden electrode; P.G., Pirani vacuum gauge; C.P., circulation pump; M.M., U-shaped mercury manometer; T_1, T_2, traps; G.R., gas reservoir; M.G., McLeod gauge; G.P., gas pipet.

The circulatory method was used when the reactions were studied at pressures of 10–100 mm Hg.[1] The reaction mixture from the gas reservoir (G.R.) was fed into the circulation loop of the known volume (ca. 560 ml) limited by the cocks E, H, I, through the cock I. Gas circulation was provided by a glass electromagnetic pump with nonreturn flaps (C.P.). The reaction rate was determined from the change of the pressure of the reaction mixture in that known volume. The pressure measurements were made by a mercury manometer (M.M.). The reading of which was recorded every 3–6 min with an accuracy of ±0.01 mm Hg.

When the reaction was carried out under a gas pressure of about 10^{-2} mm Hg, the reaction system limited by the cocks B, D, E, F, K, L (ca. 1100 ml) was used. In this case, the pressure change in the system was recorded every 6–12 min by using a McLeod gauge with an accuracy of ±0.001 mm Hg. Under such low pressures, the diffusion velocity of gas was thought to be fast enough, so the circulation pump was not used.

A Pirani gauge (P.G.) was used to measure the uptake rate of oxygen by the reduced catalyst because of the rapid decrease of the oxygen pressure. In this case, oxygen of about 10^{-2} mm Hg was introduced through the metallic cock A to the reaction tube (ca. 220 ml) limited by the metallic cocks A, D, E. The reading of the Pirani gauge, which was corrected by the McLeod gauge, was recorded every 30–60 sec.

This apparatus could be evacuated to a pressure lower than 10^{-6} mm Hg by means of a mercury diffusion pump.

The change in the ^{18}O concentration in the gases was examined as follows. During the reaction, the sample gas was withdrawn periodically from the circulation loop by a gas pipet (G.P.) through the metallic cock E, then it was analyzed immediately by a mass spectrometer (HITACHI RMS-4 TYPE).

The electric conductivity of the catalyst during the reaction was measured in the following manner (*7, 8*). The catalyst between two electrodes about 1 cm apart was weighted by a glass tube (which enclosed an iron rod of about 80 g) in order to obtain a steady and reproducible value in the electric conductivity. A constant dc potential was applied only when the current was to be recorded. The current was measured with an electric micro-micro ammeter (Takeda Riken TR-6 TYPE) with a precision within ±3%. In the preliminary experiments, the proportional relation between the currents and the applied potentials (ohm's law) was confirmed.

Molybdenum trioxide of about 12 g was put into the reaction tube. Prior to the measurements, the sample was heated to 530°C and evacuated to 10^{-6} mm Hg. This treatment caused a significant quantity of water to dehydrate from the catalyst, and the electric conductivity of the catalyst increased remarkably. However, soon after the introduction of oxygen, the rapid uptake of oxygen by the catalyst took place accompanying the abrupt decrease in the electric conductivity. Upon continued heating at 530°C for a period of approximately 3 hr in circulating oxygen of about 50 mm Hg, the catalyst gradually began to show a definite value in the electric conductivity, probably because of the stabilization of the surface lattice structure as well as the decontamination of the organic compound on the surface of the catalyst. The catalyst after this treatment showed a steady and reproducible value not only in the catalytic activity but also in the electric conductivity.

Attention was paid not to heat the catalyst above 530°C in order to avoid sintering of MoO_3. During a series of experiments, the traps were cooled continuously by liquid nitrogen or a dry ice–ethanol mixture to prevent the catalyst surface from being

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[1] Throughout this paper 1 mm Hg = 133.3 Pa.

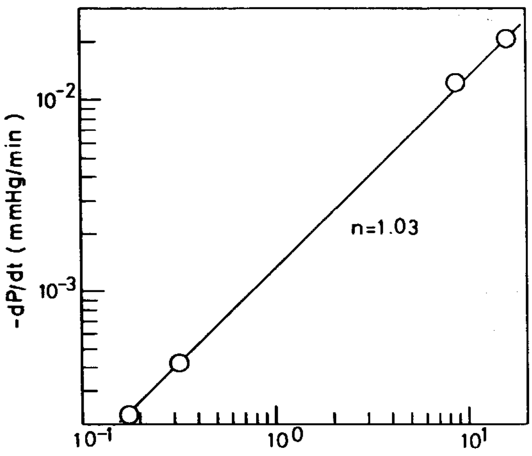

FIG. 2. Effect of total pressure on the reaction rate at 482°C (CO/O_2 = 2/1). Mercury manometer and McLeod gauge were properly used according to the pressure range.

contaminated by grease and mercury vapor.

RESULTS AND DISCUSSION

Catalysis Kinetics

After establishing the steady activity of the catalyst in the mixed gas with a stoichiometric composition of $CO/O_2 = 2/1$, the oxidation rate of carbon monoxide on MoO_3 was measured in the temperature range 400–530°C and under pressures of 10^{-2}–100 mm Hg. The oxidation rate is plotted against the total pressure in Fig. 2. The reaction is clearly of the first order with respect to the total pressure.

To examine the effects of partial pressures of carbon monoxide and oxygen on the reaction rate, a series of experiments were carried out using the various reaction mixtures where the initial CO/O_2 ratios were varied between 4/1 and 1/1. Initial values of dP/dt were taken at various partial pressures of carbon monoxide corresponding to constant oxygen partial pressure, or vice versa. In each experiment, the reaction mixture was introduced over the catalyst evacuated in the steady state in the stoichiometric reaction mixture. The results are shown in Fig. 3. It can be seen that the reaction is nearly of the first order with respect to the pressure of CO and independent of the O_2 pressure.

In order to investigate the effect of carbon dioxide on the reaction rate, measurements were carried out by using dry ice–ethanol-cooled traps to mix the formed carbon dioxide into the reactant gases. However, the reaction rate was found to be independent of carbon dioxide in the gas phase.

Therefore, the reaction rate can be expressed by the following equation:

$$d(CO_2)/dt \simeq k_{CO_2} \cdot P_{CO}^{1.0} \cdot P_{O_2}^{0.0} \quad (1)$$

where K_{CO_2} is the rate constant of carbon monoxide oxidation on MoO_3. The Arrhenius plots of k_{CO_2} are shown in Fig. 4. The activation energy calculated from the slope of these linear plots was about 27.9 $kcal_{th}/mol$.[2] This value is somewhat larger than that of Nozaki, 22 $kcal_{th}/mol$, which was measured in the flow-type apparatus (*5*).

Amount of Active Oxygen on Molybdenum Trioxide

The catalyst pretreated in circulating oxygen of about 50 mm Hg at 530°C for 3 hr

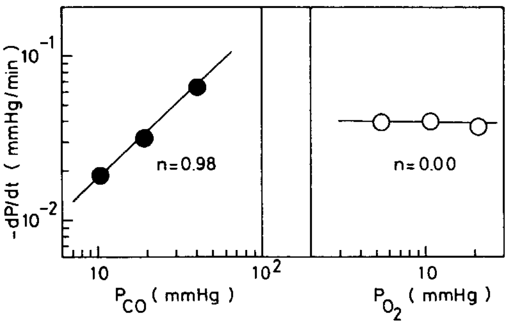

FIG. 3. Kinetics of the oxidation of carbon monoxide for MoO_3. Open circles refer to constant CO pressure (P_{CO} = 21.42 mm Hg) and varying O_2 pressures at 491°C. Filled circles refer to constant O_2 pressure (P_{O_2} = 10.05 mm Hg) and varying CO pressure at 491°C.

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[2] 1 cal_{th}/mol = 4.184 J.

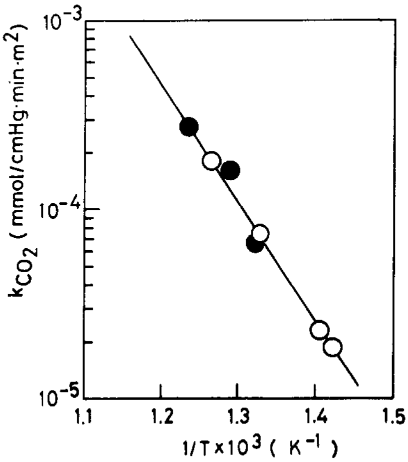

FIG. 4. Effect of temperature on the reaction rate constant, k_{CO_2}. Open circles refer to k_{CO_2} values in the pressure range of 10–20 mm Hg. Filled circles refer to those measured in the pressure range of 10^{-1}–10^{-2} mm Hg.

was cooled down to a definite temperature and evacuated. The catalyst in this state will be called "a catalyst in the starting state" hereafter. The catalyst in the starting state was exposed to carbon monoxide of 10–120 mm Hg at 330–500°C until there was practically no pressure change. The amount of surface oxygen reducible by CO was determined from that of CO_2 which was condensed in the liquid nitrogen-cooled traps. The amount of CO_2 formed in the traps is plotted against the reduction time in Fig. 5. It shows that the formation of CO_2 initially proceeded, but it ceased at a certain point, suggesting that there exists a limited amount of reactive oxygen on the surface of MoO_3. Figure 6 shows the dependence of the amount of formed CO_2 and that of adsorbed CO upon the CO pressure at 411°C. The amount of CO adsorbed on the surface was calculated by subtracting the amount of formed CO_2 from that of CO disappeared from the gas phase. It can be seen in Fig. 6 that the amount of CO adsorbed increased proportionally with increases in the CO pressure. Tanaka *et al.* reported that MoO_3 catalyst supported on β-TiO_2 starts to adsorb CO and olefine molecules when it is reduced by CO or H_2 at 500°C (*9*). Figure 6 also shows that the amount of CO_2 formed (the amount of reactive oxygen) was almost independent of CO pressure.

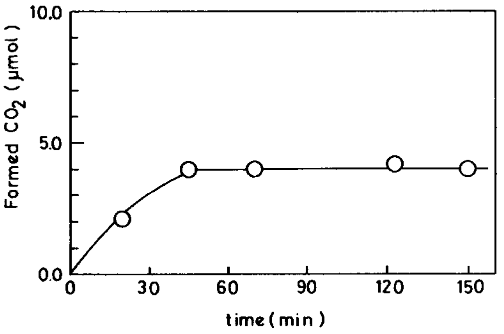

FIG. 5. The change of the amount of formed CO_2 as a function of time. The reduction was carried out at 386°C by using CO of 30–40 mm Hg.

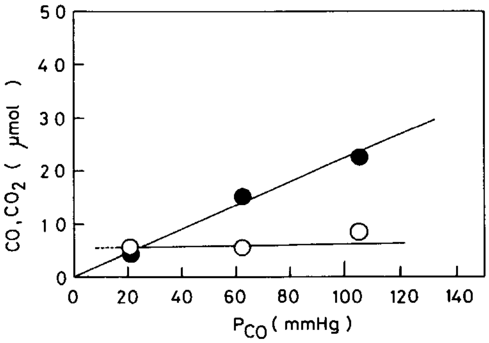

FIG. 6. Effect of CO pressure on the amount of formed CO_2 and that of adsorbed CO at 411°C. ○, the amount of CO_2; ●, the amount of adsorbed CO.

Massoth studied the kinetics of reduction of molybdena–alumina catalyst by hydrogen of atmospheric pressure over the temperature range 400–600°C and stated that pure MoO_3 was reduced more easily to Mo than MoO_3 supported on η-Al_2O_3 (*10*). Kennedy and Bevan also studied the reduction kinetics of MoO_3 by hydrogen at a pressure of 380 mm Hg in the temperature range 480–600°C and stated that MoO_3 was reduced via MoO_2 to Mo (*11*). However, reports about the study of the reduction of MoO_3 by CO can only rarely be found in publications (*12, 13*). It can be said from the results of Figs. 5 and 6 that the reduction of MoO_3 by CO virtually does not proceed beyond some extent in this pressure and temperature range.

If a limited amount of the surface oxygen of the catalyst (it may be both the lattice oxygen and the adsorbed one) is assumed to react with carbon monoxide easily, this oxygen will be called "active oxygen" hereafter. Since the results of Figs. 5 and 6 show that there exists a limited amount of reactive surface oxygen on MoO_3, it would be proper to assume that the amount of active oxygen of MoO_3 can be estimated from the amount of CO_2 condensed in the traps. The numbers of the active oxygen atoms per unit of the surface area, and their percentages to the surface lattice oxygen assuming the (100) surface of MoO_3, are listed in Table 1 (*14, 15*).

Electric Conductivity of the Catalyst in Oxygen and in the Reaction Mixture

After pretreatment in circulating oxygen at 530°C for 3 hr, the electric conductivity of the catalyst in oxygen was measured between 350 and 530°C. The electric conductivity of MoO_3 in the steady state of the catalysis was also determined in circulating mixed gas with a stoichiometric composition under a pressure of about 50 mm Hg. In this case, formed CO_2 was condensed in the liquid nitrogen traps and the total pressure was gradually deceased, but the electric conductivity did not change. The temperature dependences of electric conductivities of MoO_3 in oxygen and in the mixed gas of the stoichiometric composition are shown in Fig. 7. It can be seen that the conductivity in the steady state of the catalysis of CO oxidation is somewhat larger than that in oxygen. Experiments showed that these values were little affected by the evacuation of these gases. Since MoO_3 is generally known to exhibit n-type semiconductivity behavior, it can be said that MoO_3 is slightly reduced during the reaction by carbon monoxide in the mixed gas as compared with the starting state.

TABLE 1

Numbers of Active Oxygen Atoms and Their Percentages to the (100) Surfae Lattice Oxygen

	Temperature (°C)				
	497	441	397	350	330
Numbers × 10^{-18} (atoms/m²)	1.85	1.29	0.83	0.66	0.55
Percentage	10.9	7.59	4.88	3.88	3.24

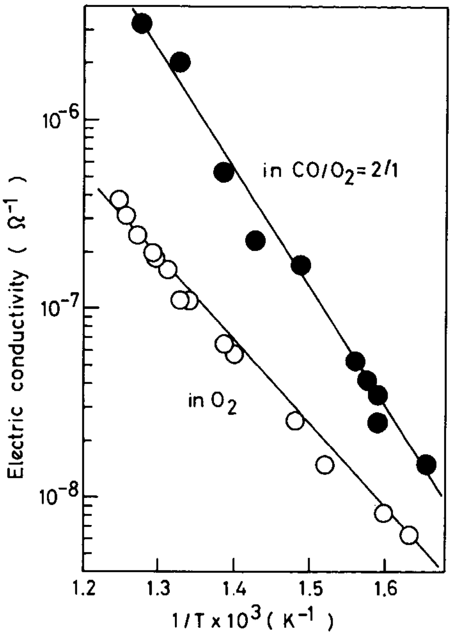

FIG. 7. Electric conductivity of MoO_3 in O_2 (ca. 80 mm Hg) and in the stoichiometric reaction mixture (initial pressure ca. 30 mm Hg).

Deficient Amount of Active Oxygen during the Catalysis of CO Oxidation

When MoO_3 in the starting state was exposed to CO under a pressure of about 10^{-2} mm Hg at a definite temperature, the active oxygen on the surface of the catalyst was reduced by CO, which caused the gradual increase in the electric conductivity of MoO_3. The reduction was continued until the conductivity became the same value as that in the steady state of the catalysis, then evacuated. The evacuation

TABLE 2

Deficiencies of Active Oxygen Atoms during the Catalysis of Carbon Monoxide Oxidation on MoO_3[a]

	Temperature (°C)			
	470	439	423	400
Numbers of deficient active oxygen atoms × 10^{-16} (atoms/m^2)	2.14	2.06	2.19	1.97
Deficiency (1-θ)%	1.40	1.64	1.92	2.07

[a] In the mixed gas with the stoichiometric composition of CO/O_2 = 2/1.

did not give a significant change in the electric conductivity. In this case, the amount of the reduction product CO_2 condensed in the traps shows the deficient amount of the active oxygen during the catalysis of CO oxidation. The numbers of the deficient active oxygen sites and their ratios to total active oxygen atoms (1-θ) are listed in Table 2; θ represents the coverage ratio of active oxygen on the catalyst, and θ is equal to 1 at the starting state. It can be found in the table that the deficient ratios of active oxygen during the catalysis are only about 1 to 2%.

Reduction and Reoxidation Process of MoO_3 as Determined by Electric Conductivity Measurements

MoO_3 in the starting state was reduced by CO of about 40 mm Hg for 6 hr at 368°C, and evacuated for 1 hr., then it was reoxidized by O_2 for 20 mm Hg. The variation of the electric conductivity of the catalyst accompanying these treatments is shown in Fig. 8. It can be seen in the figure that the electric conductivity of MoO_3 increased gradually during the reduction by CO. The evacuation of the reduced catalyst did not give significant change in the electric conductivity. However, the introduction of oxygen decreased it almost instantaneously to near the starting value. This fact suggests that the uptake rate of oxygen by reduced MoO_3 is far faster than the reduction rate of MoO_3 by CO. It can also be found in the figure that the electric conductivity of MoO_3 in the steady state of the catalysis is very near to that in the starting state. This finding shows that the catalyst is only slightly reduced during the reaction as compared with the starting state. This conclusion is consistent with the results in Table 2.

Reduction Rates of MoO_3 by CO and Reoxidation Rates of Reduced MoO_3 by O_2

When carbon monoxide of about 10^{-2} mm Hg was introduced to the catalyst in the starting state, it reacted with the active oxygen of the catalyst and carbon dioxide formed was caught in the traps, and the pressure of CO decreased. The amount of consumed carbon monoxide was ascertained to agree with that of CO_2 caught in the traps within the experimental error. This fact shows that (i) the amount of CO which may be adsorbed on the surface of the catalyst is negligible as compared with that of CO oxidized to CO_2 in this pressure range, and (ii) CO_2 formed on the surface of the catalyst immediately desorbs from there. The rate of formation of CO_2 was found to be proportional to the pressure of CO. Consequently, the reduction rate can

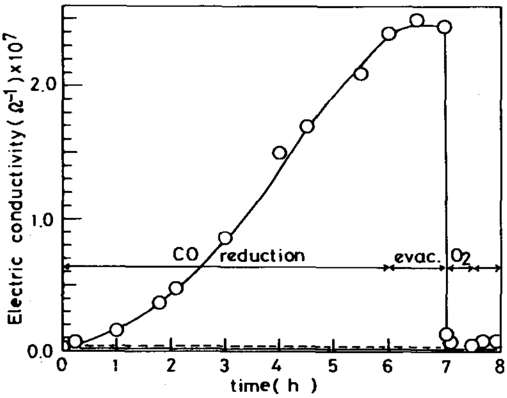

FIG. 8. The variation of the electric conductivity of MoO_3 with time by CO reduction and O_2 reoxidation at 368°C. The dotted line shows the electric conductivity at the steady state of the catalysis, and the solid line shows the starting value.

be expressed as follows:

$$d(CO_2)/dt = k_{CO} \cdot P_{CO} \cdot \theta \qquad (2)$$

where k_{CO} is the reduction rate constant of MoO_3 by CO and θ, the coverage ratio of active oxygen on the surface of the catalyst. Since the θ value during the catalysis of CO oxidation is nearly equal to 1, as is shown in Table 2, k_{CO} can be compared with k_{CO_2}. The Arrhenius plots of k_{CO} are shown in Fig. 9 together with those of k_{CO_2}. It can be seen that the reduction rates constants almost agree with the reaction rates constants.

MoO_3 in the starting state was reduced by CO of about 50 mm Hg at a definite temperature between 350 and 430°C for a period of appropriate time, and evacuated. Soon after that, oxygen of about 10^{-2} mm Hg was introduced into the reaction system. The reoxidation of the reduced catalyst occurred and the pressure of O_2 decreased rapidly. At this time, a Pirani gauge was used to determine the decreasing pressure of oxygen. In each experiment, the initial deficient ratio of active oxygen on the surface of the catalyst was calculated from the amount of CO_2 condensed in the traps.

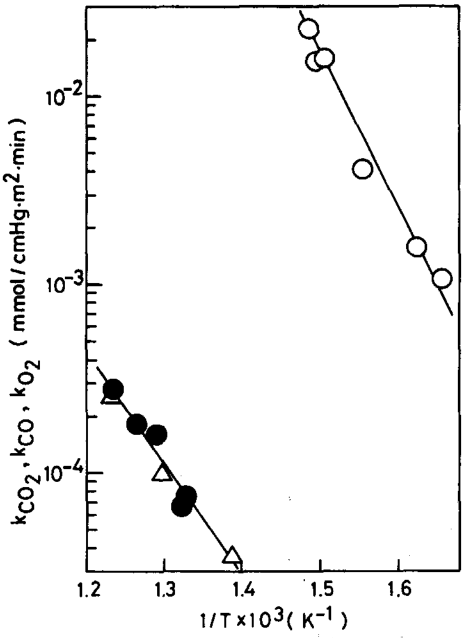

FIG. 9. Effect of temperature on the reduction rate constant, k_{CO}, at $\theta = 1.00$, and the reoxidation rate constant, k_{O_2}, at $\theta = 0.00$, and the reaction rate constant k_{CO_2}. ●, k_{CO_2}; △, k_{CO}; ○, k_{O_2}.

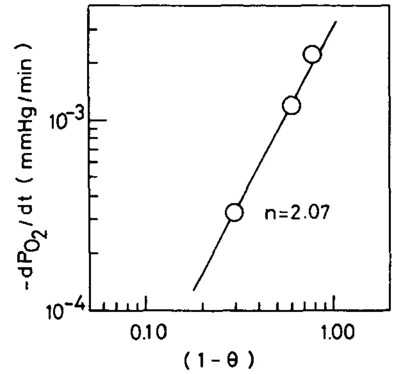

FIG. 10. Effect of deficient ratio of active oxygen on the reoxidation rate at 400°C. The initial pressure of oxygen (ca. 5 × 10^{-2} mm Hg) was kept constant.

To examine the effect of the deficient ratio of active oxygen on the reoxidation rate, the oxygen uptake rates by reduced MoO_3 were measured at a definite temperature at various deficient ratios of active oxygen, maintaining the O_2 pressure constant. Figure 10 shows the results at 400°C. It is evident that the reoxidation rate is nearly of the second order with respect to the deficient ratio of active oxygen. This result suggests the dissociative adsorption of oxygen molecule on such sites which are composed of two adjacent defects of active oxygen (*16*).

The reoxidation process during the reaction was also examined by using the tracer technique. The reaction was carried out at 507°C using the mixed gas of carbon monoxide and isotopic oxygen ^{18}O, containing about 60% ^{18}O, with the stoichiometric composition $CO/(^{16}O_2 + {}^{18}O_2) = 2/1$, by using the dry ice–ethanol-cooled traps. Figure 11 shows the change in the isotopic composition of oxygen and carbon dioxide in the gas phase in the course of the reaction. It can be seen that the percentage of $C^{16}O^{18}O$ in the produced carbon dioxide increased gradually as the reaction proceeded, but the isotopic composition of ^{18}O

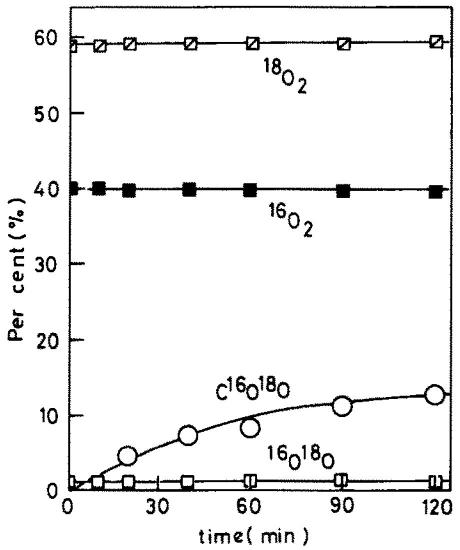

FIG. 11. The change of the isotopic composition of O_2 and CO_2 during the reaction at 507°C. The initial pressure of the reaction mixture was about 48 mm Hg.

in the gaseous oxygen remained constant during the reaction. Similar results were obtained by Hirota *et al.* in the study of the CO oxidation with an oxygen tracer over V_2O_5 catalyst (*17*). These results show, as Hirota *et al.* also proposed, that (i) the oxygen molecule does not exchange with surface lattice oxygen of MoO_3 during the reaction, and (ii) the oxygen molecule is irreversibly taken up on the surface of the catalyst during the reaction. Consequently, the oxygen molecule, during the course of the catalysis, is chemisorbed from the gas phase irreversibly and dissociatively on such sites which are composed of two adjacent defects of active oxygen on the surface of the catalyst.

The dependence of uptake rate of oxygen by reduced MoO_3 upon the oxygen pressure was examined at the constant deficient ratio of active oxygen. The result are shown in Fig. 12. It is clear that the reoxidation rate is nearly proportional to the oxygen pressure. Therefore, the reoxidation rate of reduced surface by oxygen can be expressed as follows:

$$-d(O_2)/dt = k_{O_2} \cdot P_{O_2} \cdot (1\text{-}\theta)^2 \qquad (3)$$

where k_{O_2} is the oxidation rate constant of the reduced MoO_3 by O_2 and (1-θ), the deficient ratio of active oxygen sites. The Arrhenius plots of k_{O_2} are also shown in Fig. 9 together with those of the reduction rate constants, and the reaction rate constants. It is obvious in Fig. 9 that the value of k_{O_2} is far larger than those of k_{CO} and k_{CO_2}.

Mechanism of the Carbon Monoxide Oxidation with Oxygen on MoO_3

Since (i) the reaction rate is proportional to P_{CO} and does not depend upon P_{O_2}, (ii) the reaction rate constant of the CO oxidation on MoO_3 almost agrees with that of the reduction of MoO_3 by CO, (iii) the oxygen uptake rate constant of the reduced MoO_3 is far larger than the reduction rate constant of MoO_3 by CO, and (iv) the oxygen uptake rate is nearly of the second order with respect to the deficient ratio of active oxygen, the mechanism of this reaction can be expressed as follows. The reaction consists of two processes: (i) a CO molecule which collides with the surface of the catalyst or is physisorbed on it reacts with the active oxygen of the catalyst and CO_2 thus formed immediately desorbs, leaving an oxygen defect on the surface, and (ii) two adjacent defects of active oxygen are refilled with oxygen molecule from the gas phase irreversibly and dissociatively. Therefore, the reaction steps are expressed as follows:

$$CO(g) + O(s) \rightarrow CO_2(g) + (s) \qquad (4)$$

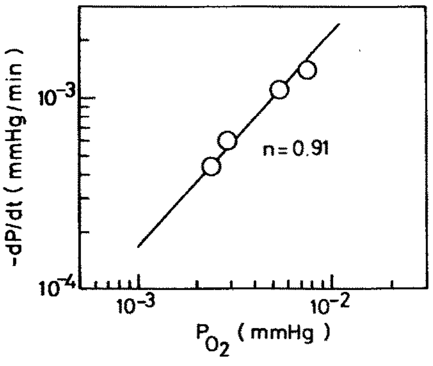

FIG. 12. Effect of oxygen pressure on the reoxidation rate of reduced MoO_3 (θ = 0.62) at 391°C.

$$2(s) + O_2(g) \rightarrow 2O(s) \qquad (5)$$

where O(s) refers to the active oxygen on the surface of MoO_3 and (s), the defect of active oxygen on the surface. The rate constant of step (5), k_{O_2}, is far larger than that of step (4), k_{CO}, so the overall reaction rate is determined by step (4).

Relation between Reduction Rate and Oxidation Rate of MoO_3 Surface in the Steady State of the Catalysis

The rate of the elementary steps (4) and (5) are expressed by Eqs. (2) and (3), respectively.

$$-d(CO)/dt = k_{CO} \cdot P_{CO} \cdot \theta \qquad (2)$$

$$-d(O_2)/dt = k_{O_2} \cdot P_{O_2} \cdot (1\text{-}\theta)^2. \qquad (3)$$

Since the θ values in the steady state of the catalysis are given in Table 2 and the values of k_{CO} and k_{O_2} between 400 and 530°C are shown in Fig. 9, the values of $k_{CO} \cdot \theta$ and $k_{O_2} \cdot (1\text{-}\theta)^2$ at the steady state of the catalysis can be calculated by using the values in Table 2 and Fig. 9. The results of the calculation are listed in Table 3. It is clear that $k_{CO} \cdot \theta$ almost agrees with $k_{O_2} \cdot (1\text{-}\theta)^2$ within the experimental error. Consequently, the following relation can be obtained in the steady state of the catalysis using the mixed gas with the stoichiometric composition:

$$k_{CO} \cdot P_{CO} \cdot \theta = 2\ k_{O_2} \cdot P_{O_2} \cdot (1\text{-}\theta)^2. \qquad (6)$$

TABLE 3

Calculated Values of $k_{CO} \cdot \theta$ and $k_{O_2} \cdot (1 - \theta)^2$ at the Surface in the Steady State of Catalysis

	Temperature (°C)			
	470	439	423	400
$k_{CO} \cdot \theta \times 10^5$ (CO_2 mmol/min · cm Hg · m^2)	4.80	2.29	1.68	0.814
$k_{O_2} \cdot (1\text{-}\theta)^2 \times 10^5$ (O_2 mmol/min · cm Hg · m^2)	5.42	2.46	1.68	0.783

The above equation shows that the reduction rate of the active oxygen on the surface of MoO_3 by CO is dynamically balanced with the uptake rate of oxygen by MoO_3 in the steady state of the catalysis in the stoichiometric reaction mixture.

The Observation of Dynamic Balance from the Measurements of Electric Conductivity

The catalyst in the steady state was evacuated at 378°C, then CO at a pressure of 2.18 mm Hg was introduced to the reaction system. As the reduction proceeded, the electric conductivity of the catalyst increased gradually, as shown in Fig. 13.

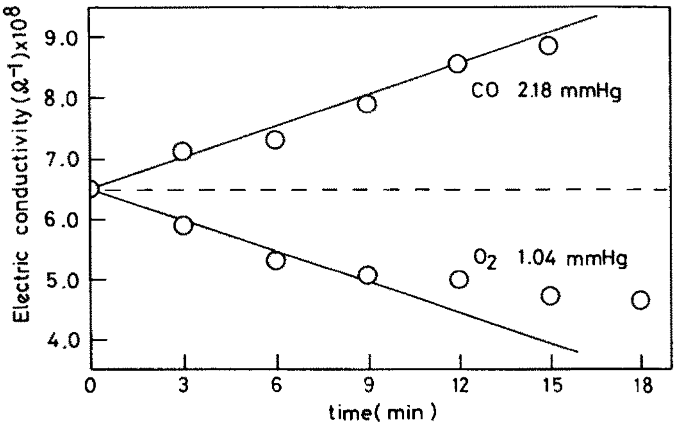

FIG. 13. The variation of the electric conductivity of MoO_3 with time by CO reduction and O_2 oxidation at 378°C. The dotted line shows the electric conductivity at the steady state of the catalysis.

After evacuation, the catalyst in the steady state was reoxidized at the same temperature by oxygen at a pressure of 1.04 mm Hg. The electric conductivity of MoO_3 decreased as also shown in Fig. 13. Although CO and O_2 altered the electric conductivity of MoO_3 to an opposite direction with each other, it is clear that the absolute values of the rates of the changes in the electric conductivities are the same in these two experiments. This finding also indicates the dynamic balance between the reduction rate and the oxidation rate at the steady state of the catalysis in the stoichiometric reaction mixture.

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