The Catalysis of Hydrogen Oxidation with Oxygen on Molybdenum Trioxide

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The mechanism of the catalytic oxidation of H_2 with O_2 on pure MoO_3 was studied kinetically in a closed circulation and static system, by measuring the electric conductivity of the catalyst during the reaction. The kinetic isotope effect with respect to hydrogen and the isotope exchange reactions between $^{18}O_2$ and $^{16}O_2$ as well as between D_2 and H_2 during the catalysis were also measured to elucidate the details of the catalysis mechanism. The experimental results were compared with those of the catalytic oxidation of CO with O_2 on this oxide carried out previously. The activation energy and the rate constant of H_2 oxidation almost coincided with those of CO oxidation. Electric conductivity measurements indicated that the catalyst was in a slightly reduced state during the steady state of the catalysis of H_2 oxidation as well as in the case of CO oxidation. The active oxygen on the surface of the catalyst which was operative in the catalysis of CO oxidation was found to be also operative in the catalysis of H_2 oxidation. The reaction scheme of H_2 oxidation with O_2 on MoO_3 could be explained in a manner similar to that of CO oxidation on this oxide. From the fact that the activation energies for the oxidations of H_2 and D_2 were very close with each other on MoO_3, molecular hydrogen, weakly bound to the active oxygen on the surface of the catalyst, was assumed to enter into the active complex in the rate-determining step of this catalysis.

INTRODUCTION

A previous paper was concerned with the study of the kinetics and mechanism of CO oxidation with O_2 on pure MoO_3 (*1*). The procedure employed was the usual kinetic method which was combined with measurements of the catalyst conductivity in the course of the reaction. This procedure enabled us to follow the variation of the catalyst state in the presence of the reaction mixture and each of the reactant gases and consequently to obtain valuable information on the mechanism of this catalysis (*2*). It seemed valuable to extend this procedure to other reactions on this oxide to examine its catalysis mechanism. In the present work, the oxidation of hydrogen has been chosen.

A few studies have been made concerning the catalysis of hydrogen oxidation on MoO_3 (*3, 4*). Goncharuk and Golodets studied the kinetics of the oxidation of H_2 with O_2 on pure MoO_3 in the temperature range 150–550°C and reported that the oxidation rate is first order with respect to the pressure of H_2 and independent of the O_2 pressure (*3*). However, they did not mention any details of the mechanism of this catalysis. Recently, Watanabe *et al.* studied the catalytic oxidations of H_2 with N_2O and CO with N_2O over the partially reduced MoO_3 catalyst supported on α-TiO_2 (*4*). The reported reaction kinetics in the catalysis of H_2 oxidation is first order with respect to H_2 and independent of the N_2O pressure. However, the rate of oxidation of CO with N_2O is independent of the CO pressure and proportional to the pressure of N_2O. On the basis of these kinetic results and EPR spectroscopy measurements, they proposed that two oxidation reactions proceed on different active sites on the surface of the catalyst.

The catalysis of hydrogen oxidation with oxygen has been examined parallel to the study of carbon monoxide oxidation on several metal oxides (*5–11*). A reaction

mechanism of hydrogen oxidation analogous to that of carbon monoxide oxidation has been proposed on NiO (5–7), TiO_2 (8), ZrO_2 (9), ZnO (10), and recently on HfO_2 (11).

The purpose of the present paper is to elucidate the kinetics and mechanism of the catalysis of H_2 oxidation with O_2 on pure MoO_3 in detail, applying the same procedure which was employed in the study of CO oxidation on this oxide and using the isotope technique with deuterium and oxygen-18.

EXPERIMENTAL

A proanalytical-grade reagent of molybdenum trioxide (99.5%), which was employed in the study of carbon monoxide oxidation, was used in the present investigation (1). It was obtained from the East Merck Company and had a specific surface area of 0.40 m^2/g. According to the Merck Company, its principal impurities were Cl, SO_4, PO_4, Pb, Fe, and NH_4 (less than 100 ppm each).

The diagram of the apparatus and details of the procedures employed to kinetics measurements were already described in the previous paper (1). Conductivity measurements of the catalyst during the reaction were performed by using almost the same procedure and instruments. In this method, the catalyst powder placed between two golden electrodes was weighted by a glass tube (which enclosed an iron rod of about 80 g) through the upper electrode 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 measured.

Hydrogen, carbon monoxide, and oxygen from commercial cylinders were purified by passing through the liquid nitrogen-cooled traps. Deuterium was prepared by decomposing heavy water (D_2O, 99.8%), which was obtained from the Commissariat a l'Energie Atomique (CEA). It was decomposed by the reaction with pure aluminum amalgam at room temperature in the evacuated vessel. Generated D_2 was purified by passing through the liquid nitrogen-cooled traps and was found to contain 97.6 at.% deuterium according to the mass-spectrometric analysis, performed by the Hitachi RMS-4-type mass spectrometer. The isotopic oxygen $^{18}O_2$ (99.1% ^{18}O) obtained from the British Oxygen Company was used without further purification.

In order to measure the isotope exchange reactions during the catalysis, the direct-inlet mass spectrometer (Anelva AGA-100 quadrupole gas analyzer) was connected to the recirculation reactor through a Granville–Phillips variable leak valve, which made it possible to analyze continuously the isotopic composition of the gas-phase mixture during the catalysis. The interior of the mass spectrometer was continuously evacuated below 10^{-6} mm Hg[1] by an ion pump.

Molybdenum trioxide of about 12 g was put into the reaction tube. Prior to the measurements, the catalyst powder was pretreated in circulating oxygen of about 50 mm Hg at 530°C for a period of approximately 3 hr until it began to show a constant value in the electric conductivity. After this treatment, the reaction mixtures of hydrogen and oxygen or deuterium and oxygen were admitted into the reaction system and water or heavy water vapors formed in the course of the reaction were caught in the liquid nitrogen-cooled traps. Kinetic measurements, except where specified, were carried out with the stoichimetric hydrogen/oxygen or deuterium/oxygen mixtures. The kinetics were followed by pressure measurements. A mercury manometer or a McLeod gauge were properly used according to the pressure range.

From the results of runs using different amounts of the catalyst, the rate of reaction per unit amount of the catalyst was estimated. It was found that, in the present experiment, the effect of the amount of the catalyst is negligible.

Attention was paid not to heat the catalyst above 535°C in order to avoid sintering of MoO_3. During a series of experiments, the traps before the catalyst were cooled continuously by liquid nitrogen or a dry ice–ethanol mixture to prevent the catalyst surface from being contaminated by grease and mercury vapor.

RESULTS AND DISCUSSION

Catalysis Kinetics

After establishing the steady activity of the catalyst in the reaction mixture, the oxidation rate of hydrogen on MoO_3 was measured in the temperature range 400–530°C and under pressures of 10^{-2}–100 mm Hg. To examine the effect of the total pressure on the reaction rate, the stoichiometric reaction mixtures at various initial pressures were introduced to the catalyst at 530°C. The values of oxidation rate at various total pressures are shown in Table 1 (Nos. 1–4). It is clear that the reaction is of the first order with respect to the total pressure.

To examine the effects of partial pressures of hydrogen and oxygen on the reaction rate, a series of experiments were carried out using the various reaction mixtures where the initial H_2/O_2 ratios were varied between 4/1 and 1/1. In each experiment, before various reaction mixtures having H_2/O_2 ratios other than 2/1 were introduced into the reaction system, the catalyst was treated by the stoichiometric reaction mixture until it began to show the steady activity. Initial values of dP/dt were taken at various partial pressures of hydrogen corresponding to constant oxygen partial pressure, or vice versa. The results shown in Table 1 (Nos. 5–10) indicate that the reaction is nearly of the first order with respect to the pressure of hydrogen and independent of the oxygen pressure, in agreement with the results of Goncharuk and Golodets ([3]).

Therefore, the reaction rate can be expressed by

$$d(H_2O)/dt \simeq k_{H_2O} \cdot P_{H_2}^{1.0} \cdot P_{O_2}^{0.0}, \quad (1)$$

where k_{H_2O} is the rate constant of oxidation of hydrogen on MoO_3. The Arrhenius plots of k_{H_2O} are shown in Fig. 1. The activation energy calculated from the slope of these plots was about 27.9 kcal/mol.[2]

The kinetics of the CO oxidation on MoO_3 were of the first order with respect to CO and independent of the O_2 pressure ([1]). The reaction rate was expressed by

$$d(CO_2)/dt \simeq k_{CO_2} \cdot P_{CO}^{1.6} \cdot P_{O_2}^{0.0}, \quad (2)$$

where k_{CO_2} is the rate constant of CO oxidation on MoO_3. Figure 1 also shows the Arrhenius plots of k_{CO_2}. It can be seen that the plots of k_{CO_2} overlap with those of k_{H_2O} over the whole range of temperature. The activation energy for the oxidation of CO was about 27.9 kcal/mol.

Electric Conductivity of the Catalyst in Oxygen and in Reaction Mixtures

After pretreatment of the catalyst in oxy-

TABLE 1

Effect of the Total Pressure and Partial Pressures of Hydrogen and Oxygen on the Rate of H_2 Oxidation on MoO_3

No.	T (°C)	Pressure (mm Hg)		Rate (mm Hg/min)
		$P_{H_2} + \frac{1}{2}P_{O_2}$		
1	530	2.03×10^{1}		6.08×10^{-2}
2	530	9.03×10^{0}		2.38×10^{-2}
3	530[a]	2.05×10^{-1}		4.13×10^{-4}
4	530[a]	8.34×10^{-2}		1.75×10^{-4}
		P_{H_2}	P_{O_2}	
5	510	23.89	5.85	8.33×10^{-2}
6	510	12.07	5.85	4.50×10^{-2}
7	510	5.56	5.85	2.00×10^{-2}
8	510	16.85	8.34	5.24×10^{-2}
9	510	16.85	5.50	5.01×10^{-2}
10	510	16.85	4.16	5.20×10^{-2}

[a] The experiments were carried out in the static reaction system, in which the change of the pressure was followed by the McLeod gauge.
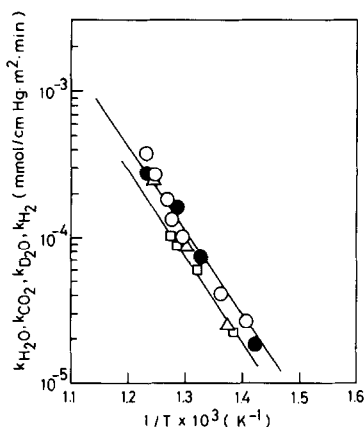
[2] 1 cal = 4.184 J.

FIG. 1. Effect of temperature on the oxidation rate constants of hydrogen, deuterium, and carbon monoxide, k_{H_2O}, k_{D_2O}, and k_{CO_2}, and the reduction rate constant of MoO_3 by H_2, k_{H_2}. $\bigcirc$, k_{H_2O} values in the pressure range of 10^{-1}–10^{-2} mm Hg; $\square$, k_{D_2O} values in the pressure range of 10^{-1}–10^{-2} mm Hg; $\bullet$, k_{CO_2} values in the pressure range of 10^{-1}–10^{-2} mm Hg; $\triangle$, k_{H_2} values in the pressure range of 10^{-1}–10^{-2} mm Hg.

gen of several centimeters of Hg at 530°C for 3 hr, the dependence of the electric conductivity of the catalyst on the oxygen pressure was examined under the pressure range of 10^{-2}–100 mm Hg with the temperature kept constant. The results are shown in Fig. 2. It is clear that the electric conductivity at a fixed temperature is practically independent of the oxygen pressure. This shows that the surface of the catalyst is saturated with oxygen, even at a pressure as low as 10^{-2} mm Hg, so the amount of surface oxygen is almost constant and independent of the oxygen pressure.

In order to compare the surface state of the catalyst treated in oxygen with those in the reaction mixtures of $H_2 + \frac{1}{2}O_2$, and CO $+ \frac{1}{2}O_2$, the electric conductivities of the catalyst during the reactions of H_2 and CO oxidations were measured. The electric conductivities of the catalyst in the reaction mixtures of $H_2 + \frac{1}{2}O_2$, and CO $+ \frac{1}{2}O_2$ were found to be practically independent of the pressures of reaction mixtures at a fixed temperature (Fig. 2). Figure 3 shows the temperature dependence of the electric conductivity of MoO_3 in circulating oxygen and in the reaction mixtures of $H_2 + \frac{1}{2}O_2$, and CO $+ \frac{1}{2}O_2$ between 350 and 530°C. Since MoO_3 is generally known to exhibit n-type semiconductivity behavior, it is clear in Fig. 3 that the catalyst is in a slightly reduced state during the steady state of the catalysis of H_2 oxidation as well as during the steady state of the catalysis of CO oxidation.
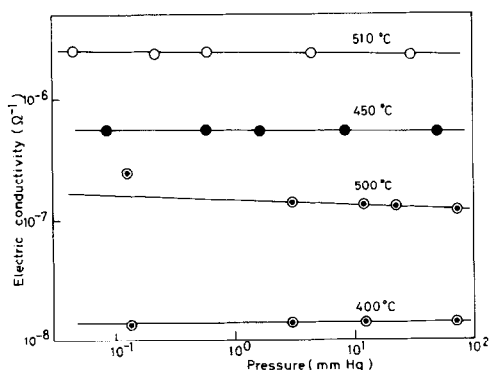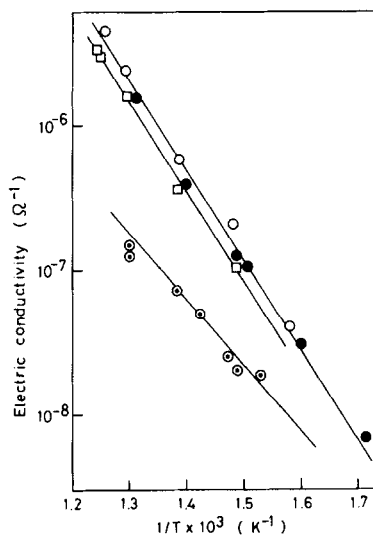

FIG. 2. Effect of pressures of oxygen, and the stoichiometric reaction mixtures on the electric conductivity of the catalyst under constant temperature. $\odot$, In O_2; $\bigcirc$, in $H_2 + \frac{1}{2}O_2$; $\bullet$, in CO $+ \frac{1}{2}O_2$.

FIG. 3. Electric conductivity of MoO_3 in oxygen and in the stoichiometric reaction mixtures. $\odot$, In O_2 (ca. 34 mm Hg); $\bigcirc$, in $H_2 + \frac{1}{2}O_2$ (initial pressure ca. 2.3×10^{-1} mm Hg); $\square$, in $D_2 + \frac{1}{2}O_2$ (initial pressure ca. 1.5×10^{-1} mm Hg); $\bullet$, in CO $+ \frac{1}{2}O_2$ (initial pressure ca. 1.8×10^{-1} mm Hg).

It can also be found in Fig. 3 that the electric conductivity of the catalyst in the steady state of H_2 oxidation overlaps fairly well with that in the steady state of CO oxidation over the whole range of temperature. This fact indicates that the extents of the reductions of the catalyst during these two oxidations are very close to each other.

The closeness of the catalyst state during the two oxidations would be responsible for the close relations between these two reactions regarding the kinetics, values of the rate constant, and activation energies. Accordingly, it may be presumed here that H_2 and CO oxidations proceed via the common active oxygen species on the surface of MoO_3.

Reduction Process of Active Oxygen by Hydrogen and Carbon Monoxide as Determined by Electric Conductivity Measurements

The studies of the reduction process of the active oxygen by H_2 and CO were performed by monitoring the change of the catalyst conductivity. The catalyst was treated in circulating oxygen of about 50 mm Hg at 535°C for an appropriate time and evacuated. Subsequently, it was reduced by hydrogen or carbon monoxide of about 10^{-2} mm Hg, maintaining the temperature at 535°C. Formed water or carbon dioxide was caught in the liquid nitrogen-cooled traps. As the reduction of the active oxygen by H_2 or CO proceeded, the electric conductivity of the catalyst gradually increased. The increase of the electric conductivity of the catalyst is plotted against the numbers of moles of hydrogen or carbon monoxide which disappeared from the gas phase in Fig. 4.

It was already mentioned in the previous paper that the amount of carbon dioxide adsorbed on the surface of the catalyst is negligibly small as compared with that of carbon dioxide caught in the traps in this pressure range (1). The adsorption of water was assumed to be also negligible because the reduction products (H_2O) were re-
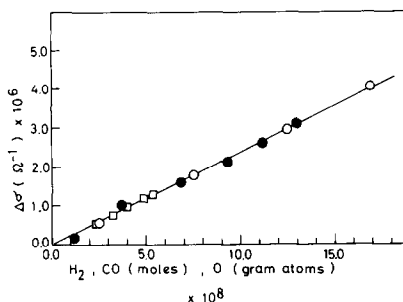

FIG. 4. The increase of the catalyst conductivity by H_2 or CO reduction or by O_2 thermodesorption at 535°C. The initial pressures of CO and H_2 were 2.17×10^{-2} and 3.43×10^{-2} mm Hg, respectively. O, H_2 reduction; ●, CO reduction; □, O_2 thermodesorption.

moved continuously by liquid nitrogen-cooled traps during the reduction processes as in the case of CO reduction.

It is clear in the figure that the active oxygen species removed from the surface of the catalyst, either by hydrogen or by carbon monoxide, had the same influence on the electric conductivity of the catalyst. Consequently, it can be said that hydrogen and carbon monoxide react with the active oxygen of electrically common species on the surface of MoO_3.

The experimental results on the thermodesorption of the surface oxygen monitored by the electric conductivity measurement are also shown in Fig. 4. Thermodesorption experiments were carried out at the same temperature as that at which H_2 and CO reduction experiments were performed (535°C). The amount of desorbed oxygen was determined by measuring the pressure of oxygen which was collected in a fixed volume by a compressing pump.

In Fig. 4 the variation of the electric conductivity of the catalyst is plotted against the numbers of gram atoms of oxygen which desorbed thermally from the surface of the catalyst. It is clear that the trend of the increase of the conductivity due to the desorption of oxygen is effectively equal to those due to the reduction processes. This finding shows that the oxygen thermodesorbed from the catalyst surface is electrically identical with the active

oxygen species which can be removed by H_2 and CO.

Amount of Active Oxygen on Molybdenum Trioxide

Since the active oxygen reducible by hydrogen was confirmed to be electrically identical with that reducible by carbon monoxide, it would be proper to assume that the active oxygen which is operative in the catalysis of CO oxidation is also operative in the catalysis of H_2 oxidation. In the previous paper, the amount of active oxygen which was operative in the catalysis of CO oxidation was estimated in the following manner (*1*). The catalyst treated in circulating oxygen at 530°C was reduced by CO of about 50 mm Hg until there was practically no pressure change, and formed CO_2 was condensed in the liquid nitrogen-cooled traps. The amount of active oxygen was estimated from the amount of CO_2 condensed in the traps.

The analogous procedure was tried in order to estimate the amount of active oxygen which was operative in the catalysis of H_2 oxidation. The catalyst pretreated in circulating oxygen of about 50 mm Hg at 530°C for 3 hr was cooled to 401°C and evacuated. The catalyst in this state was then exposed to hydrogen of 20–66 mm Hg until there was practically no pressure change. The decrease of hydrogen pressure was plotted against the reduction time in Fig. 5. It shows that the pressure of hydrogen decreased rapidly in the initial period of reduction time; however, it practically ceased to decrease after 12–18 min, suggesting that the reduction of MoO_3 by H_2 did not proceed beyond some extent at this temperature. It can also be found that the levels of the plateaus in Fig. 5 go up with the increase of the hydrogen pressure. This indicates that a part of hydrogen is adsorbed on the reduced catalyst surface.

When the reduction experiment was carried out at 500°C, hydrogen at the initial pressure of 42 mm Hg also decreased rap-
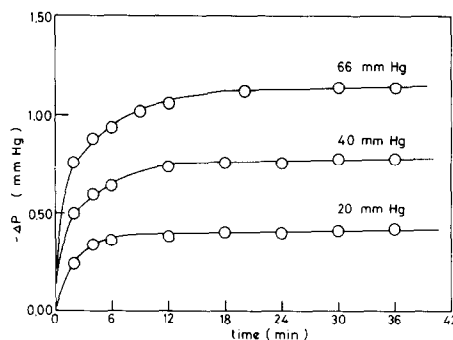

FIG. 5. The decrease of the hydrogen pressure as a function of time. The reduction of MoO_3 was carried out by H_2 at pressures of 20, 40, and 66 mm Hg at 401°C.

idly in the initial period of reduction time, and the decrease of H_2 pressure seemed to stop after 12–18 min. However, after the lapse of 30 min, the pressure of H_2 again started to decrease in proportion to reduction time. This result indicates that (i) the reactive oxygen on the surface of MoO_3 is initially reduced, and (ii) then the reduction of bulk MoO_3 by H_2 proceeded in proportion to reduction time.

Massoth studied the kinetics of reduction of molybdena–alumina catalyst by hydrogen at atmospheric pressure over the temperature range of 400–600°C and stated that pure MoO_3 was reduced more easily to Mo than MoO_3 supported on η-Al_2O_3 (*12*). Kennedy and Bevan also studied the reduction kinetics of MoO_3 by hydrogen at a pressure of 380 mm Hg in the temperature range of 480–600°C, and stated that MoO_3 was reduced via MoO_2 to Mo (*13*).

Consequently, on the basis of our results and those of Massoth, and Kennedy and Bevan, it can be said that the reduction of MoO_3 did not proceed beyond some extent when the reduction was carried out at about 400°C using hydrogen at a pressure lower than 66 mm Hg, suggesting that there exists a limited amount of reactive oxygen on the surface of MoO_3. However, when the reduction temperature was raised to 500°C, the reactive oxygen on the surface of MoO_3 seemed to be reduced initially, then the

reduction of bulk MoO_3 by H_2 proceeded in proportion to time.

After the pressure of hydrogen ceased to decrese at 401°C, hydrogen in the gas phase was evacuated, and the formed water condensed in the traps was vaporized in a fixed volume at room temperature. The amount of formed water was, then, determined volumetrically. The amount of active oxygen operative in H_2 oxidation was thus estimated.

The results were compared with those obtained by carbon monoxide reduction method (*1*). Figure 6 shows the dependence of amounts of formed CO_2 or H_2O upon H_2 or CO pressure at 401°C. It can be found that (i) the amounts of formed H_2O agree well with those of CO_2, and (ii) both of them are almost independent of the pressures of CO or H_2. It can therefore be said that there exists a limited amount of active oxygen on the surface of MoO_3 which can be reduced by CO as well as by H_2. Figure 6 also shows the dependence of the amount of adsorbed H_2 upon the pressure of H_2. The amount of H_2 adsorbed on the surface

was calculated by subtracting the amount of formed H_2O from that of H_2 that disappeared from the gas phase. Tanaka *et al.* reported that MoO_3 catalyst supported on β-TiO_2 started to adsorb CO and olefin molecule when it was reduced by CO or H_2 at 500°C (*14*). The fact that MoO_3 adsorbs CO when it is reduced by CO was already reported previously (*1*). The results of Fig. 6 show that the catalyst which is reduced by H_2 also adsorbs H_2 molecules.

In order to compare the surface reduced by hydrogen with that reduced by carbon monoxide, hydrogen was adsorbed on the catalyst which was reduced by CO. In this case, the formation of H_2O was confirmed to be negligible. It can be seen in Fig. 6 that the amount of H_2 adsorbed on the CO-reduced surface almost agreed with that adsorbed on the H_2-reduced surface. This again indicates that CO and H_2 molecules reduce the same active oxygen on the surface of MoO_3.

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, were already given in the previous paper (*1*). The percentages of active oxygen were 10 to 3% of the surface lattice oxygen between 500 and 300°C.

FIG. 6. The dependence of the amounts of formed H_2O and CO_2 and those of adsorbed H_2 upon H_2 or CO pressures. The reductions were carried out at 401°C. □, The amount of formed H_2O; ■, the amount of formed CO_2; △, the amount of adsorbed H_2 on the surface reduced by H_2; ▲, the amount of adsorbed H_2 on the surface reduced by CO.

Deficient Amount of Active Oxygen in the Steady State of the Catalysis of Hydrogen Oxidation

It would be proper to assume that the deficient amounts and ratios of active oxygen during the catalysis of H_2 oxidation are practically equal to those in the steady state of the catalysis of CO oxidation, because (i) the electric conductivities of MoO_3 in the steady state of the catalyses of H_2 and CO oxidations are almost overlapped over the whole range of temperature, as shown in Fig. 3, and (ii) the amount of active oxygen on the surface of MoO_3 reducible by H_2 almost coincided with that reducible by CO.
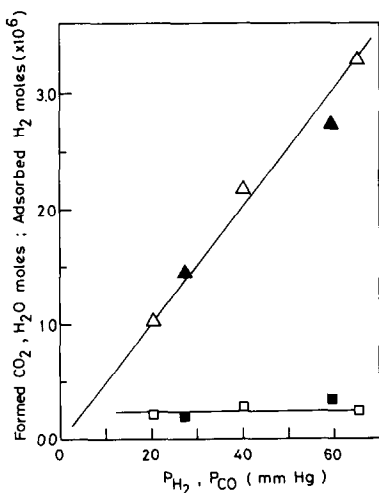
The numbers of the deficient active oxy-

gen atoms during the catalysis and their ratios to total active oxygen atoms in the temperature range of 400–470°C were already given in the previous paper (*1*). The deficient ratios of active oxygen during the catalysis were only about 1 to 2%. This fact shows that the catalyst under the reaction conditions is very near to the oxidized state. Similar results were reported by Boreskov *et al.* who measured the equilibrium oxygen pressure on oxides of 4th period elements in the study of oxidations of hydrogen and methane (*15*).

Relation between Reduction Rate and Oxidation Rate of Active Oxygen at the Steady State of the Catalysis

The catalyst pretreated in circulating oxygen of about 50 mm Hg at 530°C for 3 hr was cooled down to a definite temperature and evacuated. When H_2 of about 10^{-2} mm Hg was introduced to the catalyst in this state, it reacted with the active oxygen of the catalyst and the formed water was caught in the traps, and the pressure of H_2 decreased. The decreasing rate of the H_2 pressure was found to be proportional to the pressure of H_2. Consequently, the reduction rate can be expressed as

$$-d(H_2)/dt = k_{H_2} \cdot P_{H_2} \cdot \theta, \qquad (3)$$

where k_{H_2} is the reduction rate constant of MoO_3 by H_2 and θ, the coverage fraction of active oxygen on the surface of the catalyst. The Arrhenius plots of k_{H_2} are shown in Fig. 1 together with those of k_{H_2O}. Since the θ value during the steady state of the catalysis of H_2 oxidation is nearly equal to 1, as is mentioned above, k_{H_2} can be compared with k_{H_2O}. It can be seen that the reduction rate constant almost agrees with the reaction rate constant over the whole range of temperature. The activation energy for the reduction of MoO_3 by H_2 was about 27.9 kcal/mol, which agreed well with that of the oxidation of H_2 with O_2 on MoO_3.

The activation energy for the reduction process obtained in the present work is in

good agreement with the value (113 kJ/mol) reported by Kennedy and Bevan (*12*), who studied the kinetics of the reduction of MoO_3 to MoO_2 by H_2 in the temperature range of 480–600°C.

The kinetics of the reoxidation process of the reduced MoO_3 by oxygen were reported previously (*1*). The reoxidation rate was proportional to the oxygen pressure and nearly of second order with respect to the deficient ratio of active oxygen, suggesting the dissociative adsorption of an oxygen molecule on a site which is composed of two adjacent vacancies of active oxygen (*16*). The reoxidation rate of the reduced surface by oxygen could be expressed by

$$-d(O_2)/dt = k_{O_2} \cdot P_{O_2} \cdot (1 - \theta)^2, \qquad (4)$$

where k_{O_2} is the oxidation rate constant of the reduced MoO_3 by O_2 and $(1 - \theta)$, the deficient ratio of active oxygen sites. The values of k_{O_2} were far larger than those of k_{H_2} and k_{H_2O}.

At the steady state of the catalysis, the reduction rate of active oxygen of MoO_3 by H_2 is expected to be dynamically balanced with the uptake rate of oxygen by MoO_3. Therefore, confirmation of the dynamic balance between the reduction rate and oxidation rate at the steady state of the catalysis was attempted from the measurements of the electric conductivity.

The catalyst in the steady state of the catalysis of H_2 oxidation was evacuated at 451°C, then H_2 at a pressure of 0.86 mm Hg was introduced to the reaction system. As the reduction of the active oxygen by H_2 proceeded, the electric conductivity of the catalyst increased gradually, as shown in Fig. 7. After evacuation, the catalyst in the steady state was reoxidized by oxygen at a pressure of 0.42 mm Hg. The electric conductivity of MoO_3 decreased as also shown in Fig. 7. Although H_2 and O_2 altered the electric conductivity of MoO_3 to opposite directions from each other, it is clear that the absolute value of the inclination of the conductivity plots are essentially the same in these two experiments. This finding indi-
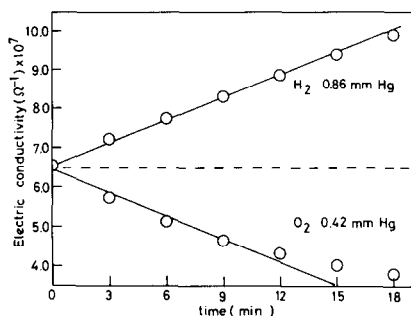
FIG. 7. The variations of the electric conductivity of MoO_3 as a function of time, which are accompanied by H_2 reduction and O_2 oxidation at 451°C. The broken line shows the electric conductivity at the steady state of the catalysis.

cates the dynamic balance between the reduction rate and the oxidation rate at the steady state of the catalysis.

Kinetic Isotope Effects Measurements

In order to obtain the more detailed information about the mechanism of the catalysis of H_2 oxidation with O_2 on MoO_3, the kinetic isotope effects with respect to hydrogen were measured. The reaction mixture of deuterium and oxygen with the stoichiometric composition of about 10^{-2} mm Hg was introduced into the reaction system. After establishing the steady activity of the catalyst, the oxidation rate of deuterium with oxygen on MoO_3 was measured in the temperature range 400–530°C. The Arrhenius plots of the oxidation rate constant of deuterium, k_{D_2O}, were shown in Fig. 1 together with those of k_{H_2O}. It can be seen in the figure that (i) the values of k_{D_2O} are lower than those of k_{H_2O} at identical temperatures by a factor of about 1.4, and (ii) the activation energies of the oxidations of H_2 and D_2 on MoO_3 are practically equal.

Bulgakov *et al.* studied the mechanism of the catalytic oxidation of H_2 with O_2 on Fe_2O_3 by measuring the kinetic isotope effect with respect to H_2 (*16*). It was established that (i) the rate of oxidation of D_2 is lower than that of H_2 and (ii) the reaction orders with respect to H_2 and D_2 and activa-

tion energies of the oxidations of both isotopes were practically equal. On the basis of kinetic results and the theoretical analysis of the values of the kinetic isotope effects, they considered that a molecule of hydrogen, weakly bound to the surface oxygen, is most probable to enter into the active complex of the first stage of the reaction.

As the activation energies for the oxidations of H_2 and D_2 with O_2 are practically equal on MoO_3, it would be probable that a molecular hydrogen, weakly bound to the active oxygen on the surface of MoO_3, comprises the active complex in the rate-determining step of this catalysis (*17*).

The electric conductivity of the catalyst during the steady state of the catalysis of D_2 oxidation was measured to examine the influence of the kinetic isotope effect on the surface state of the catalyst. The electric conductivity of MoO_3 during D_2 oxidation was shown in Fig. 3 together with those during H_2 and CO oxidations and in O_2. As the electric conductivities of the catalyst are almost independent of the pressures of oxygen and reaction mixtures, it can be said that the surface of MoO_3 during the oxidation of D_2 is less reduced than those in the steady state of the H_2 and CO oxidations. This finding supports the conclusion that the reduction rate of active oxygen by reducing gas is dynamically balanced with the reoxidation rate of MoO_3 by oxygen at the steady state of the catalysis. It can also be found that the results in Fig. 3 are consistent with the kinetic results in Fig. 1.

The Isotope Exchange Measurements during the Catalysis of Hydrogen Oxidation

In order to examine the catalysis mechanism of H_2 oxidation with O_2 in further detail, the isotope exchange reactions in the course of the catalysis were measured. Samples of the gas were leaked into the AGA-100 quadrupole mass filter for mass-spectrometric analysis.

The hydrogen–deuterium exchange reac-

tion in the gas phase during the catalysis was measured. A mixture of hydrogen and deuterium (1/1) with oxygen ($H_2 + D_2/O_2 = 2/1$) was introduced over the catalyst at 491°C. It was established that there was practically no deuterium–hydrogen exchange on MoO_3 under the conditions of the catalysis. This finding indicates the absence of the reversible dissociative adsorption of hydrogen on the surface of MoO_3 during the catalysis.

The oxygen isotope exchange reaction during the catalysis was also examined by using the mixed gas of H_2 with $^{18}O_2 + {}^{16}O_2$, containing about 40% ^{18}O, with the stoichiometric composition. Table 2 shows the variation of the isotopic composition of oxygen in the gas phase during the oxidation. It can be seen that the isotopic composition of ^{18}O remained constant during the reaction. This fact shows that (i) the oxygen molecule does not exchange with surface lattice oxygen on MoO_3 during the catalysis, and (ii) the oxygen molecule is irreversibly taken up on the surface of the catalyst during the reaction.

Mechanism of the Hydrogen Oxidation with Oxygen on Molybdenum Trioxide

Since (i) the reaction rate is proportional to P_{H_2} and does not depend upon P_{O_2}, (ii) the reaction rate constant and activation energy of the H_2 oxidation with O_2 on MoO_3

TABLE 2

The Isotopic Composition of Gaseous Oxygen during the Catalysis of H₂ Oxidation with $^{18}O_2 + {}^{16}O_2$ at 491°C

Time (min)	Composition (%)		
	$^{16}O_2$	$^{18}O^{16}O$	$^{18}O_2$
0	57.0	1.7	41.3
30	56.7	1.8	41.4
60	57.2	1.7	41.0
90	55.1	1.9	43.0
120	56.8	1.9	41.3
150	57.5	1.4	41.0
180	57.3	1.6	41.4

almost agree with those of the reduction of MoO_3 by H_2, (iii) the oxygen uptake rate constant of the reduced MoO_3 is far larger than the reduction rate constant of MoO_3 by H_2, 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 catalysis can be expressed as follows. The reaction consists of two processes: (i) a molecule of hydrogen which collides with the surface of the catalyst or is physisorbed on it reacts with the active oxygen of the catalyst and H_2O thus formed immediately desorbs, leaving an oxygen vacancy on the surface, and (ii) two adjacent vacancies of active oxygen are refilled with oxygen molecule from the gas phase irreversibly and dissociatively. Therefore, the reaction steps are expressed as follows:

$$H_2(g) + O(s) \rightarrow H_2O(g) + (s) \quad slow, \quad (5)$$

$$2(s) + O_2(g) \rightarrow 2O(s) \quad fast, \quad (6)$$
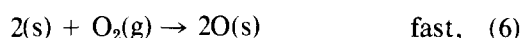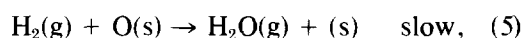
where $O(s)$ refers to the active oxygen on the surface of MoO_3 and (s), the vacancy of active oxygen on the surface. The rate constant of step (6), k_{O_2}, is far larger than that of step (5), k_{H_2}, so the overall reaction rate is determined by step (5). In the rate-determining step, molecular hydrogen, weakly bound to the active oxygen on the surface, is presumed to enter into the active complex because the activation energies for the oxidations of H_2 and D_2 are very close to each other on MoO_3.

The reaction mechanism presented here is closely analogous to that proposed for CO oxidation with O_2 on this oxide (1). A close analogy in the reaction mechanism between CO and H_2 oxidations has been proposed on ZnO (10), NiO (5–7), TiO₂ (8), ZrO₂ (9), and recently of HfO₂ (11). Jamieson et al. explained this feature by assuming that the difference between hydrogen and carbon monoxide reactivity has only a small effect and that the reactivity of active

oxygen in the surface layer of the oxide plays the predominant kinetic role in the two reactions (7). Our result that MoO_3 has a limited amount of active oxygen which operates reactively in both the catalyses of oxidations of H_2 and CO is compatible with the assumption of Jamieson et al.

Recently, Bielanski and Haber mentioned that MoO_3 practically does not adsorb oxygen but shows the ability to use its lattice oxygen in reactions with gaseous reactants, and that oxides which show no activity in oxygen exchange, do not adsorb oxygen (18). Since MoO_3 practically does not show the ability to exchange isotopes of oxygen during the catalysis (Table 2), surface lattice oxide ions of MoO_3 are thought to be active in the catalysis of H_2 oxidation. The experimental results that the reduction rate constant of MoO_3 by H_2 almost agrees with the oxidation rate constant of H_2 on MoO_3 also supports the participation of lattice oxide ions in the catalysis. However, as not all of the surface lattice oxide ions are active, the active oxygen may be presumed to be associated with lattice defects on the surface of MoO_3.

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