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The Catalytic Oxidation of Carbon Monoxide on Titanium Dioxide; Anatase and Rutile

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For the purpose of examining the surface state of titanium dioxide during the catalytic oxidation of carbon monoxide, the electric conductivities of anatase and rutile at 350—800°C, the amount of active oxygen on the catalyst surface at 400—600°C, and oxygen deficiency during the reaction were measured. The temperature-dependence of electric conductivities are represented by the formula $\sigma = A \cdot e^{-E/RT}$ in narrow temperature ranges. The amounts of active oxygen per unit surface area of rutile were 3—5 times as much as those of anatase at same temperatures, and 1—3% of them desorbed during the reaction. When the coverage fraction of active oxygen on the catalyst, θ, is assumed to be equal to 1 in oxygen, the following equation can express the relation between the rate constant of the reduction of titanium dioxide by carbon monoxide, k_{CO}, and that of the oxidation of reduced titanium dioxide by oxygen k_{O_2}, during the oxidation of carbon monoxide:

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

In the preceding paper,[1] the following results have been reported: the rate constant of oxidation of carbon monoxide on titanium dioxide is proportional to P_{CO} and it does not depend upon P_{O_2} nor P_{CO_2}, the rate-determining step is the reaction between the surface oxygen on the catalyst and carbon monoxide, and the difference between activation energies of the uptake of surface oxygen atoms by carbon monoxide from anatase and rutile is about 10 kcal/mol. Several papers[2–5] have discussed an amount of surface oxygen, oxygen defect, and active sites on the catalyst in the oxidation of carbon monoxide on metallic oxide catalysts. For the titanium dioxide, the oxygen defect is formed on its surface during the reaction, and there are surface oxygen which react easily with carbon monoxide, *i.e.*, active oxygen.[1]

In this paper, the amount of active oxygen and its deficient amount during the oxidation of carbon monoxide on the surface of two crystal forms will be determined. The relation between the amount of active oxygen and the rate constants of the reduction of titanium dioxide by carbon monoxide and the oxidation of the reduced titanium dioxide by oxygen will be studied.

Experimental

The samples used were anatase (A) and rutile (R). The latter was obtained by heating A at 1150°C for 3 hr.[1] The apparatus and the preparation of the reactant gas were described in the preceding paper.[1] The sample was evacuated and treated with a circulating oxygen at 600°C for 3 hr in the reaction system before the measurements.

The electric conductivity of the sample was calculated from the observed current under a constant D.C. voltage applied to a pair of gold electrodes which were pressed to the sample with a definite weight.

Results and Discussion

Dependence of Electric Conductivity of the Catalyst upon Temperature. The electric conductivity of the catalyst pretreated in oxygen at 600°C for 3 hr was determined in oxygen under pressure of 70 mmHg or in circulating mixed gas with a composition of $CO/O_2 = 2/1$ under pressure of 70 mmHg[6] at a constant temperature. The temperature-dependence of electric conductivities for anatase and rutile determined at 350—800°C are shown in Figs. 1 and 2. The measured points at 600°C and lower are almost linear for two samples and the conductivity σ can be represented

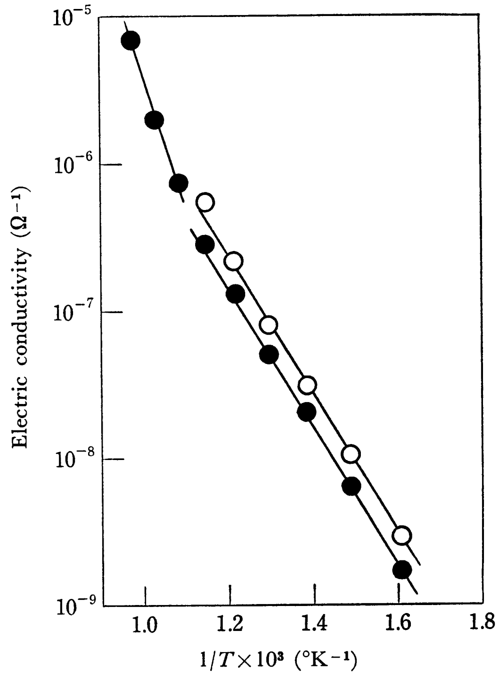

Fig. 1. Effect of temperature on electric conductivity of anatase.
●: in O_2 ○: in $CO/O_2 = 2/1$

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[1] Y. Onishi and T. Hamamura, This Bulletin, **43**, 996 (1970).

[2] G. Parravano, *J. Amer. Chem. Soc.*, **75**, 1448 (1953).

[3] E. R. S. Winter, *J. Chem. Soc.*, **1955**, 2726.

[4] F. S. Stone, *Advan. Catal.*, **13**, 1 (1962).

[5] K. Tarama, S. Teranishi, and A. Yasui, *Kogyo Kagaku Zasshi*, **60**, 1222 (1957).

[6] In this case, carbon dioxide formed was condensed in the liquid nitrogen trap and the total pressure gradually decreased, but the electric conductivity did not change.

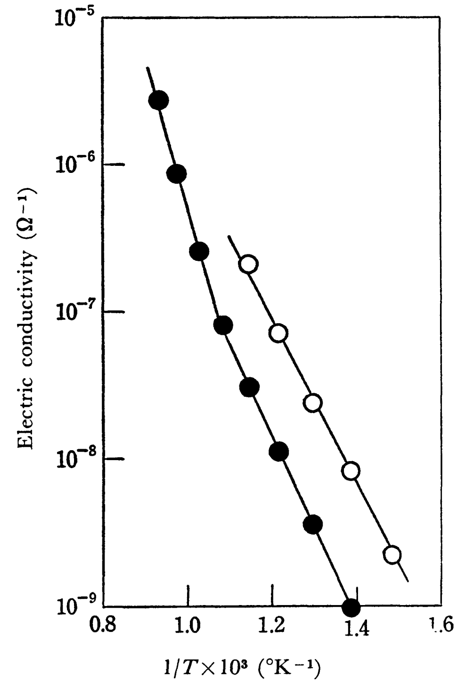

Fig. 2. Effect of temperature on electric conductivity of rutile.

● : in O_2 ○ : in $CO/O_2=2/1$

by the following equation:

$$\sigma = A \cdot e^{-E/RT} \quad (1)$$

where A is a constant, and E an activation energy, respectively. The plots at higher temperatures than 600°C gradually deviate upward from linear lines, but in narrow temperature ranges, Eq. (1) may be applied. The obtained values of E are listed in Table 1.

TABLE 1. ACTIVATION ENERGIES FOR ELECTRIC CONDUCTIVITIES OF CATALYSTS

Temp. (°C)	350—600		600—800
	$CO/O_2=2/1$	O_2	O_2
Anatase (kcal/mol)	21.3	21.3	38.5
Rutile (kcal/mol)	25.7	29.5	46.9

The value of rutile determined under temperatures lower than 600°C in oxygen almost agrees with that of Gorelik,[7] and the value above 600°C, with those of Earle,[8] Cronemeyer,[9] and Hauffe.[10] The conductivity in the mixed gas is larger than that in oxygen for both anatase and rutile because of the reduction with carbon monoxide, and this fact shows that titanium dioxide is an n-type oxide semi-conductor.

Amount of Active Oxygen of the Catalyst. When the catalyst pretreated in oxygen at 600°C for 3 hr was cooled, their conductivities were function of the temperature, and these values almost unchanged upon the evacuation. Therefore, it is considered that the catalyst surface is clean and stable by this treatment, and the catalyst thus treated will be called its starting state hereafter.

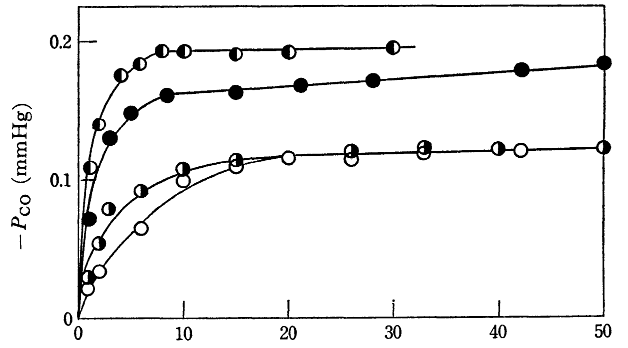

Fig. 3. Amounts of carbon monoxide reacted *vs.* time curves on anatase.

◐ : $P_{CO}=149$ mmHg at 550°C
◑ : $P_{CO}=75$ mmHg at 500°C
● : $P_{CO}=16$ mmHg at 550°C
○ : $P_{CO}=14$ mmHg at 500°C

When titanium dioxide of the starting state was exposed to carbon monoxide under pressures of 10—150 mmHg at 400—600°C, carbon dioxide formed was condensed in the liquid nitrogen trap, and the CO pressure decreased, but the rate of decrease fell down with the time as is shown in Fig. 3. The total amount of carbon dioxide condensed was almost equal under the different initial pressure of carbon monoxide at the same temperatures. If a limited amount of the surface oxygen of the catalyst (it may be the oxygen of both crystal-lattice point and adsorbed one) is assumed to react easily with carbon monoxide (these oxygen will be called active oxygen hereafter), the amount of the active oxygen can be estimated from the amount of carbon dioxide condensed. The number of the active oxygen atoms per unit surface area, and its percentage to the surface lattice oxygen assuming that the surface is (011) for anatase and (110) for rutile,[11] are listed in Table 2.

TABLE 2. NUMBERS OF ACTIVE OXYGEN ATOMS AND THEIR PERCENTAGES TO SURFACE LATTICE OXYGEN ON ANATASE AND RUTILE

	Temp. (°C)	600	550	500	450	400
A	Numbers $\times 10^{-17}$ (atoms/m^2)	5.14	3.26	2.07	1.25	0.66
	%	4.63	2.94	1.87	1.13	0.60
R	Numbers $\times 10^{-17}$ (atoms/m^2)	16.2	11.3	8.35	5.66	—
	%	15.6	10.8	8.01	5.44	

Deficient Amount of thr Active Oxygen during the Oxidation of Carbon Monoxide. When titanium dioxide of the starting state is exposed to carbon monoxide

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[7] S. I. Gorelik, *Zhur. Eksptl. i Teoret. Fiz.*, **21**, 826 (1951); *Chem. Abstr.*, **49**, 1395f (1955).

[8] M. D. Earle, *Phys. Rev.*, **61**, 56 (1942).

[9] D. C. Cronemeyer, *ibid.*, **87**, 876 (1952).

[10] K. Hauffe, "Reaktionen in und an festen Stoffen," Springer, Berlin (1955), p. 136.

[11] A. N. Winchell and H. Winchell, "Elements of Optical Mineralogy, Part II," John Wiley and Sons Inc., New York (1951), pp. 66, 69.

under a pressure of about 10^{-2} mmHg at a definite temperature, it is reduced by carbon monoxide and its conductivity increases with the time. Therefore, the amount of the reduction product CO_2 formed until the conductivity becomes the same value in the mixed gas shows the deficient amount of the active oxygen during the reaction. The number of the deficient active oxygen sites and its ratio to total active oxygen atoms, $(1-\theta)$, are listed in Table 3; θ represents the coverage fraction of active oxygen on the catalyst and θ is equal to 1 at the starting state.

TABLE 3. DEFICIENCIES OF ACTIVE OXYGEN ATOMS DURING THE OXIDATION OF CARBON MONOXIDE ON ANATASE AND RUTILE

	Temp. (°C)	600	550	500	450
A	Deficiency $\times 10^{-15}$ (atoms/m^2)	8.61	5.93	3.98	2.47
	$(1-\theta)\times 10^2$	1.68	1.82	1.92	1.98
R	Deficiency $\times 10^{-16}$ (atoms/m^2)	2.09	1.98	1.89	1.78
	$(1-\theta)\times 10^2$	1.29	1.75	2.26	3.14

Relation between Reduction Rate and Oxidation Rate of Titanium Dioxide. If the reduction starts from its starting state ($\theta=1$) in the above case, the value of θ at any point can be calculated by measuring the amount of carbon monoxide consumed. Therefore, the rate of decrease of carbon monoxide at any θ value can be estimated by measuring the CO pressure as a function of time. Similarly, when oxygen is introduced over the reduced titanium dioxide, it is oxidized by oxygen (some of the oxygen may be adsorbed on it), and the O_2 pressure decreases. Therefore, the oxidation rate of titanium dioxide of any θ value can be estimated by measuring the O_2 pressure. From these measurements, the following equations are obtained:

$$-\mathrm{d(CO)}/\mathrm{d}t = k_{\mathrm{CO}}\cdot P_{\mathrm{CO}}\cdot\theta \tag{2}$$

$$-\mathrm{d(O_2)}/\mathrm{d}t = k_{\mathrm{O_2}}\cdot P_{\mathrm{O_2}}\cdot(1-\theta)^2 \tag{3}$$

where k_{CO} and $k_{\mathrm{O_2}}$ are the rate constants of reduction and oxidation of titanium dioxide, respectively. The values of k_{CO} and $k_{\mathrm{O_2}}$ are listed in Table 4; k_{CO} are the same values shown in Fig. 3 of the preceding paper[1)] in which they have been shown as k'. The oxidation rate of titanium dioxide by oxygen (the adsorption rate of oxygen) is far faster than the reduction rate by carbon monoxide.

TABLE 4. ESTIMATED VALUES OF k_{CO} AND $k_{\mathrm{O_2}}$

Temp. (°C)	600	550	500	450
$k_{\mathrm{CO}}\times 10^5$ (CO_2 mmol/min·cmHg·m^2)				
Anatase	7.50	3.96	1.76	0.896
Rutile	30.1	22.4	18.3	13.6
$k_{\mathrm{O_2}}\times 10$ ($-O_2$ mmol/min·cmHg·m^2)				
Anatase	2.35	1.20	0.55	0.25
Rutile	18.0	7.50	3.40	1.33

The values of $k_{\mathrm{CO}}\cdot\theta$ and $k_{\mathrm{O_2}}\cdot(1-\theta)^2$ calculated from Eqs. (2) and (3) using the values in Tables 3 and 4 are listed in Table 5. The following relation is obtained at 450—600°C for both anatase and rutile during the catalytic oxidation of carbon monoxide using the mixed gas with the composition of $CO/O_2=2/1$:

TABLE 5. CALCULATED VALUES OF $k_{\mathrm{CO}}\cdot\theta$ AND $k_{\mathrm{O_2}}\cdot(1-\theta)^2$

Temp. (°C)	600	550	500	450
$k_{\mathrm{CO}}\cdot\theta\times 10^5$ (CO_2 mmol/min·cmHg·m^2)				
Anatase	7.38	3.90	1.73	0.87
Rutile	29.7	22.0	17.8	13.1
$k_{\mathrm{O_2}}\cdot(1-\theta)^2\times 10^5$ ($-O_2$ mmol/min·cmHg·m^2)				
Anatase	6.70	4.00	2.03	0.98
Rutile	29.8	23.0	17.4	13.1

$$k_{\mathrm{CO}}\cdot P_{\mathrm{CO}}\cdot\theta = 2k_{\mathrm{O_2}}\cdot P_{\mathrm{O_2}}\cdot(1-\theta)^2\,. \tag{4}$$

Above equation shows that the present reaction consists of both the reduction and the oxidation processes of the catalyst by carbon monoxide and oxygen.

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