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

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For the purpose of investigating the correlation between the crystal structure of titanium dioxide and its catalytic activity, the catalytic oxidation rate of carbon monoxide and the desorption rate of oxygen from the sample surface have been measured on anatase, rutile, and an anatase-rutile mixture. The oxidation of carbon monoxide was investigated by a static method at temperatures of 250—550°C and under gas pressures of $10^{-2}$—150 mmHg. The desorption of oxygen was carried out at 600—750°C. The reaction rate was proportional to $P_{CO}$ and did not depend on either $P_{O_2}$ or $P_{CO_2}$. The activation energy was 16.0 kcal/mol for anatase and 6.7 kcal/mol for rutile. The catalytic activity per unit of the surface area of rutile was 3—6 times as much as that of anatase. The reaction rate almost coincided with the rate of the reduction of titanium dioxide by carbon monoxide. The electric resistance of the sample was little affected by the $P_{O_2}$. The following reaction mechanism is proposed to explain the results. The rate-determining step is the reaction between the surface oxygen of the sample and the carbon monoxide physisorbed or that which has just collided with the surface coming from the gas phase; the oxygen vacancy thus formed on the surface is quickly filled with oxygen of the gas phase. The difference in the activation energy of the catalytic action between the two structures is based upon the difference in the activation energy of the oxygen desorption from the surface structure; the activation energies are 57.8 kcal/mol for anatase and 38.4 kcal/mol for rutile.

It is generally accepted that there is an intimate relationship between the catalytic activity of a solid catalyst and its crystal structure. Many investigations[1-4] as to these points have been carried out on the metals, but few on metallic oxide catalysts; thus, we have chosen titanium dioxide, $TiO_2$, as the subject of the present investigation. Titanium dioxide has three polymorphic forms, that is, anatase, rutile, and brookite; among these, rutile can be transformed from anatase by heating it to high temperatures, and so it is easy to obtain samples with the same chemical constitutions but different polymorphic forms. Therefore, titanium dioxide is suitable as a sample to investigate the relationship between the catalytic activity and the crystal structure.

The aim of this series of investigations is to ascertain the difference between anatase and rutile in their catalytic activity in response to the oxidation reaction. This paper will be concerned with the oxidation of carbon monoxide on the surface of titanium dioxide.

There have been several reports[5] on the pure or doped titanium dioxide catalyst used for the CO-oxidation, but there seems to have been no systematic investigation of the catalyst relating to the polymorphic forms. Moreover, most of the investigations of the catalytic reactions reported so far were carried out using an apparatus with greased stop cocks; these might contaminate the catalyst and so might cause some errors in the results. For this reason, the present experiments were performed with strict care taken to prevent the sample from contamination with grease vapor.

## Experimental

The samples used in the present experiment are listed in Table 1. The sample $A_1$ was a reagent of a guaranteed grade obtained from the East Merck Company. Anatase transforms into rutile[6] and decreases in specific surface area when it is heated to high temperatures, so the samples of anatase, rutile, or an anatase-rutile mixture with the desired surface areas were obtained by selecting a suitable temperature and period

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[1] J. A. Becker, *Advan. Catal.*, **7**, 135 (1955).

[2] A. T. Gwathmey and R. E. Cunningham, *ibid.*, **10**, 57 (1958).

[3] G. Ehrlich, *ibid.*, **14**, 255 (1963).

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

[5] I. L. Mikhailova, I. S. Sazonova and N. P. Keier, *Kinet Katal.*, **6**, 704 (1965). *Chem. Abstr.*, **63**, 17197a (1965).

[6] A. W. Czanderna, C. N. R. Rao and J. M. Honig, *Trans. Faraday Soc.*, **54**, 1069 (1958).

Table 1. Samples

| No. | Temperature and time of heating | | Poly-morphic forms | Weight % | Specific surface areas ($m^2/g$) |
|---|---|---|---|---|---|
| $A_1$ | — | — | Anatase | 100 | 10.3 |
| $A_2$ | 900°C | 1 hr | Anatase | 100 | 7.7 |
| $A_3$ | 1000 | 1 hr | Anatase | 100 | 4.3 |
| $R_1$ | 1150 | 1 hr | Rutile | 100 | 1.3 |
| $R_2$ | 1150 | 3 hr | Rutile | 100 | 1.0 |
| $AR_1$ | 1050 | 1 hr | Anatase<br>Rutile | 87.3<br>12.7 | 3.8 |
| $AR_2$ | Mixture of<br>$A_1$ and $R_2$ | | Anatase<br>Rutile | 87.4<br>12.6 | 4.7 |

of heat treatment. The heat treatments were carried out as follows. The sample $A_1$ (about 60 g) in a fused quartz tube 3 cm in diameter was put in an electric furnace which had been preheated to a desired temperature, and kept there for the desired period. It was then taken out of the furnace, quenched in air, and pulverized by using an agate mortar. The temperature, time of heating, weight percentages of anatase and rutile, and specific surface areas of the samples are listed in Table 1. The weight percentages of anatase and rutile were estimated by the ordinary method of X-ray analysis, while the specific surface areas were determined by the B.E.T. method,[7,8] using nitrogen as the adsorbate. The crystal structures of $A_2$ and $A_3$ are the same as that of $A_1$, but the specific surface areas of $A_2$ and $A_3$ are less than that of $A_1$. The crystal structures of $R_1$ and $R_2$ are rutile, but the specific surface areas differ from each other. The $AR_1$ is $A_1$ partly transformed into rutile.

Carbon monoxide prepared by the decomposition of sodium formate by sulfuric acid, and oxygen prepared from a commercial bomb, were purified by fractional distillation using liquid nitrogen.

The apparatus shown schematically in Fig. 1. was used for the experiment under pressures of 10—150 mmHg. It was made of glass and had a circulating pump of the piston type. The stop cocks, A, B, and C, were metallic cocks, with Viton used as the sealing material to keep grease vapor out. The trap $T_1$ was cooled by liquid nitrogen in order to collect the reaction product, ($CO_2$), while the trap $T_2$ was cooled to keep grease and mercury vapor out of the sample. This apparatus could be evacuated to a pressure lower than $10^{-6}$ mmHg by means of a mercury-diffusion pump. A sample tube of fused quartz, in which a pair of electrodes of gold were mounted, was connected with the glass system by means of a graded seal.

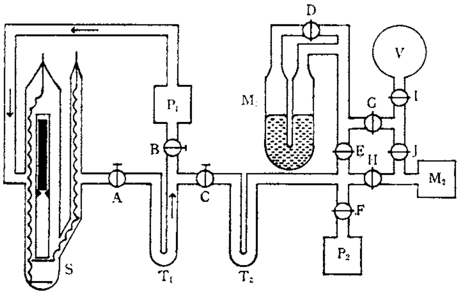

Fig. 1. The apparatus.
A—C: Metal cocks D—J: Grease cocks
$M_1$: Mercury manometer $M_2$: McLeod gauge
$P_1$: Circulating pump $P_2$: Mercury diffusion pump
S: Sample tube $T_1$, $T_2$: Traps V: Gas reservoir

The electric resistance of the catalyst was measured as follows. The catalyst (about 10 g) was put between two electrodes, about 1 cm apart, and was loaded with an iron rod (about 80 g) enclosed in a glass tube; then a constant D.C. voltage was applied, and the current was measured with an electric micro-micro ammeter produced by Takeda-Riken, type TR-16. The voltage was applied only when the current was to be measured.

By preliminary experiments, the followings were confirmed: the electric resistance of the sample was proportional to its length, the contact resistance between the electrodes and the catalyst was negligible, and both the catalytic reaction on the gold electrodes and the gas-phase reaction were negligible.

The apparatus used for the experiments under a gas pressure of about $10^{-2}$ mmHg consisted of a reaction tube, a Pirani gauge, and a liquid nitrogen trap. Under such low pressures, the diffusion velocity of gas was fast enough, so the circulating pump was not used.

When a mixture of carbon monoxide and oxygen was introduced into the reaction system, a catalytic oxidation reaction occurred to form carbon dioxide, which then condensed in the trap; the rate of reaction could be determined by measuring the rate of decrease of the total pressure. When the reaction rate was too small, however, the following method was employed to get the reaction rate: at the end of the run, the residual carbon monoxide and oxygen were pumped out, the carbon dioxide condensed in the trap was vaporized to a definite volume, and the pressure was measured. The rate of the reaction was obtained from the amount of carbon dioxide thus determined.

In the experiment with a powder catalyst, the rate of reaction is, in general, apt to be affected by the rate of the diffusion of gas into the catalyst, so the rate of the reaction should vary with the amount of the catalyst and this effect should become more remarkable as the reaction rate becomes faster. In order to examine this effect, the rate of reaction per unit amount of the catalyst was estimated from the results of runs using different amounts of the catalyst; it was thus found that, in the present experiment, the effect of the amount of the catalyst is negligible. However, the same amount of the catalyst was used in each of the series of experiments.

Gebhardt and Herrington[9] reported that, in order to clean the rutile surface, it was necessary to heat it at 600°C in oxygen for 30 min. In the present experiments, too, this fact was confirmed on both rutile and anatase. The pretreatment carried out in the present

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[7] S. Brunauer, P. H. Emmett and E. Teller, *J. Amer. Chem. Soc.*, **60**, 309 (1938).

[8] K. Kodera and Y. Onishi, This Bulletin, **33**, 338 (1960).

[9] J. Gebhardt and K. Herrington, *J. Phys. Chem.*, **62**, 120 (1958).

experiment was to heat the sample at 600°C for 3 hr in circulating oxygen at a pressure of 70 mmHg until the electric resistance became constant. In the experiment under the lower pressure, the gas could not be forced to circulate in the apparatus, so the pretreatment of the sample was carried out by renewing the oxygen several times.

For obtaining reproducible results with a sample of a low catalytic activity, such as titanium dioxide, it seems necessary to use an apparatus without greased stop cocks and to clean the sample with oxygen prior to the experiment.

## Results and Discussion

**The Relation of Catalytic Activities to Specific Surface Areas and Polymorphic Forms.** The catalytic activity of each sample was measured by using reacting gas with a composition of $CO/O_2=2/1$. At temperatures of 250—550°C and under gas pressures of $10^{-2}$—150 mmHg, the reaction rates were found to be proportional to the total pressure of the reacting gas; they can be expressed by the following equation:

$$d(CO_2)/dt = 2/3\,k\cdot P \qquad (1)$$

where $k$ is a constant. The Arrhenius plots of each sample are shown in Fig. 2. It can be seen from the figure that the $k$ value of the sample $A_1$ is almost equal to that of the smaple $A_3$ and that the $k$ value of $R_1$ is almost equal to that of $R_2$. Therefore, the catalytic activity per unit of the surface area is the same for all samples with the same crystal form, even when they have different surface areas per unit of weight. The sample $AR_1$ consists of particles with both anatase and rutile forms in each particle. The ratio of the area of anatase-type faces to that of rutile-type faces in the sample may be estimated on the assumption that the catalytic activity of an anatase-type face in $AR_1$ is equal to that in $A_1$ and that the catalytic activity of a rutile-type face in $AR_1$ is equal to that in $R_2$. From the data at 550°C, the ratio was estimated to be: anatase/rutile=86.8/13.2. At temperatures other than 550°C, the $k$ values of $AR_1$ can be calculated by using the surface-area ratio presented above, assuming that the $k$ values of the two crystalline faces on $AR_1$ are equal to those of $A_1$ and $R_2$ respectively. These calculated values are plotted as the curve $AR_1$ in Fig. 2; this curve is convex downward. On the other hand, the measured values of $k$ are plotted in Fig. 2 by the mark ○; this mrak shows that the calculated values agree well with the measured values at every temperature.

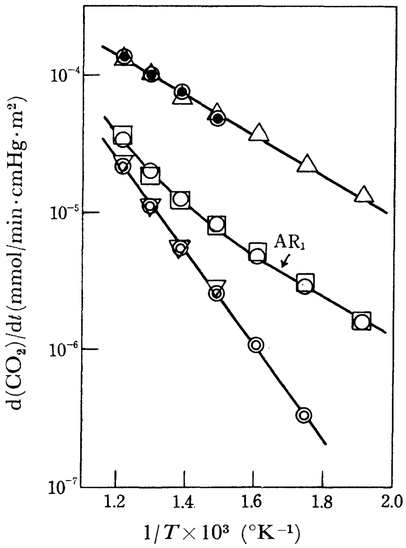

Fig. 2. Effect of temperature on the reaction rate constant.
◎: $A_1$ ▽: $A_3$ ⊙: $R_1$: △: $R_2$ ○: $AR_1$
□: $AR_2$

From these results, it was found that the $k$ value was characteristic for the crystal form and was not affected by the value of the specific surface area nor by the coexistence of two crystalline faces.

**The Relation between the Reaction Rate and the Partial Pressure of Carbon Monoxide.** The effect of the partial pressures of oxygen and carbon monoxide upon the reaction rate was studied at temperatures of 350—550°C and under gas pressures of $10^{-2}$—100 mmHg by changing the $CO/O_2$ ratio at each pressure. It follows that the reaction rate is proportional to $P_{CO}$ and that it does not depend on the $P_{O_2}$ for all samples and does not change even if a small amount of $CO_2$ is intentionally introduced into the reaction system. From these results, together with Eq. (1), the following equation can be obtained:

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

The activation energies of the reaction using anatase and rutile, as calculated from Fig. 2, are 16.0 kcal/mol and 6.7 kcal/mol respectively.

**The Reaction of Carbon Monoxide with the Surface Oxygen of Titanium Dioxide.** The catalyst pretreated in oxygen at 600°C was cooled down to the reaction temperature and evacuated.*1 When carbon monoxide, at a pressure of about $10^{-2}$ mmHg, was introduced into the reaction system, it reacted slowly with the surface oxygen of the catalyst and the carbon dioxide thus formed was caught in the trap. In this experiment, the amount of carbon monoxide which disappeared from the gas phase agreed well with that of the carbon dioxide caught in the trap, showing that the consumed carbon monoxide is entirely converted to carbon dioxide and that the amount of carbon monoxide adsorbed on the surface of the catalyst is negligible compared with that of the carbon monoxide oxidized to carbon dioxide. It was found that the rate of the formation of carbon dioxide

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*1 At this time, the electric resistance of the catalyst did not change upon the evacuation.

is proportional to $P_{CO}$:

$$d(CO_2)/dt = k' \cdot P_{CO} \qquad (3)$$

The $k'$ values determined for all the samples are shown in Fig. 3. On the other hand, when reacting gas with the composition of $CO/O_2=2/1$ is introduced into the reaction system at a pressure of $10^{-2}$ mmHg, catalytic oxidation occurs. The $\boldsymbol{k}$ values of this reaction, as calculated by Eq. (1), are shown in Fig. 3. It is clear that the rate constant of the catalytic oxidation of carbon monoxide, $\boldsymbol{k}$, almost agrees with that of the reaction of carbon monoxide with the surface oxygen of titanium dioxide, $\boldsymbol{k'}$.

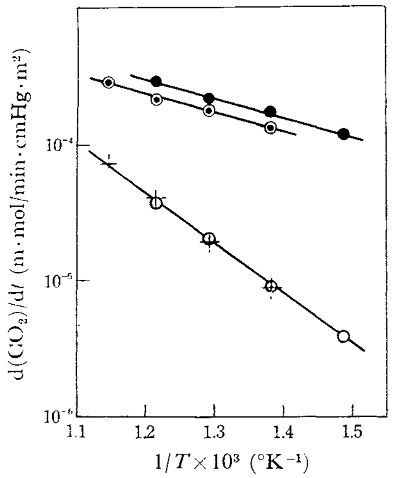

Fig. 3. Effect of temperature on the reaction rate constant.
Anatase, +: $k'$ ○: $k$ Rutile, ⊙: $k'$ ●: $k$

On the catalytic oxidation of carbon monoxide on cupric oxide and nickel oxide,[10-15] it has been reported that the rate of the formation of carbon dioxide is proportional to $P_{CO}$ and independent of $P_{O_2}$, and that the reaction consists of two processes: 1) carbon monoxide which collides with the surface of the catalyst or is physisorbed on the surface reacts with the surface oxygen of the catalyst, and the carbon dioxide thus formed is desorbed immediately, leaving an oxygen vacancy on the surface, and 2) the oxygen vacancy thus formed is filled with oxygen from the gas phase. Therefore, the reaction mechanism can be expressed as follows:

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

$$(s) + 1/2\,O_2 \rightarrow O(s) \qquad (5)$$

where O(s) refers to the surface oxygen of the catalyst and (s), to the oxygen vacancy on the surface. The rate of step (5) is much faster than that of step (4); therefore, the overall reaction rate is proportional only to $P_{CO}$.

In the present investigation, it is believed that the catalytic oxidation of carbon monoxide on titanium dioxide proceeds through the steps (4) and (5), as is the case with cupric oxide or nickel oxide, because the rate of the formation of carbon dioxide is proportional to $P_{CO}$ and the uptake rate of oxygen on the catalyst is much faster than that of carbon monoxide, as will be discussed below.

**The Pressure of Oxygen and the Amount of Surface Oxygen.** The electric resistance of the catalyst which had been pretreated in oxygen at 600°C was measured under the oxygen pressures from $10^{-2}$ to 100 mmHg, with the temperature kept constant. The results, given in Fig. 4, can be represented by:

$$R = R_0 \cdot P_{O_2}^n$$

where $R_0$ is a constant at each temperature and $n$ is 0.02—0.10. It is clear from this result that the electric resistance 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 $10^{-2}$mmHg, so the amount of surface oxygen is almost constant, independent of the oxygen pressure. This fact seems to show that the uptake rate of oxygen is extremely fast.

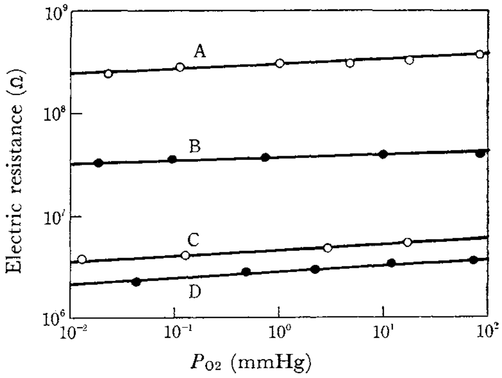

Fig. 4. Effect of oxygen pressure on electric resistance of the catalyst under the constant temperature.
A: 350°C ($n$=0.04) B: 450°C ($n$=0.02) C: 550°C ($n$=0.09) D: 600°C ($n$=0.10)

**The Desorption of the Surface Oxygen.** The catalyst pretreated in oxygen at 600°C was evacuated at this temperature until the gas desorption became almost imperceptible. When the catalyst thus pretreated was heated to a temperature above 600°C, the oxygen desorption was detected and the desorption rate of oxygen could be deter-

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

[11] G. Parravano and M. Boudart, *Advan. Catal.*, **7**, 47 (1955).

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

[13] I. Matsuura, Y. Kubokawa and O. Toyama, *Nippon Kagaku Zasshi*, **81**, 1003 (1960).

[14] A. Kanome and T. Chitani, *ibid.*, **63**, 36 (1942).

[15] S. Nakata, *ibid.*, **63**, 41 (1942).

mined by measuring the pressure of the oxygen, which was collected in a fixed volume by a compressing pump. In this experiment, reproducible results could be obtained as long as the catalyst was pretreated in oxygen for each run and the desorption rate was not too large. The experimental results on anatase and rutile are shown in Fig. 5. The activation energies for anatase and rutile are 57.8 kcal/mol and 38.4 kcal/mol respectively. The difference in activation energy between anatase and rutile is about 20 kcal/mol.

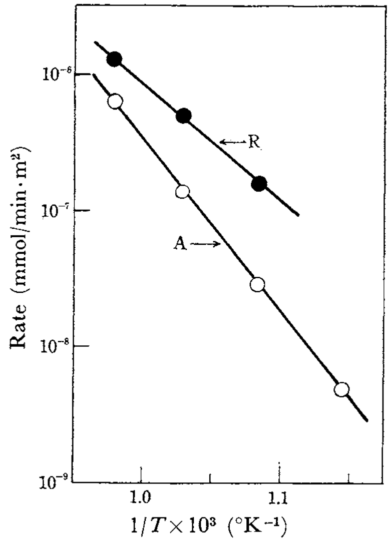

Fig. 5. Effect of temperature on the oxygen desorption rate.

As it is believed[4,16] that the surface oxygen of catalyst exists in the form of $O^{2-}$ at these high temperatures, the desorption of the surface oxygen can be expressed by $2\ O^{2-} \rightarrow O_2(g)+4e$; the difference of 20 kcal/mol mentioned above would result from this process. Therefore, the difference becomes about 10 kcal/mol for the process $O^{2-} \rightarrow 1/2\ O_2(g)+2e$. This value is comparable to the 10 kcal/mol difference between the activation energy of anatase and that of rutile which was found in the catalytic oxidation of carbon monoxide and also in the reaction of carbon monoxide with the surface oxygen of the catalyst.

The authors wish to express their deep thanks to Professor Kumasaburo Kodera of Kyoto University for his kind advice and discussions.

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16) E. R. S. Winter, *Advan. Catal.*, **10**, 196 (1958).