The Catalytic Oxidation of Hydrogen on Titanium Dioxide; Anatase and Rutile

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To clarify the reaction mechanism of catalytic oxidation of hydrogen on titanium dioxide, the rate of catalytic oxidation of hydrogen by oxygen and the reduction rate of titanium dioxide by hydrogen have been measured by a static method in temperature range of 400—650°C at 10^{-2} mmHg. The results were compared with those of carbon monoxide which were reported in the previous papers. The oxidation reactions of hydrogen on anatase and rutile were first order with respect to hydrogen and independent of the oxygen pressure. The oxidation rate was almost the same as the reduction rate of titanium dioxide by hydrogen. The activation energy was 29.2 kcal/mol for anatase and 17.8 kcal/mol for rutile, and the difference between these values for two crystal forms was nearly equal to that of the oxidation of carbon monoxide. Therefore, it may be considered that the mechanism of oxidation of hydrogen is analogous to that of carbon monoxide. The electric conductivity of the catalyst during the oxidation of hydrogen was larger than that in oxygen at the same temperature, and was still larger than that during the oxidation of carbon monoxide except for a few cases on anatase. There were close correlations between the electric conductivity and the amount of active oxygen of the catalyst and the reduction rate constant of titanium dioxide by both hydrogen and carbon monoxide.

As a series of investigations of the catalytic action of titanium dioxide, the catalytic oxidation of carbon monoxide[1,2] and the catalytic decomposition of nitrous oxide[3] have been carried out. It was confirmed from the results that the difference between anatase and rutile in the catalytic action is owing to the difference in the desorption rates of the active oxygen from the catalysts. Furthermore, in order to examine whether the reaction mechanism of carbon monoxide is applied to other reactions, the catalytic oxidation of hydrogen was examined because hydrogen is a reducing gas analogous to carbon monoxide.

There have been published several papers concerning the oxidation of hydrogen on the metallic oxide catalysts,[4-12] and some of them [4-7,10] compared the reaction mechanisms of the oxidation of hydrogen with those of carbon monoxide. But except for a few papers on the adsorption of hydrogen on titanium dioxide,[13] there is none which treated systematically the catalytic oxidation of hydrogen on titanium dioxide.

Experimental

The catalysts[1] used in the present investigation were anatase (A) and rutile (R) which was obtained from the sample A by heating it at 1150°C for 3 hr. The specific surface areas of anatase and rutile estimated by B.E.T. method using nitrogen as the adsorbate were 10.3 m^2/g and 1.0 m^2/g, respectively. Polymorphic forms of two samples were confirmed by X-ray diffraction. Hydrogen, oxygen, and carbon monoxide from the commercial cylinders were purified by passing through a liquid nitrogen cooled trap. The apparatus had a trap, a Pirani gauge, a McLeod gauge, and a sample tube of fused quartz. Pressure of gas was usually measured by the Pirani gauge but sometimes by the McLeod gauge. The trap in the apparatus was cooled by liquid nitrogen in order to protect the sample from grease and mercury vapors and also to catch the oxidation product of hydrogen, H_2O.

The catalyst heated to 600°C for 3 hr in oxygen under a pressure of about 70 mmHg was called to be in its starting state.[2] After this treatment, the catalytic oxidation of hydrogen was measured at a definite temperature and under pressure of about 10^{-2} mmHg by using a mixed gas with a composition of $H_2/O_2=2/1$. The reaction product H_2O is condensed in the liquid nitrogen trap, and the oxidation rate of hydrogen can be determined by measuring the rate of decrease of the pressure. The distance between the trap and the sample tube was so small and the pressure in the reaction system was so low that the reaction product was caught rapidly in the trap. Therefore, even without a circulating pump, there was no trouble for the measurement. For the purpose of estimating the order of reaction, the reaction rate was also determined by using a mixed gas with a composition of $H_2/O_2=3/1$. The electric conductivity of the catalyst was measured by using the apparatus for the experiment under gas pressures of 10 mmHg and above, which was described in the previous paper.[1]

Results and Discussion

Dependence of Catalytic Activity on Specific Surface Area and Crystal Form. The rates of the catalytic oxidation of hydrogen on two crystal forms were determined in temperature range of 400—650°C and under pressure of about 10^{-2} mmHg. The reaction was first order with respect to the total pressure of the reac-

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tant gas P, and its rate can be expressed as follows:

$$d(H_2O)dt = 2/3k \cdot P \qquad (1)$$

where k is a constant. The Arrhenius plots on two crystal forms are shown in Fig. 1 by △. As shown in this figure the experimental points of k are linear for both anatase and rutile, and activation energies were calculated to be 29.2 kcal/mol and 17.8 kcal/mol, respectively.

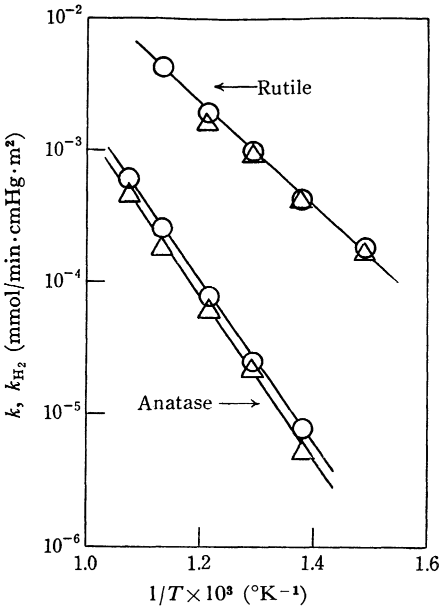

Fig. 1. Effect of temperature on the rate constant of oxidation of hydrogen.

△: k ○: k_{H_2}

Dependence of Reaction Rate and Partial Pressures of Hydrogen and Oxygen. To examine the effect of the partial pressures of hydrogen and oxygen on the reaction rate, the oxidation rate of hydrogen was measured in temperature range of 400—650°C and under pressure of about 10^{-2} mmHg keeping the initial partial pressure of oxygen constant and changing the partial pressure of hydrogen, or *vice versa*. The results are shown in Figs. 2 and 3. It is found from the figures that the oxidation rate of hydrogen is first order with respect to the hydrogen pressure P_{H_2} and independent of the oxygen pressure P_{O_2}, therefore, the following equation is obtained:

$$d(H_2O)/dt = k \cdot P_{H_2} \qquad (2)$$

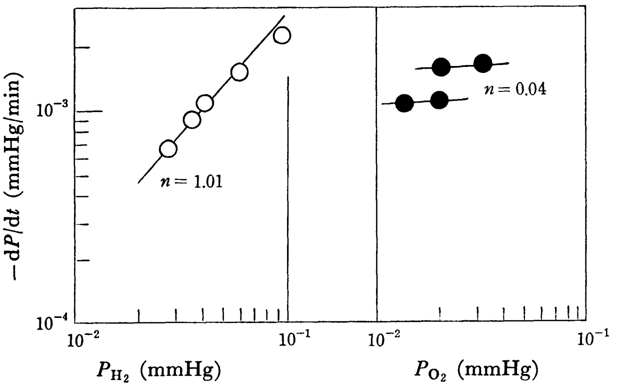

Fig. 2. Kinetics of the oxidation of hydrogen for anatase at 600°C. Open circles refer to constant O_2 partial pressure and changing H_2 pressures. Filled circles refer to constant H_2 partial pressure and changing O_2 pressures. n is the order of reaction.

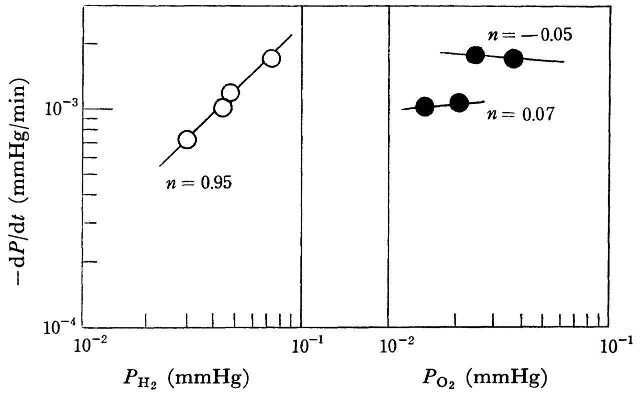

Fig. 3. Kinetics of the oxidation of hydrogen for rutile at 450°C. Open circles refer to constant O_2 partial pressure and changing H_2 pressures. Filled circles refer to constant H_2 partial pressure and changing O_2 pressures. n is the order of reaction.

Reaction of Active Oxygen of Catalyst with Hydrogen. When the catalyst in the starting state was exposed to hydrogen under pressure of about 10^{-2} mmHg at a definite temperature, hydrogen reacted slowly with the active oxygen of the catalyst and water vapor thus formed was condensed in the trap and the pressure of hydrogen decreased. It was found from the results that the formation rate of water depends upon P_{H_2} and is expressed as follows:

$$d(H_2O)/dt = k_{H_2} \cdot P_{H_2} \qquad (3)$$

where k_{H_2} is a rate constant of reduction of titanium dioxide by hydrogen. The Arrhenius plots on two crystal forms are shown in Fig. 1 by ○, and the value k_{H_2} is almost the same as the rate constant of the catalytic oxidation of hydrogen k above mentioned.

Electric Conductivity of the Catalyst. The temperature-dependence of electric conductivities for the catalysts of two crystal forms measured in various conditions are shown in Figs. 4 and 5. It is seen that the values in $H_2/O_2=2/1$ are larger than those in oxygen in the measured temperature range and are still larger than those in $CO/O_2=2/1$ except for the values at the temperatures lower than 450°C on anatase. From the results, it is considered that the catalyst during the oxidation of hydrogen would be in more reduced state than in the case of the oxidation of carbon monoxide except for the case at the lower temperatures mentioned above for anatase. As is listed in Table 1, the trend in conductivity coincides well with the trend in the rate constants k_{H_2} and k_{CO}.

As the slopes of the temperature-dependence of electric conductivity in oxygen and in vacuum are parallel to each other for two crystal forms, as shown in Figs. 4 and 5, it is probable that the surface state of titanium dioxide preheated at 600°C in oxygen is stable under the experimental temperatures. In the previous papers,[1,2] it is mentioned that the electric conductivity of the catalyst during the oxidation of carbon monoxide is larger than that in oxygen be-

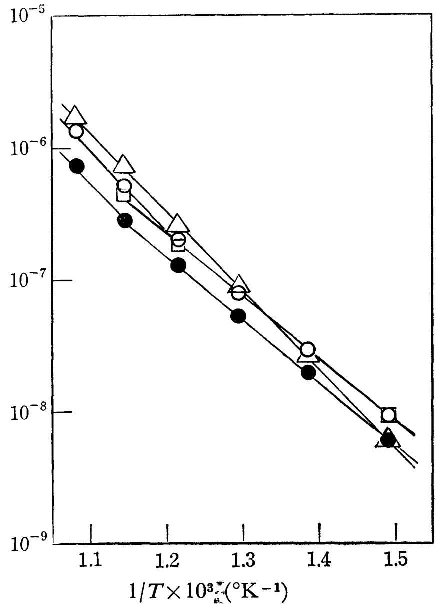

Fig. 4. Effect of temperature on electric conductivity of anatase.
△: in $H_2/O_2=2/1$ (10^{-2} mmHg)
○: in $CO/O_2=2/1$ (70 mmHg)
●: in O_2 (70 mmHg)
□: in vacuum (10^{-6} mmHg)

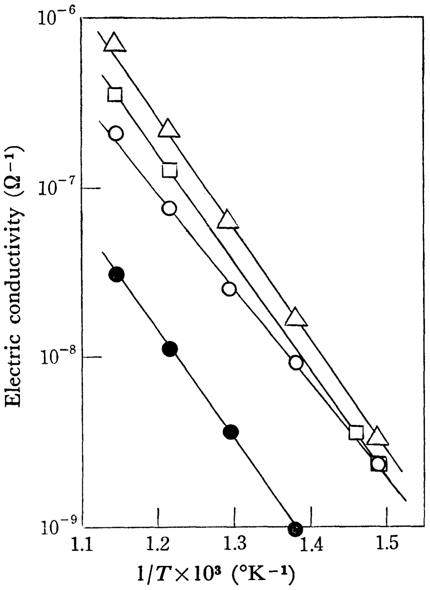

Fig. 5. Effect of temperature on electric conductivity of rutile.
△: in $H_2/O_2=2/1$ (10^{-2} mmHg)
○: in $CO/O_2=2/1$ (70 mmHg)
●: in O_2 (70 mmHg)
□: in vacuum (10^{-6} mmHg)

cause a part of active oxygen on the catalyst is removed by the reaction with the carbon monoxide in the mixed gas. Therefore, from the same reason, the electric conductivity of the catalyst during the oxidation of hydrogen is larger than that in oxygen and, in narrow conductivity range, the amount of increase of conductivity will depend upon the number of the active oxygen defect. By utilizing this relation, the deficiency of active oxygen during the oxidation of hydrogen can be estimated from the electric conductivities in oxygen and in $CO/O_2=2/1$.

Table 1. Rate constants of reduction of catalysts by hydrogen and carbon monoxide

Temp. (°C)	650	600	550	500	450	400
$k_{H_2} \times 10^4$ (H_2O mmol/min·cmHg·m^2)						
Anatase	5.8	2.5	0.88	0.27	0.074	—
Rutile	—	41.0	21.5	10.8	4.6	1.9
$k_{CO} \times 10^4$ (CO_2 mmol/min·cmHg·m^2)						
Anatase	—	0.75	0.396	0.176	0.0896	—
Rutile	—	3.01	2.24	1.83	1.36	—

On the other hand, it was mentioned in the previous paper[2)] that when titanium dioxide in the starting state is exposed to carbon monoxide under pressure of 10—150 mmHg at a definite temperature, after a certain period, all the surface oxygen which reacts easily with carbon monoxide is used up and the decrease of CO pressure stops. The reactive surface oxygen is called active oxygen on the oxidation of carbon monoxide. Similarly an amount of active oxygen for the oxidation of hydrogen can be determined. When the catalyst in the starting state was exposed to a circulating hydrogen under pressure of about 50 mmHg, hydrogen reacted with the surface oxygen of the catalyst to form water which was condensed in the trap, and H_2 pressure decreased. But the decrease stopped after a definite period as is the case of carbon monoxide. Thus the amount of active oxygen for the oxidation of hydrogen was estimated from the total decrease of the H_2 pressure. The amounts for two catalysts at various temperatures agreed within the experimental error with those of carbon monoxide. Therefore, the amount of active oxygen for the oxidation of hydrogen seems to be approximately equal to that for carbon monoxide at the same temperature. Therefore, the values of active oxygen listed in the previous paper[2)] are also applicable to the oxidation of hydrogen. In Table 2, the deficiency of active oxygen on the oxidati on o hydrogen $(1-\theta)$, the rate constant of oxidation of the reduced titanium dioxide by oxygen k_{O_2} listed in the previous paper,[2)] and the values of $k_{O_2}\cdot(1-\theta)^2$ are shown, where θ is the fraction of coverage of active oxygen. θ is equal to 1 at the starting state. The value $k_{O_2}\cdot(1-\theta)^2$ agrees almost with k_{H_2} which is listed in

Table 2. Calculated values of $(1-\theta)$, k_{O_2}, and $k_{O_2}\cdot(1-\theta)^2$

k_{O_2} and $k_{O_2}\cdot(1-\theta)^2$ ($-O_2$ mmol/min·cmHg·m^2)				
Temp. (°C)	600	550	500	450
Anatase				
$(1-\theta) \times 10^2$	3.27	2.80	2.14	1.54
$k_{O_2} \times 10$	2.35	1.20	0.55	0.25
$k_{O_2}\cdot(1-\theta)^2 \times 10^4$	2.5	0.93	0.25	0.059
Rutile				
$(1-\theta) \times 10^2$	4.90	5.83	5.43	5.70
$k_{O_2} \times 10$	18.0	7.50	3.40	1.33
$k_{O_2}\cdot(1-\theta)^2 \times 10^4$	43	26	10	4.2

Table 1, and from these values, the following equation may be satisfied approximately because the value θ is nearly equal to 1 during the oxidation of hydrogen:

$$P_{H_2} \cdot k_{H_2} \cdot \theta = 2P_{O_2} \cdot k_{O_2} \cdot (1-\theta)^2 \tag{4}$$

The above equation is entirely similar with that for the oxidation of carbon monoxide. Therefore, the catalytic oxidation of hydrogen seems to proceed with the same mechanism as that of the oxidation of carbon monoxide, as will be mentioned below.

Reaction Mechanism of Oxidation of Hydrogen. It has been described in the previous paper[1)] that the electric conductivities of the catalysts of two crystal forms in oxygen at a definite temperature are constant independently of oxygen pressure. This shows that the surface of the catalyst is saturated with oxygen under pressure above 10^{-2} mmHg. It seems from this fact that the oxidation rate of the reduced catalyst by oxygen is extremely fast. In fact, these values are 920—4400 times as large as the reduction rates of the catalyst by hydrogen in temperature range of 450—600°C. Therefore, from Eqs. (1), (2), and (3), and from the results shown in Fig. 1, the reaction of the oxidation of hydrogen may consist of two steps; 1) the active oxygen of the catalyst reacts with hydrogen which is physisorbed or has just collided with the surface from the gas phase, and water thus formed is desorbed leaving an oxygen defect on the surface, and 2) the oxygen defect is quickly refilled with oxygen from the gas phase. The reaction steps are expressed by the following equations:

$$\mathrm{H_2(g) + O(s)} \mathrel{\rlap{\;A}\longrightarrow} \mathrm{H_2O(g) + (s)} \tag{5}$$

$$\mathrm{(s) + 1/2\,O_2(g) \rightarrow O(s)} \tag{6}$$

where O(s) refers to the active oxygen of the catalyst and (s) the oxygen defect on the surface. The rate of step (6) is extremely faster than that of step (5), therefore, the rate of water formation depends upon only P_{H_2}.

For the oxide catalysts other than titanium dioxide, there are several papers[4–8)] which state that the rate of catalytic oxidation of hydrogen depends upon only P_{H_2}, and some papers[4–7,10)] compared the reaction mechanism with that of carbon monoxide and found the similar mechanism for both gases. For titanium dioxide, the mechanism of oxidation of hydrogen is entirely similar to that of carbon monoxide, and the electric conductivities of the catalysts during the oxidation of both gases are larger than those in oxygen at the same temperatures. Moreover, the effect of crystal form for the oxidation of hydrogen and carbon monoxide is similar, *i.e.*, the activation energy of the oxidation of hydrogen on anatase is larger about 10 kcal/mol than that on rutile, as is the case for carbon monoxide. The reason of this agreement is explained by the fact that the rate-determining steps of two oxidation reactions are considered to be the reaction between the active oxygen of the catalyst and hydrogen or carbon monoxide. Therefore, the difference of 10 kcal/mol comes from the difference in the readiness of reaction between the gases and the active oxygen of the two forms, *i.e.*, the readiness of desorption of the active oxygen from the catalysts, and has almost no correlation with the kinds of the reactant gases. The activation energy of the thermal desorption of the active oxygen atoms of anatase is about 10 kcal/mol larger than that of rutile[1)] and this difference can be compared with the difference in activation energies of the oxidation of hydrogen by two crystal forms.

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