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The Catalytic Oxidation of Carbon Monoxide on Zirconium Dioxide

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The catalytic oxidation of carbon monoxide on zirconium dioxide was kinetically examined in order to compare with the results of titanium dioxide. The experiment was carried out under gas pressures of 10^{-2}—100 mmHg at 400—550°C. The reaction rate was proportional to P_{CO} and did not depend upon P_{O_2}, and there was no retarding effect by carbon dioxide. The rate constant of this oxidation reaction almost agreed with that of the reduction of zirconium dioxide by carbon monoxide. The reaction mechanism could be explained in the same manner as that on titanium dioxide. The catalytic activity of zirconium dioxide for this reaction was almost the same as that of rutile. The activation energy was about 12.5 kcal/mol, and this value was intermediate between those of anatase and rutile. The same relation was obtained in the activation energies of the thermal desorption of surface oxygen from these catalysts.

The correlation between the crystal form and the catalytic activity of titanium dioxide has been examined in this laboratory using rutile and anatase.[1-4] It was found that both rutile and anatase showed the same reaction mechanism for the oxidations of carbon monoxide and hydrogen, but the activity of rutile was much larger than that of anatase for the two reactions. The activation energies of two reactions on anatase were larger by about 10 kcal/mol than those on rutile, and these differences almost coincided with that in activation energies of the thermal desorption of surface oxygen atoms from the catalysts between two crystal forms.

Zirconium, likewise titanium, belongs to the group IVA elements in the periodic table, and its electronic configuration (Kr core) $4d^25s^2$ is very similar to that of titanium (Ar core) $3d^24s^2$. Therefore, it is interesting to study the catalytic action of zirconium dioxide for comparison to that of titanium dioxide. The report about

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1) Y. Onishi and T. Hamamura, This Bulletin, **43**, 996 (1970).
2) Y. Onishi, *ibid.*, **44**, 1460 (1971).
3) Y. Onishi, *ibid.*, **44**, 912 (1971).
4) Y. Onishi and T. Hamamura, *Memoirs of the Faculty of Industrial Arts, Kyoto Technical University, Science and Technology*, **19**, 44 (1970).

the carbon monoxide oxidation on zirconium dioxide can scarcely be found in the literature.[5]

Experimental

Two kinds of samples were used in the present investigation. One was obtained from the Nippon Gaishi Company (ZrO_2-1), and the other from the Zirconium Corporation of America (ZrO_2-2). Both samples are pure zirconium dioxide from which hafnia was separated. These samples were heated at 1200°C for 3 hr in a fused quartz tube to vaporize the volatile contaminants as well as to develop their crystal lattices. The BET surface areas of ZrO_2-1 and -2 were 3.8 and 1.0 m^2/g, respectively. Both of them were found to have the monoclinic crystal forms by the X-ray powder method.

Carbon monoxide and oxygen from commercial cylinders were purified by fractional distillation using liquid nitrogen. The apparatus used was essentially the same as before.[1] Since the formed carbon dioxide was caught in the trap, the rate of reaction was determined by measuring the total pressure. The experiments were carried out under the pressure range of 1—10 cmHg, and the pressure change was measured by using a mercury manometer. The McLeod gauge was used for the reaction at the gas pressure of about 10^{-2} mmHg. At such a low pressure the gas diffusion was thought to be so fast that the circulating pump was cut from the reaction system.

The sample of about 5 g was introduced into the apparatus and evacuated to 10^{-6} mmHg. Prior to the measurements, the sample was heated at 800°C in circulating oxygen of 5 cmHg for 3 hr to clean its surface.

Results and Discussion

Catalytic Activity. The oxidation rate of carbon monoxide on zirconium dioxide was measured by using a mixed gas with a composition of $CO/O_2=2/1$ in temperature range of 400—550°C and under pressures of 10^{-2}—100 mmHg. The oxidation rate is plotted against the total pressure in Fig. 1. The reaction is clearly of the first order with respect to the total pressure. In order to examine the effect of carbon dioxide, measurements were carried out by using a dry ice trap to mix the formed carbon dioxide into the reactant gas. However, no retarding effect by carbon dioxide was found. Therefore, the reaction rate can be expressed by the following equation:

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

where k is a constant. The Arrhenius plots of k on ZrO_2-1 and -2 are given in Fig. 2 together with those on rutile and anatase. The ZrO_2-1 and -2 show almost the same values in their catalytic activities per unit of the surface area and in their activation energies, although they are different both in their specific surface areas and their conditions of formations.

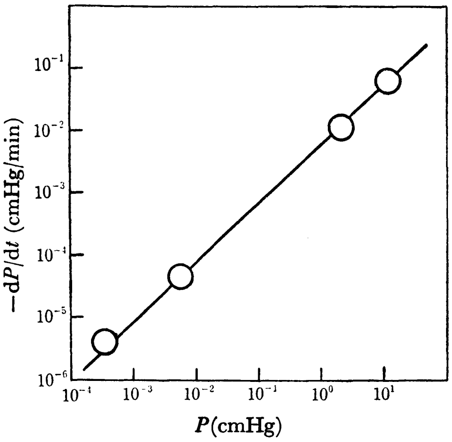


Fig. 1. Effect of total pressure on the reaction rate at 550°C on ZrO_2-1.

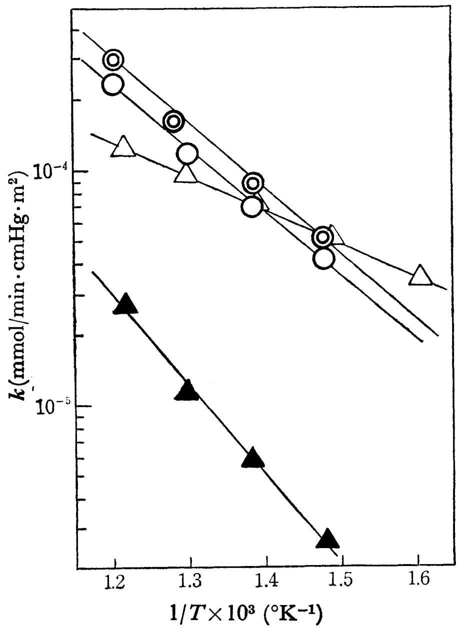
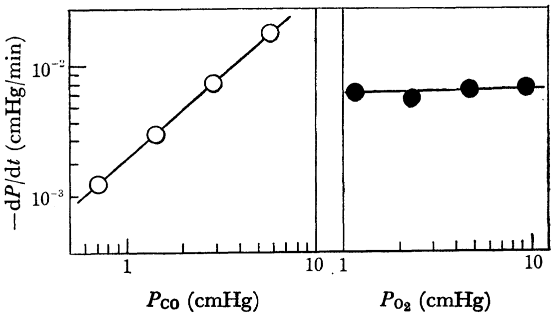


Fig. 2. Effect of temperature on the reaction rate constant. ○: ZrO_2-1 ◎: ZrO_2-2 ▲: Anatase △: Rutile

Comparing with titanium dioxide,[1] the catalytic activity of zirconium dioxide is approximately on the same level with that of rutile. As for the activation energy, zirconium dioxide shows the intermediate value of 12.5 kcal/mol between rutile, 6.7 kcal/mol, and anatase, 16.0 kcal/mol.

Effect of Partial Pressures of Carbon Monoxide and Oxygen on the Reaction Rate. To examine the effect of partial pressures of carbon monoxide and oxygen on the reaction rate, the reaction rate was measured keeping the initial partial pressure of oxygen constant and



Fib. 3. Kinetics of the oxidation of carbon monoxide for ZrO_2-2 at 550°C. Open circles refer to constant O_2 pressure ($P_{O_2}=2.84$ cmHg) and varying CO pressures. Filled circles refer to constant CO pressure ($P_{CO}=2.35$ cmHg) and varying O_2 pressures.

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5) C. J. Engelder and L. E. Miller, *J. Phys. Chem.*, **36**, 1345 (1932).

changing the partial pressure of carbon monoxide, or *vice versa*. The results are shown in Fig. 3. The reaction rate is nearly of the first order with respect to the carbon monoxide pressure P_{CO} and independent of the oxygen pressure P_{O_2}. Consequently, the reaction rate can be expressed by the following equation:

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

where $\boldsymbol{k}$ is a constant which is the same as that in Eq. (1).

Reaction of Carbon Monoxide with Surface Oxygen of Zirconium Dioxide. The catalyst pretreated in oxygen at 800°C for 3 hr was cooled to the reaction temperature and evacuated. When carbon monoxide, at a pressure of about 10^{-2} mmHg, was introduced into the reaction system, it reacted with the surface oxygen of the catalyst and the formed carbon dioxide was caught in the trap. It was confirmed that the amount of consumed carbon monoxide agreed well with that of the carbon dioxide caught in the trap. This fact shows that the amount of carbon monoxide which may be adsorbed on the surface of the catalyst is negligible compared with that of carbon monoxide oxidized to carbon dioxide and that the carbon dioxide formed on the surface of the catalyst immediately desorbs from there. The rate of formation of carbon dioxide was found to be proportional to P_{CO}:

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

where $\boldsymbol{k}_{CO}$ is the reduction rate constant of zirconium dioxide by carbon monoxide. The Arrhenius plots of $\boldsymbol{k}_{CO}$ on ZrO_2-1 are shown in Fig. 4 together with that of the oxidation rate constant $\boldsymbol{k}$. It is obvious that $\boldsymbol{k}_{CO}$ almost agrees with $\boldsymbol{k}$.

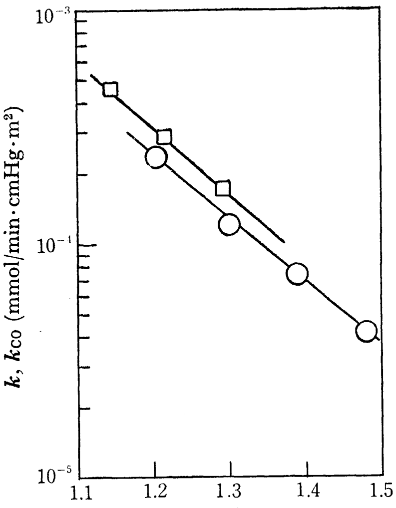

Fig. 4. Effect of temperature on the rate constant of oxidation of carbon monoxide $\boldsymbol{k}$ and that of reduction of ZrO_2 by carbon monoxide $\boldsymbol{k}_{CO}$.
○: $\boldsymbol{k}$ □: $\boldsymbol{k}_{CO}$

The catalyst was reduced by carbon monoxide of about 3 cmHg for 30 min, then oxygen of about 10^{-2} mmHg was introduced to measure the uptake rate of oxygen by the catalyst. It was found that the uptake rate of the reduced zirconium dioxide was far faster than the reduction rate of the catalyst by carbon monoxide.

Mechanism of the Oxidation of Carbon Monoxide on Zirconium Dioxide. Since 1) the reaction rate is proportional to P_{CO} and does not depend upon P_{O_2}, 2) the rate constant of the oxidation of carbon monoxide on zirconium dioxide almost agrees with that of the reduction of zirconium dioxide by carbon monoxide, and 3) the oxygen uptake rate of the reduced zirconium dioxide is much faster than the reduction rate of zirconium dioxide by carbon monoxide, the mechanism of this reaction can be explained in the same manner as that on titanium dioxide,[1,2] cupric oxide,[6] and nickel oxide.[7]

The reaction consists of two processes; 1) carbon monoxide which collides with the surface of the catalyst reacts with the surface oxygen of the catalyst and the carbon dioxide thus formed immediately desorbs, leaving an oxygen defect on the surface and 2) the oxygen defect thus formed is refilled with oxygen from the gas phase. Therefore, the reaction steps can be expressed as follows:

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

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

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

Desorption of the Surface Oxygen. The catalyst pretreated in oxygen at 800°C was cooled down to 600°C and evacuated 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 could be determined by measuring the pressure of oxygen, which was collected in a fixed volume by a compressing pump. The experimental results on zirconium dioxide are shown in Fig. 5 together with those on anatase

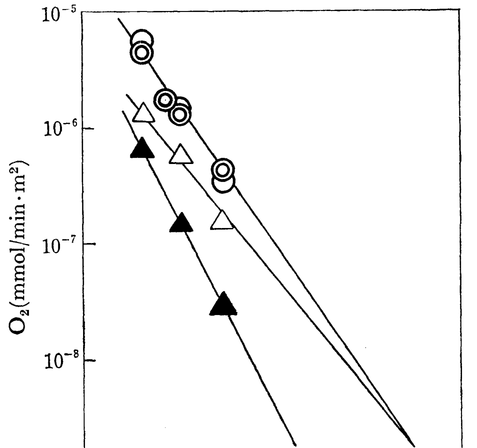

Fig. 5. Effect of temperature on the thermal desorption rate of surface oxygen.
○: ZrO_2-1 ◎: ZrO_2-2 ▲: Anatase △: Rutile

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6) A. Kanome and T. Chitani, *Nippon Kagaku Zasshi*, **63**, 36 (1942); S. Nakata, *ibid.*, **63**, 41 (1942).

7) G. Parravano and M. Boudart, *Advan. Catal.*, **7**, 47 (1955); E. R. S. Winter, *J. Chem. Soc.*, **1955**, 2726; I. Matsuura, Y. Kubokawa, and O. Toyama, *Nippon Kagaku Zasshi*, **81**, 1003 (1960).

and rutile. The activation energy of the desorption of the surface oxygen of zirconium dioxide was about 44.0 kcal/mol. This value lies between those of anatase, 57.8 kcal/mol and rutile, 38.4 kcal/mol, which seems to correspond to the relation about the activation energies of the oxidation of carbon monoxide on these oxides. Furthermore, extrapolating the data to the temperature range of the oxidation reaction, it is found that zirconium dioxide shows almost the same level of the desorption rate of oxygen as rutile. This fact again seems to correspond to the resemblance between rutile and zirconium dioxide with respect to their catalytic activities. All these results indicate that there is a close relation between titanium dioxide and zirconium dioxide in their catalytic actions.

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