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The Catalytic Oxidation of Hydrogen on Zirconium Dioxide

Takuya HAMAMURA, Yoshito ONISHI, and Yasuo IIZUKA*

Department of Chemistry, Faculty of Industrial Arts, Kyoto Technical University, Matsugasaki, Sakyo-ku, Kyoto 606

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The previous paper was concerned with the catalytic oxidation of carbon monoxide on zirconium dioxide.[1] The experimental results were there compared with those for anatase and rutile[2~5] in order to examine the correlation between zirconium dioxide and titanium dioxide with respect to their catalytic actions. It was found that the reaction mechanism could be explained in entirely the same manner as that on titanium dioxide.

The oxidation mechanism of hydrogen on titanium dioxide was extremely analogous to that of carbon monoxide,[4] and titanium and zirconium belong to the same group in the periodic table. Therefore, the oxidation mechanism of hydrogen on zirconium dioxide can also be expected to be similar to that of carbon monoxide.

Experimental

Two kinds of samples of ZrO_2–1 (3.8 m^2/g) and ZrO_2–2 (1.0 m^2/g) used in the previous experiment were again employed.[1] The apparatus, procedure, and method of pretreatment of the catalysts used were essentially the same as before.[2] The reaction rate was measured by using a mixed gas with a composition of $H_2/O_2=2/1$ in the temperature range of 450—600 °C and under pressures of 10^{-1}—10^{-3} mmHg.

Results and Discussion

The oxidation rate of hydrogen on zirconium dioxide was nearly of the first order with respect to P_{H_2} and was independent of P_{O_2}. Consequently, the reaction rate can be expressed by the following equation:

$$d(H_2O)/dt = k\cdot P_{H_2} \tag{1}$$

where k is a constant. The Arrhenius plots of k on ZrO_2–1 and -2 are given in Fig. 1, together with those on anatase and rutile.[4] The ZrO_2-1 and -2 show almost the same values in their catalytic activities. The activation energy of zirconium dioxide is the value of 22.6 kcal/mol, intermediate between anatase, 29.2 kcal/mol, and rutile, 17.8 kcal/mol.

When instead of a mixture of H_2 and O_2, hydrogen, 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 water vapor thus formed was caught in the trap. The rate of the formation of water was found to be proportional to P_{H_2}:

$$d(H_2O)/dt = k_{H_2}\cdot P_{H_2} \tag{2}$$

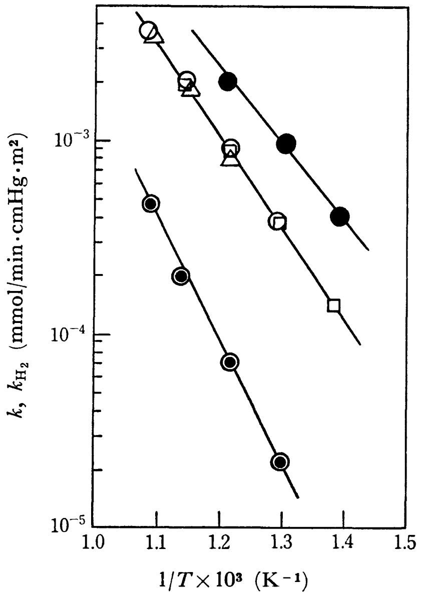

Fig. 1. Effect of temperature on the reaction rate constant.
□: ZrO_2-1 ○: ZrO_2-2 ◉: Anatase ●: Rutile

where k_{H_2} is the reduction rate constant of zirconium dioxide by hydrogen. The Arrhenius plots of k_{H_2} on ZrO_2-1 are shown in Fig. 1 by the mark △. It is obvious that k_{H_2} agrees with k. It was reported in the preceding paper that the oxygen-uptake rate of the reduced zirconium dioxide was much faster than the reduction rate of zirconium dioxide.[1]

From all these results, the mechanism of the oxidation of hydrogen on zirconium dioxide can be expressed as follows. The reaction consists of the following two steps;

$$H_2(g) + O(s) \mathrel{\rlap{\;\;\wedge}\longrightarrow} H_2O(g) + (s) \tag{3}$$

$$(s) + 1/2\,O_2(g) \longrightarrow O(s) \tag{4}$$

where O(s) refers to the surface oxygen of the catalyst and (s) the oxygen defect on the surface. Step (4) is much faster than Step (3), so the overall reaction rate is proportional to P_{H_2}. This reaction mechanism is extremely analogous to that of the oxidation of carbon monoxide.

The activation energies of the oxidations of carbon monoxide and hydrogen on anatase, rutile, and zir-

TABLE 1. ACTIVATION ENERGIES FOR THE OXIDATIONS OF CO AND H_2 AND THOSE FOR THE THERMAL DESORPTION OF SURFACE OXYGEN FROM THE CATALYSTS (kcal/mol)

Catalysts	Oxidation of CO	Oxidation of H_2	Thermal desorption of surface oxygen
Anatase	16.0	29.2	57.8
Rutile	6.7	17.8	38.4
ZrO_2	12.5	22.6	44.0

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* Present address: Asahi Glass Co., Ltd., Ichihara, Chiba.

[1] T. Hamamura, Y. Onishi, and Y. Iizuka, This Bulletin, **45**, 1288 (1972).

[2] Y. Onishi and T. Hamamura, *ibid.*, **43**, 996 (1970).

[3] Y. Onishi, *ibid.*, **44**, 1460 (1971).

[4] Y. Onishi, *ibid.*, **44**, 912 (1971).

conium dioxide are summarized in Table 1, together with the activation energies of the thermal desorption of the surface oxygen from these three catalysts.[1,2,4,5] The values of activation energies in each column of Table 1 decrease in this order: anatase, zirconium dioxide, and rutile. These facts suggest that the activation energies of the two oxidation reactions are connected with the bond strength between the surface oxygen and the catalyst surface.

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5) Y. Onishi and T. Hamamura, *Memoirs of the Faculty of Industrial Arts, Kyoto Technical University, Science and Technology*, **19**, 44 (1970).