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The Catalytic Reactions on Hafnium Dioxide

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Synopsis. The mechanisms of the catalytic oxidations of carbon monoxide and hydrogen on hafnium dioxide are similar to those on titanium dioxide (anatase and rutile) and zirconium dioxide, and the activation energies of these reactions have been correlated with the oxygen bond energies of these four oxides.

In previous papers, the catalytic reactions on zirconium dioxide were reported in comparison with those on titanium dioxide. There exist however little data on the catalytic reactions on hafnium dioxide.[1,2] This paper will report the catalytic reactions on hafnium dioxide in connection with those on titanium dioxide and zirconium dioxide.

Experimental

The procedure and apparatus employed were almost the same as those used previously.[3] Hafnium dioxide obtained from Ventron Alfa Products Corporation was employed as the catalyst. The sample was of spectroscopic grade and free from zirconia. From X-ray powder analysis, the specimen was shown to exist in the monoclinic form. The BET surface area was 0.66 m^2/g (N_2 at −196 °C). Hafnium dioxide (9.5 g) was used as the catalyst.

Prior to measurement, the sample in the reaction tube was evacuated to 10^{-6} mmHg** and subsequently heated at 870 °C in oxygen (75 mmHg) for 3 h to clean the surface. A mixture of carbon monoxide and oxygen or a mixture of hydrogen and oxygen when introduced to the heated hafnium dioxide produced cataytic oxidation giving carbon dioxide or water, which then condensed into the liquid nitrogen cooled traps. The reaction rate was determined by measuring the decrease in the total pressure.

Results and Discussion

Kinetic studies of the carbon monoxide oxidation on hafnium dioxide were conducted using a mixed gas of carbon monoxide and oxygen in the temperature range 400—550 °C and in the pressure range 10^{-3}—100 mmHg. The oxidation rate was proportional to the carbon monoxide pressure and independent of the oxygen pressure. Therefore, the reaction rate may be expressed by the following equation:

$$\mathrm{d(CO_2)}/\mathrm{d}t = k_{\mathrm{CO_2}} \cdot P_{\mathrm{CO}}, \tag{1}$$

where $k_{\mathrm{CO_2}}$ is the oxidation rate constant of carbon monoxide on hafnium dioxide.

The oxidation rate of hydrogen on hafnium dioxide was measured using a mixed gas of hydrogen and oxygen in the temperature range 450—600 °C and in the pressure range 10^{-3}—10^{-1} mmHg. The reaction rate may be expressed as follows:

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

where $k_{\mathrm{H_2O}}$ is the oxidation rate constant of hydrogen on hafnium dioxide.

The catalyst pretreated in oxygen (75 mmHg) at 870 °C for 3 h was cooled to the reaction temperature and evacuated. Carbon monoxide or hydrogen, at a pressure of approximately 10^{-2} mmHg, was introduced into the reaction system, whereby it reacted with the active oxygen of the catalyst and the formed carbon dioxide or water was caught in the traps. The rate of the formation of carbon dioxide and water was found to be proportional to P_{CO} or $P_{\mathrm{H_2}}$, respectively:

$$\mathrm{d(CO_2)}/\mathrm{d}t = k_{\mathrm{CO}} \cdot P_{\mathrm{CO}}, \tag{3}$$

$$\mathrm{d(H_2O)}/\mathrm{d}t = k_{\mathrm{H_2}} \cdot P_{\mathrm{H_2}}, \tag{4}$$

where k_{CO} and $k_{\mathrm{H_2}}$ are the rate constants of the reductions of hafnium dioxide by carbon monoxide and hydrogen, respectively. The Arrhenius plots of k_{CO} and $k_{\mathrm{H_2}}$ are shown in Fig. 1 together with those of the oxidation rate constants $k_{\mathrm{CO_2}}$ and $k_{\mathrm{H_2O}}$. It may be seen that k_{CO} reasonably agrees with $k_{\mathrm{CO_2}}$, and $k_{\mathrm{H_2}}$ with $k_{\mathrm{H_2O}}$ at each corresponding temperature.

The catalyst was reduced by carbon monoxide at approximately 40 mmHg for 1 h. Oxygen at approximately 10^{-2} mmHg was then introduced to measure the oxidation rate of the reduced hafnium dioxide by oxygen. The oxidation rates were 1100—5300 times as large as the reduction rates of hafnium dioxide by carbon monoxide and hydrogen in the temperature range 450—600 °C.

Thus the mechanism of the oxidation of carbon monoxide on hafnium dioxide may be expressed by the following equations:

$$\mathrm{CO(g)} + \mathrm{O(s)} \mathrel{-\!\!\!\wedge\!\!\!\rightarrow} \mathrm{CO_2(g)} + \mathrm{(s)}, \tag{5}$$

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

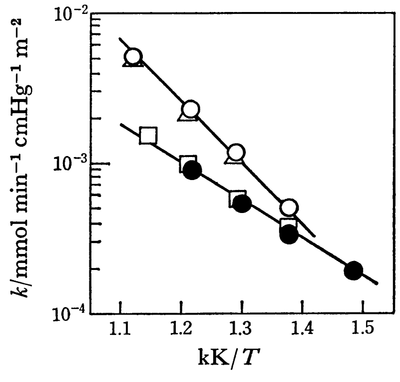

Fig. 1. Effect of temperature on the rate constant. ●: $k_{\mathrm{CO_2}}$, ○: $k_{\mathrm{H_2O}}$, □: k_{CO}, △: $k_{\mathrm{H_2}}$.

**1 mmHg=133.322 Pa.

where O(s) refers to the active oxygen of the catalyst and (s) the oxygen defect on the surface. Step (6) is much faster than step (5), so that step (5) becomes the rate-determining step of the overall reaction. This mechanism is closely analogous to those for titanium dioxide[3)] and zirconium dioxide.[4)]

The oxidation of hydrogen on hafnium dioxide may be expressed as follows:

$$\mathrm{H_2(g) + O(s)} \mathrel{\rlap{\;\;\Lambda}\longrightarrow} \mathrm{H_2O(g) + (s)}, \qquad (7)$$

$$\mathrm{(s) + 1/2\,O_2(g)} \longrightarrow \mathrm{O(s)}, \qquad (8)$$

and similar mechanisms have been published on titanium dioxide[5)] and zirconium dioxide.[6)]

The thermodesorption rate of oxygen from hafnium dioxide was measured by a procedure described in previous papers.[3,4)]

The activation energies of the two oxidation reactions and that of the thermodesorption of oxygen from hafnium dioxide are summarized in Table 1 together with those on anatase, rutile, and zirconium dioxide. It may be seen from Table 1 that hafnium dioxide agrees well with zirconium dioxide in the activation energies not only on the oxidations of carbon monoxide and hydrogen but also on the thermodesorption of oxygen. This is possibly a direct result of the remarkable resemblances between hafnium dioxide and zirconium dioxide in crystal structures.[7)]

There have been several studies to elucidate the correlations between the strength of the metal oxygen bond of the oxidation catalysts and their activities in the several types of oxidation reaction. According to Seiyama,[8)] the reactivity of oxygen on the metal oxide catalyst may be estimated by determining the equilibrium oxygen pressures of the oxide at several temperatures. Sachtler *et al.*[9,10)] studied the catalytic oxidation reactions on several metal oxides, and concluded that the activity of the oxide is related to its ability to release oxygen. Boreskov *et al.*[11-15)] investigated the catalytic properties of Period IV transition metal oxides, and stated that the rates of the catalytic oxidations of carbon monoxide depend upon the surface oxygen bond energies of these oxides estimated by the thermodesorption method and that a linear correlation is established between the oxygen bond energies and the activation energies of the catalytic oxidations of hydrogen and methane.

TABLE 1. ACTIVATION ENERGIES (E/kcal$_{\mathrm{th}}$ mol^{-1})[a)] FOR THE OXIDATIONS OF CO AND H_2 AND THOSE FOR THE THERMODESORPTION OF OXYGEN

Catalyst	Oxidation of CO	Oxidation of H_2	Thermodesorption of oxygen
Hafnia	11.7	19.8	42.8
Zirconia	12.5	22.6	44.0
Anatase	16.0	29.2	57.8
Rutile	6.7	17.8	38.4

a) 1 cal$_{\mathrm{th}}$ = 4.184 J.

From Table 1, it may be seen that the four oxides can be arranged in the same order anatase zirconia hafnia rutile with respect to their activation energies in the catalytic oxidations of carbon monoxide and hydrogen and the thermodesorption rate of oxygen. Consequently, the activation energies of the oxidations of carbon monoxide and hydrogen on anatase, rutile, zirconium dioxide, and hafnium dioxide may be correlated with the oxygen bond energies of these four oxides.

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