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Abstract

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ON THE ROLE OF HYDROGEN ATOMS IN THE REACTION OF CATALYTIC OXIDATION OF HYDROGEN ON PALLADIUM

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Although the reaction of the catalytic oxidation of hydrogen on metals of the platinum group has been studied by a large number of authors, the mechanism of this reaction is still not clear at the present time. It is not even clear whether the reaction proceeds by a chain ($^{1-3}$), radical ($^{4-6}$), or molecular (^{2,7}) mechanism. Ionic mechanisms are also possible (^{8}). In the work of Wagner and Hauffe (^{2}), a study was undertaken of the mechanism of the catalytic oxidation of hydrogen on metallic palladium by comparing the stationary concentration of hydrogen atoms on the catalyst surface during the reaction with the equilibrium concentration. In this case the authors came to the conclusion that a chain mechanism of this reaction is possible. Recently, in a number of works, the question of chain mechanisms in heterogeneous catalysis has again been subjected to detailed theoretical consideration. In this connection it seemed of interest to us to test the conclusions of Wagner and Hauffe independently, using another experimental method.

According to present-day views, during the adsorption and dissolution of hydrogen in metallic palladium, dissociation of hydrogen molecules occurs at the metal surface with the formation of adsorbed atoms. The dissolution and diffusion of hydrogen in the bulk of the metal apparently occur in the form of ions (^{9}). In the case of equilibrium, the concentration of hydrogen atoms adsorbed on the metal surface can be determined from the equality of the rates of the processes of dissociation and recombination per unit surface area:

$$W_{\mathrm{dis}} = K_{\mathrm{r}}[H_{\mathrm{eq}}]^2. \tag{1}$$

Here K_{r} is the recombination constant, and H_{eq} is the equilibrium concentration of adsorbed hydrogen atoms. In the molecular mechanism of the reaction of catalytic oxidation of hydrogen on the surface of palladium, hydrogen atoms are not consumed in the reaction. In this case, despite the fact that, owing to oxygen adsorption, the total number of hydrogen atoms on the catalyst surface decreases, the concentration of hydrogen atoms on the free sites will correspond to the equilibrium one. In the radical mechanism of the reaction, two hydrogen

Fig. 1. Schematic of the apparatus

Figure 1: Fig. 1. Schematic of the apparatus

atoms are expended in the formation of each water molecule, and for the part of the surface not occupied by oxygen, equality (1) will be written in the form:

$$W_{\mathrm{dis}} = K_{\mathrm{r}}[H_{\mathrm{stat}}]^2 + W_{\mathrm{ox}}, \tag{2}$$

where H_{stat} is the stationary concentration of hydrogen atoms on the catalyst surface. When the reaction proceeds by an unbranched chain mechanism with chain length ν, the entry of one primary hydrogen atom into the reaction leads to the formation of ν water molecules. In accord—

In connection with this, when the chain is terminated on oxygen, the balance equation for hydrogen atoms is written as follows:

$$W_{\mathrm{dis}} = K_{\mathrm{p}}[H_{\mathrm{stat}}]^2 + \frac{W_{\mathrm{ox}}}{\nu}. \tag{3}$$

If chain termination occurs by recombination of hydrogen atoms, equality (3) becomes equality (1). From equations (1), (2), and (3), one can derive relationships between the steady-state and equilibrium concentrations of hydrogen atoms on the free part of the catalyst surface for a radical reaction mechanism:

Fig. 1. Schematic of the apparatus

$$\frac{H_{\mathrm{stat}}}{H_{\mathrm{eq}}} = \sqrt{\frac{W_{\mathrm{dis}} - W_{\mathrm{ox}}}{W_{\mathrm{dis}}}}, \tag{4}$$

for an unbranched chain reaction mechanism with first-order chain termination:

$$\frac{H_{\mathrm{stat}}}{H_{\mathrm{eq}}} = \sqrt{\frac{W_{\mathrm{dis}} - \frac{W_{\mathrm{ox}}}{\nu}}{W_{\mathrm{dis}}}}, \tag{5}$$

for an unbranched chain reaction mechanism with quadratic chain termination:

$$\frac{H_{\mathrm{stat}}}{H_{\mathrm{eq}}} = 1. \tag{6}$$

It can be shown that, when the reaction proceeds by a branched chain mechanism, the concentration of hydrogen atoms must be greater than the equilibrium concentration. It follows from what has been said that certain conclusions about the reaction mechanism can be drawn on the basis of comparing the steady-state concentration of hydrogen atoms on the catalyst surface with the equilibrium concentration.

Such a comparison for hydrogen atoms adsorbed on palladium was carried out in our experiments by means of the diffusion process. The experiments were conducted in a vacuum circulation apparatus that made it possible to carry out the reaction under steady-state conditions (^{10}) (Fig. 1). The catalyst was a palladium capillary 1, on the outer surface of which the reaction was conducted. The surface area of the catalyst was about 15 cm^2. The internal volume of the capillary was connected to manometer 2, whose readings were taken with a cathetometer.

The mixture of hydrogen with oxygen was stirred by a glass circulation pump 4; the water formed as a result of the reaction was frozen out in traps 5 and 6, cooled with solid carbon dioxide. The volume of the gas-circulation loop was about 400 cm^3. The loss of reactants as a result of the reaction was compensated by means of electrolyzer 3. The electrolysis current was selected in such a way that the total pressure during the reaction, measured by manometer 7, remained constant. The stationary reaction rate was determined directly from the magnitude of the electrolysis current.

Table 1

Temperature, °C	Reaction rate, mm Hg/min	Partial pressure O_2, mm Hg	Partial pressure H_2, mm Hg	Stationary pressure H_2, mm Hg, inside the capillary
220	9	50	100	94
190	4.2	49	101	89
180	2.5	51	98	78

The experiments were carried out as follows. With taps 9 and 10 open, connecting the internal volume of the capillary with the gas-circulation loop, hydrogen was admitted into the evacuated measuring part of the apparatus. The catalyst was kept in hydrogen until the process of its dissolution in palladium ceased. Then tap 10 was closed, hydrogen was pumped out of the communications, and oxygen was introduced into the circulation loop of the apparatus. After this, with tap 9 closed, stirring of the gases was begun and the electrolyzer was switched on. It then turned out that, despite equality of the partial pressures inside and outside the capillary, diffusion of hydrogen through the palladium wall was observed in the direction of the reacting mixture. The diffusion process continued until a stationary state was established. In this case the hydrogen pressure inside the capillary corresponded to the stationary concentration of hydrogen atoms on the catalyst surface during the reaction. The decrease in the equilibrating hydrogen pressure upon attainment of the stationary state, compared with its partial pressure in the reaction zone, served as a measure of the deviation of the stationary concentration of hydrogen atoms from the equilibrium one. The results of some of our experiments are given in Table 1. From the data of Table 1 it is seen that the stationary concentration of hydrogen atoms in the reaction zone is substantially smaller than the equilibrium concentration, which indicates that hydrogen atoms are consumed in the oxidation reaction. For a more detailed investigation of the reaction mechanism, we calculated the deviation of the stationary concentration of hydrogen atoms on the catalyst surface from the equilibrium one for the radical mechanism of the reaction (formula (4)), and the calculated quantities were compared with experiment. The rate of dissociation of hydrogen on the palladium surface was determined by us from the rate of the hydrogen-deuterium exchange reaction, which proceeds by dissociation of hydrogen molecules on the catalyst surface followed by recombination of hydrogen atoms ([11]). Special experiments showed that oxygen only slightly (by 10–20%) lowers the rate of the exchange reaction and, consequently, does not change the mechanism of this reaction. Table 2 gives the results of calculations carried out with this circumstance taken into account. The good agreement between the experimentally measured and calculated values indicates a radical mechanism of the hydrogen-oxidation reaction on metallic palladium under the conditions studied by us. It should be noted that, as the calculation shows, chains even of very small length (5–6 links) would lead, under our conditions, to the practical coincidence of the stationary and equilibrium concentrations of hydrogen atoms.

Table 2

Temperature, °C	Reaction rate, mm Hg/min	$W_{\mathrm{H/D}} = 2W_H$	$\frac{P_{\mathrm{stat}}}{P_{\mathrm{part}}} = \frac{[H_{\mathrm{stat}}]^2}{[H_{\mathrm{eq}}]^2}$ (experiment)	$\frac{W_{\mathrm{dis}} - W_{\mathrm{ox}}}{W_{\mathrm{dis}}}$ (theory)
220	9	115	0.94	0.91
190	4.2	32	0.88	0.87
180	2.5	18	0.80	0.86

Thus, in contrast to Wagner and Hauffe, as well as other authors who assumed the participation of hydrogen molecules in the reactions of its catalytic oxidation on metals of the platinum group, our data unambiguously indicate that, in the case of palladium, the reaction proceeds through the interaction of hydrogen atoms adsorbed on the surface of the catalyst with oxygen.

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CITED LITERATURE

1. R. P. Donnely, C. N. Hinshelwood, J. Chem. Soc., **1929**, 1727.
2. C. Wagner, K. Hauffe, Zs. Elektrochem., **45**, 409 (1939).
3. G. K. Boreskov, J. Chim. Phys., **51**, 759 (1954).
4. I. Langmuir, Trans. Farad. Soc., **17**, 621 (1922).
5. T. Tucholski, Zs. Phys. Chem., B **40**, 333 (1938).
6. S. Yu. Elovich, V. S. Rozeng, *Problems of Kinetics and Catalysis*, vol. 3, L., 1937, p. 499.
7. R. P. Donnely, J. Chem. Soc., **1929**, 2438.
8. O. V. Krylov, S. Z. Roginskii, Izv. AN SSSR, OKhN, **1956**, 145.
9. R. Barrer, *Diffusion in Solids*, IL, 1948, p. 172.
10. G. K. Boreskov, M. G. Slinko, A. G. Filippova, DAN, **92**, No. 2, 353 (1953).
11. V. B. Kazanskii, R. E. Mardaleishvili, V. P. Strunin, V. V. Voevodskii, ZhFKh, **30**, issue 4, 821 (1956).

Note: Figure translations are in progress. See original paper for figures.