Reports of the Academy of Sciences of the USSR

Yu. A. BALOVNEV, Corresponding Member of the Academy of Sciences of the USSR S. Z. ROGINSKY,

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 158, No. 4

PHYSICAL CHEMISTRY

Yu. A. BALOVNEV, Corresponding Member of the Academy of Sciences of the USSR S. Z. ROGINSKY, I. I. TRETYAKOV

ON THE NATURE OF THE CATALYTIC ACTIVITY OF PLATINUM IN THE OXIDATION OF HYDROGEN

The catalytic action of platinum on the interaction of hydrogen with oxygen was discovered by Döbereiner ([1]) more than 140 years ago and since then has been studied by many investigators. However, the data obtained by them, concerning both the nature of the catalyzing surface and the kinetics of the process itself, are highly contradictory. In contrast to Faraday ([2]), who came to the conclusion that high catalytic activity is a property of a clean platinum surface, later investigators attributed it to platinum activated by absorbed gases ([3–5]). Since in all experiments carried out up to now contamination of the surface by foreign substances (impurities in the gases, vapors of grease, mercury) could not be completely excluded, we attempted to study the catalytic properties of an extremely degassed platinum surface.

The experiments were carried out in an ultrahigh-vacuum apparatus, in which the conditioning of massive specimens and the evaporation of the metal in obtaining films were performed at a residual-gas pressure of the order of $1—2 \cdot 10^{-10}$ mm Hg, and vapors of grease and mercury were completely absent. The ultrahigh vacuum was obtained after conditioning the entire apparatus at 450°C by means of titanium electrodischarge pumps and a Bayard–Alpert tube. The latter also served as a manometer at pressures below 10^{-4} mm Hg. The pressures of the reacting gases from 10^{-1} to 10^{-4} mm Hg were measured with Pirani manometers. Instead of stopcocks, seals with a liquid alloy based on gallium were used. Pure hydrogen and oxygen were admitted by diffusion through heated capillaries made respectively of palladium and silver. The reaction kinetics was studied under static conditions at pressures from 10^{-1} to 10^{-3} mm Hg.

A study of the chemisorption properties of clean platinum films showed that already at −196° they interact practically instantaneously with hydrogen and

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

with oxygen, with strong coverage of almost the entire surface (close to a monolayer) at pressures below 10^{-4} mm Hg. Measurements of the contact potential difference made during adsorption indicate that oxygen forms a negative dipole layer on the surface, while hydrogen at the beginning of adsorption (up to $\theta = 0.1$—0.2) also gives a negative layer, and then, at higher coverages, a positive dipole layer.

The interaction of hydrogen with oxygen on clean platinum films not subjected to preliminary activation by gases proceeds at room temperature at a very high rate, irrespective of whether both gases are admitted simultaneously or successively in any order.

Owing to the high activity of the films, the reaction kinetics was studied on platinum wires with a surface area of 0.1—1 cm^2. They were cleaned by heating at 1000° in ultrahigh vacuum until gas evolution ceased, followed by heating in oxygen to remove possible organic contaminants and carbon from the surface, heating in hydrogen for complete removal of oxygen, and, finally, repeated heating in ultrahigh vacuum. Wires prepared in this way possessed reproducibly high activity, which changed almost not at all after heating in hydrogen or oxygen.

In parallel with the experiments in the ultrahigh-vacuum apparatus, studies were also carried out in an ordinary vacuum apparatus, in which, during conditioning of the samples, a vacuum of $2–3 \cdot 10^{-7}$ mm Hg was achieved. The catalyst, in the form of a wire, was suspended on metal leads through glass, and it could be strongly heated by an electric current while keeping the reactor walls cold. The latter were conditioned to 450° before each series of experiments. Under these conditions, prolonged heating of platinum in hydrogen or in vacuum led to a decrease in its activity, which, however, returned to its former value after calcination in oxygen. This may indicate activation by the burning off of organic contaminants formed on the surface of the catalyst.

Fig. 1. Dependence of the reaction rate on the ratio of the reactant pressures. Initial pressure of the mixture $1 \cdot 10^{-2}$ mm Hg.

Fig. 2. Dependence of the reaction rate on the pressure of O_2 at $p_{H2} = 7.2 \cdot 10^{-3}$ mm Hg.

In studying the influence of the partial pressures of the reaction components on its kinetics, the existence of optimal ratios between oxygen and hydrogen was found. Fig. 1 shows the dependence, obtained in the ultrahigh-vacuum

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

apparatus at 20°, of the initial reaction rates on this ratio. A clear maximum of the rate is seen at about 3 : 1. Figs. 2 and 3 show analogous dependences recorded in the ordinary apparatus while varying, over a wide range, the partial pressure of one of the components and keeping constant the partial pressure of the other component. As is evident from these graphs, the reaction rates depend strongly on the ratio between the pressures of hydrogen and oxygen and also pass through a maximum near $p_{O2}/p_{H2} \sim 3$. At other temperatures, as is seen from Fig. 4, the maximum rate is preserved, but with increasing temperature it shifts–

Fig. 3. Dependence of the reaction rate on the pressure of H_2 at $p_{O2} = 2.1 \cdot 10^{-2}$ mm Hg.

Fig. 4. Dependence of the reaction rate on the pressure of O_2 at different temperatures. $p_{H2} = 7 \cdot 10^{-3}$ mm Hg. 1 –1000°, 2 –500°, 3 –220°, 4 –140°, 5 ––78°C.

toward smaller values of the ratio p_{O2}/p_{H2}. The presence of a maximum in the reaction rate at a definite ratio between the partial pressures of the components of the reacting mixture was also found by us in the oxidation of hydrogen on palladium.

If one takes into account that the maximum rate of hydrogen oxidation on platinum is observed at a sixfold excess of oxygen relative to stoichiometry, it becomes clear why it was not noted for this system by other authors, and why some of them arrive at the conclusion that the reaction is accelerated by oxygen ([3–5]), while others–by hydrogen ([6,7]). Indeed, since in none of the works known to us, when varying the ratio between hydrogen and oxygen, was a sixfold excess of oxygen reached, this effect could not have been observed; and conclusions about the influence of the reaction components on its rate were drawn in the works of different authors on the basis of experiments apparently belonging either to the ascending or to the descending branch of the curve. The phenomenon observed by us can also explain the "incomplete combustion" effect of the reaction mixture at an excess of oxygen, discovered by a number of authors ([3]), since in this case, during the course of the reaction, the excess of oxygen increases and a sharp slowing of the rate of interaction of hydrogen with oxygen occurs, which can create the false impression that the reaction has ended before the hydrogen has been completely consumed.

It is interesting to note that, according to the data of G. K. Boreskov et al. ([7]),

the rate of hydrogen oxidation on platinum at large excesses of hydrogen is proportional to the partial pressure of oxygen, while at large excesses of oxygen it increases with the pressure of hydrogen. At intermediate ratios of hydrogen and oxygen one would naturally expect a maximum of the rate, but this region was not investigated by the authors. In another work by G. K. Boreskov ([8]), a maximum in the rate of hydrogen oxidation on iron, cobalt, and nickel was found at low oxygen contents in hydrogen. A maximum of the reaction rate at a definite ratio between the reaction components was also observed by Hinshelwood and Prichard for the interaction of hydrogen with carbon monoxide on platinum ([9]).

The data presented do not give direct indications of the origin of the observed maxima. They could be formally explained by an equation of Langmuir kinetics of the type

$$w = \frac{k a_{O2} p_{O2}^m a_{H2}^n p_{H2}^n}{(1 + a_{O2} p_{O2} + a_{H2} p_{H2})^{m+n}},$$

from which it follows, in agreement with the experimental results, that at large values of the adsorption coefficients the reaction rate passes through a maximum, which must occur at a constant value of the ratio of the partial pressures of oxygen and hydrogen

$$\frac{p_{O2}}{p_{H2}} = \frac{m}{n} \frac{a_{H2}}{a_{O2}}.$$

However, this explanation is in some contradiction with the data on kinetics and kinetic isotope effects obtained under somewhat different conditions ([4]). Therefore, in order to choose between this and other explanations, further investigation is required.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
23 V 1964

CITED LITERATURE

1. I. W. Döbereiner, *Ann. Chem.*, **24**, 94 (1823).

2. M. Faraday, *Experimental Researches in Electricity*, Vol. 1, Publishing House of the Academy of Sciences of the USSR, 1947, p. 227.

3. S. Z. Roginskii, V. S. Rozin, Collection *Refractories, Scientific Research Institute of the Academy of Sciences of the USSR for 1940*, L., 1941, p. 116.

4. O. V. Krylov, S. Z. Roginskii, *Izv. AN SSSR, OKhN*, 1956, No. 2, 145.

5. D. L. Chapman, P. W. Reynolds, *Proc. Roy. Soc.*, A **156**, 284 (1936).

6. G. K. Boreskov, M. G. Slin' ko, V. S. Chesalova, *ZhFKh*, **30**, 2787 (1956).

7. E. N. Kharkovskaya, G. K. Boreskov, M. G. Slin'ko, *DAN*, **127**, 145 (1959).

8. G. K. Boreskov, *ZhFKh*, **31**, 937 (1957).

9. Hinshelwood, Prichard, *J. Chem. Soc.*, 1925, 806.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.