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Abstract

Full Text

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THE ELECTRICAL-CONDUCTIVITY METHOD IN THE STUDY OF POWDERED METALLIC CATALYSTS IN THE LIQUID PHASE

In a number of works (^{1}) attention was drawn to the possibility of the formation of conducting "bridges" in suspensions of conductors and semiconductors in dielectrics when a certain "critical" voltage is reached at the electrodes. For platinum, conductivity was already detected at $E_{\text{cr}} = 20$ V/cm.

In measuring the resistance of platinum suspensions, we became convinced that it varies within limits from several ohms to hundreds of ohms. Reproducible values could not be obtained. On the other hand, it was observed that, as the suspension settled, its resistance became ordered. In connection with this, the idea arose of measuring the resistance of metallic powders after their settling.

The objects of investigation chosen were skeletal nickel and platinum black; as solvent, *n*-heptane was taken, having low specific electrical conductivity ($1 \cdot 10^{-13}$ ohm$^{-1}\cdot$cm^{-1}). Experiments were also carried out in benzene, 96% alcohol, and glacial acetic acid.

Fig. 1. Change in the resistance of skeletal nickel during settling

The basis of the cell for determining the electrical conductivity of powders was a catalytic "duck." At the level of its bottom, electrodes were sealed in—two platinum wires each 6 cm long, with a distance between them of 5 mm. The resistance was measured with a direct-current bridge (UMB type), at a battery voltage of 6 V.

It turned out that the high conductivity of active nickel powder is due to the hydrogen contained in it. In freshly prepared skeletal nickel the resistance may vary from several ohms to a thousand ohms, while a powder that has stood for several days under alcohol may conduct no current at all. However, when the powder is saturated with hydrogen its resistance falls until the powder absorbs

Figure 2

Figure 2: Figure 2

hydrogen; after this a definite low value of the resistance is established, which we have conventionally called the "saturation resistance."

When the system is shaken it does not conduct current, but as early as 10 sec after shaking is stopped the resistance of the powder can be measured; it slowly decreases with time (Fig. 1).

This change is associated both with compaction of the precipitate that forms and with an increase in the total number of settled particles.

The resistance of skeletal nickel is directly proportional to the distance between the electrodes and decreases regularly with increasing taken charge—

powder sample. For each sample, analogous sedimentation curves are obtained, each of which corresponds to its own "saturation resistance" (0.75 g: 3.5 Ω; 1 g: 2.5 Ω; 3 g: 0.8 Ω; 15 g: 0.4 Ω).

The influence of oxygen, acetylene, and methylethylacetylene carbinol on the resistance of 0.75 g of hydrogen-saturated skeletal nickel powder at 20° was studied. In all cases, removal of hydrogen from the catalyst surface by these substances led to an increase in its resistance. When a stream of acetylene was passed through a suspension of skeletal nickel in *n*-heptane, the resistance of the catalyst rose sharply and within 15–20 min reached one million ohms and remained at this level. If the acetylene was then displaced from the gas phase by hydrogen and hydrogenation of the adsorbed acetylene and the products of its partial polymerization was carried out, then hydrogen was absorbed at a high rate, without at first affecting the conductivity of the powder (see Fig. 2, *A*, *a*). Only after decolorization of the solution was a sharp decrease in the rate of hydrogen absorption observed, together with an equally sharp increase in the conductivity of the powder. Approximately 30 min after the start of hydrogenation, the "saturation resistance" was established.

Fig. 2. Change in the resistance of skeletal nickel during hydrogenation of acetylene (*A*) and methylethylacetylene carbinol (*B*). Kinetic curves for acetylene (*a*) and carbinol (*b*).

When the powder was shaken in air, the resistance also reached one million ohms; moreover, if the contact with air was brief, then upon saturation with hydrogen the bulk of it was absorbed at a resistance of 1 MΩ, and the remaining, smaller part at the "saturation resistance." The entire saturation process lasted several minutes. With prolonged contact with oxygen, subsequent saturation with hydrogen was prolonged to 2–3 hours, and the bulk of the hydrogen was absorbed at the "saturation resistance" (Fig. 2, *B*, *b*).

When methylethylacetylene carbinol was introduced into the "duck" under a

Fig. 3

Figure 3: Fig. 3

nitrogen atmosphere, the resistance of the powder increased and reached a constant value corresponding to the fraction of hydrogen removed. During subsequent hydrogenation the resistance even increased somewhat while hydrogen was being absorbed intensively, and then fell sharply. Hydrogenation of the carbinol by hydrogen from the gas phase likewise led to a considerable increase in the resistance of the powder while hydrogen was absorbed at a substantial rate. It is characteristic that, for skeletal nickel, the jump in resistance from 10 to 1,000,000 Ω occurs upon removal of only 15% of the hydrogen sorbed by it (18 ml H_2 per 1 g of skeletal nickel).

It is evident that hydrogen adsorbed on the surface (possibly molecular hydrogen), which determines the mechanism of the high conductivity of the powder,

nickel. Its amount, determined by the electrical-conductivity method, agrees well with the data of potentiometric measurements (^{2}). In hydrogenation on skeletal nickel the resistance is almost always in the region corresponding to removal of more than 15% of the hydrogen. Cyclohexene is an exception. Similar results were obtained with platinum black. However, in contrast to nickel, oxygen increases the resistance only up to 2000 Ω.

With increasing temperature, as is seen from Fig. 3, the conductivity of Ni and Pt powders in coordinates $\lg \sigma \left(\frac{1}{T}\right)$ increases rectilinearly, and the absolute magnitude of this change depends on the nature of the substance adsorbed on the surface. In the case of nickel the conductivity begins to decrease after 50°, whereas in the case of platinum it continues to increase above 70°.

Fig. 3. Dependence of the electrical conductivity of skeletal nickel and platinum black on temperature. *a*—the powder is saturated with hydrogen; *b*—hydrogen has been partially removed from the powder surface

The course of the temperature curve of the electrical conductivity of skeletal nickel and platinum black is characteristic of semiconductors (^{3}). The slope of the rectilinear portion makes it possible to calculate the dissociation energy of the current carriers. In the case of skeletal nickel and platinum black, this energy proves to be very close to the activation energies of hydrogen and unsaturated compounds on these catalysts. For skeletal nickel in *n*-heptane, when its surface is covered with hydrogen, the dissociation energy of the current carriers is 1200 cal/mol, while when hydrogen is removed from the surface by an unsaturated compound it reaches 9000 cal/mol.

If one takes into account that for skeletal nickel after 45–50° negative temperature coefficients are often observed in hydrogenation reactions, whereas for platinum such a coefficient is characteristic at temperatures above 100°, one may conclude that the electrical conductivity of these catalysts is connected with their catalytic activity. Moreover, if not the entire mass of the catalyst particle, then at least its surface layers exhibit semiconductor properties. Hydrogen or an unsaturated compound adsorbed on the surface of the powders may play the role of surface impurities, on whose donor or acceptor character the absolute magnitude of the conductivity of these catalysts depends (^{3}).

It may be noted that the specific conductivity of these powders, calculated for a layer 6 cm × 1 mm in the case of adsorption of hydrogen on their surface, has a value of the order of $10^{-2}\ \Omega^{-1} \cdot \text{cm}^{-1}$, and decreases by 6 orders of magnitude in the case of adsorption of an unsaturated compound, which is characteristic of semiconductors. The proposed method, distinguished by high sensitivity, makes it possible to judge the concentration of reacting substances on the surface of catalysts and to study the regularities of adsorption of unsaturated compounds. With the aid of the method it has been shown that the change in the electrical conductivity of powdered metals is characteristic of semiconductors and is connected with their catalytic activity.

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