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Abstract

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THE EFFECT OF ZINC IONS ON THE SORPTION OF HYDROGEN AND THE CATALYTIC ACTIVITY OF PALLADIUM

The question of the effect of ions on the activity of catalysts is of great importance for the further development of the theory of liquid-phase catalytic processes. A number of authors ([1]-[3]), who investigated the effect of various salts on the rate and selectivity of the hydrogenation of organic compounds on platinum, palladium, and nickel, noted changes in the rate and selectivity of the processes, without going deeply into the mechanism of ion action. Investigations carried out by us showed that many ions are capable of being adsorbed on the surface of catalysts and of substantially changing their adsorption and catalytic properties ([4]-[6]).

In the present work, the effect of zinc sulfate and zinc chloride on the sorption of hydrogen on palladium in acidic and neutral media, and on the activity of Pd black in the hydrogenation reactions of dimethylacetylenylcarbinol, was studied. The sorption of hydrogen on palladium in acidic solutions of zinc salts was studied by the method of charging curves at 20, 40, and 60°. The electrode consisted of a platinum plate (1 cm^2), on which 0.00662 g of palladium was deposited electrolytically. The solutions were prepared with bidistilled water. The concentration of zinc salts was varied from 0.01 N to 2 N. Figure 1 presents the charging curves of a Pd electrode in 1 N H_2SO_4 and with additions of zinc sulfate and zinc chloride. In 1 N H_2SO_4 the curve has the characteristic form with a phase-transition plateau at 68 mV. In 0.01 N and 0.1 N zinc sulfate the course of the charging curves does not change in comparison with 1 N H_2SO_4. When the concentration of zinc sulfate is increased to 1 N, the plateau of the α β transition shifts to the anodic side by 7 mV, while the hydrogen region of the charging curve is somewhat reduced. In 2 N $ZnSO_4$ there is an even greater strengthening of the Pd—H bond, and the amount of sorbed hydrogen decreases to 0.56 ml as compared with 0.60 ml in 1 N H_2SO_4. In the case of zinc chloride, the change in the shape of the charging curve occurs already in a 0.1 N solution, i.e., adsorption of zinc ions from chloride salts is more pronounced than from sulfate salts. When the temperature is raised to 40 and 60°, zinc ions are not adsorbed on palladium in an acidic medium.

The amount of hydrogen sorbed by palladium in a neutral medium in the presence of zinc salts was determined by direct measurement of the hydrogen con-

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

sumed in the reduction and saturation of palladium oxide (0.1 g). Figure 2 gives the curves for the reduction of palladium oxide to Pd black at 20°. Palladium oxide in water is reduced at a high rate; when zinc sulfate is introduced, no noticeable change in the rate of reduction is observed.

In solutions of zinc chloride there is some slowing of the reduction of palladium oxide, and in 1 N $ZnCl_2$, during the first 7-8 min, reduction does not occur at all. During the reduction of palladium oxide to Pd black in the presence of zinc salts, a significant acidification of the medium from pH 6 to 2-3 was found, which is connected with the ionization of part of the sorbed hydrogen as a result of adsorption of zinc ions on palladium ([6]). As a result of this, the amount of hydrogen sorbed by Pd black decreases—

decreases from 87.2 ml/g of palladium in water to 70.1 ml/g in 1 N $ZnSO_4$; in zinc chloride solutions the amount of hydrogen decreases still more sharply (56.1 ml/g in 1 N $ZnCl_2$).

The catalytic properties of Pd black in the presence of zinc sulfate and zinc chloride were studied using the hydrogenation of dimethylacetylenylcarbinol at 20 and 30° as an example. Fig. 3 shows the kinetic and potential curves for the hydrogenation of dimethylacetylenylcarbinol in water and in solutions

Fig. 1. Charging curves of a Pd electrode at 20° in acidic solutions: *a*—$ZnSO_4$, *b*—$ZnCl_2$. Current density $5 \cdot 10^{-4}$ A/cm^2. 1—0.1 N H_2SO_4; 2—0.01 N Zn^{2+}; 3—0.1 N Zn^{2+}; 4—1 N Zn^{2+}; 5—2 N Zn^{2+}

Fig. 2. Reduction of palladium oxide in the presence of zinc sulfate at 20°. 1—in H_2O; 2—in 0.01 N $ZnSO_4$; 3—in 0.1 N $ZnSO_4$; 4—in 1 N $ZnSO_4$

$ZnSO_4$ of various concentrations at 20°. In water, carbinol is hydrogenated on Pd black at a constant rate of 15.0 ml/min with a shift of the catalyst potential by 103 mV in the positive direction. In 0.01 N zinc sulfate the rate of hydrogenation of the carbinol increases to 19 ml/min; in 0.1 N $ZnSO_4$ a maximum rate of 21 ml/min was found. In 1 N $ZnSO_4$ a bend is observed on the kinetic curve at approximately half uptake of hydrogen. The triple bond is hydrogenated at a rate of 21.4 ml/min, while the rate of hydrogenation of the double bond decreases by approximately half—to 11 ml/min. On the potential curve a sharp break is likewise observed; the double bond of the carbinol is hydrogenated at more positive potentials than the triple bond; thus, the potential shift during hydrogenation of the C C bond is 125 mV, and that of the C=C bond is 160 mV. In zinc chloride solutions these regularities are expressed still more sharply (Fig. 4).

By potentiometric titration we carried out analyses for the triple bond after uptake of 1/2 of the amount of hydrogen. It was

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

It was found that dimethylacetylene carbinol on palladium is hydrogenated selectively in water (99.3%), although there are no breaks in the kinetic curve. However, the selectivity of the process can be judged qualitatively from the course of the potential curve; if the triple bond of the carbinol in water is hydrogenated with a potential shift of 103 mV, then the double bond is hydrogenated at $\Delta\varphi = 115$ mV. Previously, the high selectivity of carbinol hydrogenation on palladium was shown

Fig. 3. Hydrogenation of dimethylacetylene carbinol on Pd black in the presence of cerous zinc oxide at 20°. Designations are as in **Fig. 2**

Fig. 4. Hydrogenation of dimethylacetylene carbinol on Pd black in the presence of zinc chloride. 1 –in water; 2 –in 0.01 N $ZnCl_2$; 3 –in 0.1 N $ZnCl_2$; 4 –in 1 N $ZnCl_2$

by I. N. Nazarov and Kh. V. Bal' yan with co-workers (7, 8). In the presence of zinc salts, the selectivity remains very high (99.6-99.8%).

The cause of the sharp increase in the rate of hydrogenation in the presence of Zn^{2+} ions is adsorption of the cation on the catalytic surface and an increase in the Pd–H bond energy.

A slight change in the bond energy of sorbed hydrogen creates more favorable conditions for the hydrogenation process, since it leads to an increase in the adsorption of the unsaturated compound. If, during hydrogenation of the triple bond in water, the shift in the potential of Pd black is 103 mV, then in 1N it is 125 mV; for the double bond in water $\Delta\varphi = 115$ mV, and in 0.1N it is 150 mV. However, at high concentrations of zinc salts the rate of hydrogenation of the double bond begins to fall, despite the considerable adsorption of dimethylvinylcarbinol ($\Delta\varphi = 160$ mV), which is probably connected with difficulty in the interaction of the double bond with hydrogen of higher bond energy. Earlier, such a regularity was shown by us (9) in the presence of cadmium ions.

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