EFFECT OF CHROMIUM AND NICKEL SALTS ON THE SORPTION AND CATALYTIC PROPERTIES OF Pd BLACK

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Figure 1

Figure 1: Figure 1

Abstract

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EFFECT OF CHROMIUM AND NICKEL SALTS ON THE SORPTION AND CATALYTIC PROPERTIES OF Pd BLACK

Continuing the work (1–4), we investigated the effect of additions of sulfuric-acid chromium chloride and nickel on the sorption of hydrogen and on the activity of Pd black in the hydrogenation of dimethylacetylene carbinol and acetonitrile. To determine the amount of hydrogen and its bond energy, the method of charging curves was used (5,6).

Figure 1 presents the charging curves of Pd black in acidic solutions of chromium chloride at 20°. In 1 N H_2SO_4 the charging curve has the usual form (5). In the presence of additions of chromium chloride, the hydrogen region of the charging curve is shortened, and in 1 N $CrCl_3$ the plateau of the α–β transition shifts by 6 mV in the anodic direction compared with 1 N H_2SO_4. From the data of Table 1 it is evident that the amount of hydrogen dissolved in palladium does not change on going from sulfuric acid to solutions of $Cr_2(SO_4)_2$, whereas the adsorption of hydrogen decreases somewhat. In chromium chloride solutions, the amount of hydrogen dissolved in palladium also decreases, which is apparently connected with the penetration of chlorine ions into the depth of the crystal lattice of the metal. The considerable penetration of Cl^- ions is due to the experimental procedure. The charging curves for each salt were recorded with one weighed portion of Pd black, and the solution was changed in the region of the double layer (0.5—0.6 V). Such a dependence of the penetration into the depth of bromine and iodine ions on the potential of the Pt electrode had earlier been shown by N. A. Balashova (7). Adsorption of chlorine ions also shifts the potential of the onset of oxidation of the palladium surface in the more negative direction: whereas in 1 N H_2SO_4 oxygen deposition begins at 720 mV, in 0.01 N $CrCl_3$ it begins at 670 mV, and in 1 N $CrCl_3$ at 520 mV.

Fig. 1. Charging curves of Pd black in acidic solutions of chromium chloride at 20°.

1 –in 1 N H_2SO_4; 2 –0.1 N $CrCl_3 + 1$ N H_2SO_4; 3 –0.1 N $CrCl_3 + 1$ N H_2SO_4; 4 –1 N $CrCl_3 + 1$ N H_2SO_4.

Figure 2 presents the charging curves of Pd black in aqueous solutions of nickel chloride. In a 1 N solution the charging curve is slightly distorted owing to a certain nonequilibrium of the process; in 2 N $NiCl_2$ the plateau of the phase α $-\beta$ transition lies more anodically than in 1 N H_2SO_4. The change–

Table 1

Effect of chromic sulfate and chromic chloride on the sorption of hydrogen on Pd black in an acidic medium

Electrolyte	Potential of the α–β transition, mV	Amount of sorbed hydrogen*, ml	Amount of dissolved hydrogen, ml	Amount of adsorbed hydrogen, ml
1 N H_2SO_4	50	5.47	4.36	1.16
0.01 N $Cr_2(SO_4)_3$ + 1 N H_2SO_4	50	5.43	4.32	1.11
0.1 N $Cr_2(SO_4)_3$ + 1 N H_2SO_4	54	5.15	4.35	0.8
1 N H_2SO_4	50	5.34	3.95	1.39
0.01 N $CrCl_3$ + 1 N H_2SO_4	52	4.6	3.50	1.11
0.1 N $CrCl_3$ + 1 N H_2SO_4	56	4.74	3.69	1.05
1 N $CrCl_3$ + 1 N H_2SO_4	56	4.7	3.50	1.20

* Per 0.05 g of Pd black.

The decrease in the amount of sorbed hydrogen from 6.0 ml in H_2SO_4 to 4.6 ml in 2 N $NiCl_2$ occurs mainly because of a decrease in the dissolution of hydrogen in Pd black. Measurement of the pH of aqueous solutions of nickel and chromium salts before and after saturation of palladium with hydrogen shows that acidification of the medium occurs. The latter agrees with previously obtained data on the ionization of hydrogen during adsorption of cations on the

Fig. 2. Charging curves of Pd black in aqueous solutions of nickel chloride at 20°. 1—in 1 N H_2SO_4; 2—in 1 N $NiCl_2$; 3—in 2 N $NiCl_2$

Figure 2: Fig. 2. Charging curves of Pd black in aqueous solutions of nickel chloride at 20°. 1—in 1 N H_2SO_4; 2—in 1 N $NiCl_2$; 3—in 2 N $NiCl_2$

Figure 3

Figure 3: Figure 3

catalyst surface (4). However, as follows from the charging curves, nickel and chromium ions have almost no effect on the bond energy Mo—H and on the potential of the α—β transition.

Fig. 2. Charging curves of Pd black in aqueous solutions of nickel chloride at 20°. 1—in 1 N H_2SO_4; 2—in 1 N $NiCl_2$; 3—in 2 N $NiCl_2$.

Figure 3 gives the curves obtained during hydrogenation of acetonitrile on Pd black in 1 N H_2SO_4 and with additions of chromic sulfate at 20°. In sulfuric acid, acetonitrile is initially hydrogenated at a rate of 10 ml/min, but then the rate drops sharply and, after absorption of half the amount of hydrogen, hydrogenation proceeds at an order close to zero. The potential curve is a mirror reflection of the kinetic one. The potential shift at the beginning of the reaction is 165 mV; as acetonitrile is hydrogenated the potential increases and, by the time 75 ml of hydrogen has been absorbed, reaches 250 mV (relative to the N.H.E.). Addition of 0.01 and 0.1 N chromic sulfate leads to a certain increase in the rate of hydrogenation of acetonitrile, but a further increase in the salt concentration to 0.5 N begins to inhibit the process.

Dimethylacetylenylcarbinol on Pd black at 20° in water is hydrogenated with zero order at a rate of 12.5 ml/min (Fig. 4). On the potential—

curve after the absorption of 75 ml of hydrogen, a break is observed toward more positive potentials, which indicates the selectivity of the process on palladium.

In 0.01 N chromic sulfate, the rate of hydrogenation of carbinol increases to 16 ml/min and reaches a maximum in 0.1 N $Cr_2(SO_4)_3$, where the rate increases almost twofold in comparison with the reaction in water. With a further increase in the salt concentration, the hydrogenation rate decreases. The shift of the potential of palladium black during hydrogenation in salt solutions is approximately 20-30 mV smaller than in water. In the presence of nickel salts, an analogous but less pronounced pattern is observed.

Thus, despite the adsorption of chromium and nickel ions on the palladium surface, the bond energy and the potential of the phase transition of sorbed hydrogen change insignificantly in comparison with (4). In sulfuric-acid solutions, where the amount of hydrogen

Fig. 3. Hydrogenation of acetonitrile on Pd black at 20°:

Figure 4

Figure 4: Figure 4

1 –in 1 N H_2SO_4; 2 –in 0.01 N $Cr_2(SO_4)_3$ + 1 N H_2SO_4; 3 –in 0.1 N $Cr_2(SO_4)_3$ + 1 N H_2SO_4; 4 –in 0.5 N $Cr_2(SO_4)_3$ + 1 N H_2SO_4

Fig. 4. Hydrogenation of dimethylacetylenylcarbinol on Pd black at 20°.
1 –in water; 2 –in 0.01 N $Cr_2(SO_4)_3$; 3 –in 0.1 N $Cr_2(SO_4)_3$; 4 –in 0.5 N $Cr_2(SO_4)_3$; 5 –in 1 N $Cr_2(SO_4)_3$

in palladium practically does not decrease, the maximum catalytic activity in the hydrogenation of acetonitrile and dimethylacetylenylcarbinol is observed in a 0.1 N salt solution. Under conditions of constancy of the amount

of sorbed hydrogen, the appearance of a maximum in the activity of the catalyst can be attributed only to an increase in the Me–H bond and to a change in the potential of the α–β transition (Table 1). Indeed, if in 1 N H_2SO_4 the adsorbed hydrogen is completely removed at a potential of 225 mV, then in 1 and 2 N $NiCl_2$ the end of the hydrogen region corresponds to 250 mV (Fig. 2). This makes it possible to suppose that the decisive role for palladium, in the change in its activity and selectivity, is played by the bond energy of the adsorbed hydrogen and by the potential of the phase α–β transition.

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