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Abstract

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SELECTIVE HYDROGENATION OF DIMETHYLACETYLENYLCARBINOL ON Pd BLACK IN THE PRESENCE OF CADMIUM IONS

In studying the influence of zinc ions on the adsorption and catalytic properties of palladium ([1]), it was shown earlier that in normal solutions of zinc salts at 20° the hydrogenation of the triple and double bonds of carbinol proceeds selectively, at different rates. The large difference in the rates of hydrogenation was explained by us as a strengthening of the bond energy of sorbed hydrogen, caused by the specific adsorption of zinc ions on the catalytic surface.

Fig. 1 Fig. 2

Fig. 1. Charging curves of a palladized Pd electrode in solutions of various concentrations of cadmium sulfate at 20°. Current density $5 \cdot 10^{-4}$ a/cm^2

Fig. 2. Hydrogenation of dimethylacetylenylcarbinol on Pd black (from 0.1 g PdO) in solutions of cadmium sulfate at 20°

On the basis of the results obtained, an assumption was made about the possibility of complete suppression of the reactivity of the double bond of the carbinol by a significant increase in the bond energy Pd—H.

In the present work we investigated the influence of cadmium sulfate and chloride on the sorption of hydrogen and the catalytic activity of Pd black in the hydrogenation of dimethylacetylenylcarbinol.

Figure 1 presents charging curves of palladium in solutions of various concentrations of cadmium sulfate at 20°. From Fig. 1 it is seen that the introduction of cadmium sulfate at a concentration of 0.01 N changes the course of the curve.

charging, shifting the ionization and desorption potential of hydrogen in the anodic direction both in the β region and in the β–α phase. If in 1 N H_2SO_4 the α –β transition of palladium occurs at a potential of 75 mV, then in 0.01 N $CdSO_4$ it occurs at 85 mV. A further increase in the concentration of the cadmium ion in the catalytic system leads to still greater hindrance of the β–α transition and increases the binding energy of the adsorbed hydrogen.

From Fig. 2, which gives the kinetic and potential curves for the hydrogenation of dimethylacetynylcarbinol on Pd black in solutions of cadmium sulfate at 20°, it follows that in water the carbinol is hydrogenated according to zero order, at a rate of 9 ml/min, with a potential shift of 100 mV. After the absorption of one

Fig. 3. Hydrogenation of five successive portions of carbinol on one charge of Pd black in 0.1 N CdSO4 at 20°

Figure 1: Fig. 3. Hydrogenation of five successive portions of carbinol on one charge of Pd black in 0.1 N CdSO4 at 20°

mole of hydrogen, a bend is observed on the potential curve, which indicates the beginning of hydrogenation of the double bond, although there are no changes on the kinetic curve. The high selectivity of hydrogenation of dimethylacetynylcarbinol in this case can be judged from the change in potential. Upon addition of cadmium sulfate (10^{-3} N), the rate of hydrogenation of the carbinol increases to 14.6 ml/min, with a maximum potential shift of 60 mV. However, whereas in water hydrogenation of the triple bond proceeds at a constant value of the potential, in 10^{-3} N $CdSO_4$ during the reaction the potential of the Pd black shifts monotonically toward negative values, and addition of the second mole of hydrogen to the carbinol occurs with a potential shift of only 26 mV from the initial value. The small shift indicates hindrance of the reaction, despite the fact that the rate of the hydrogenation process for the double bond is the same as for the triple bond. Indeed, when the concentration of cadmium sulfate in the solution was increased to 0.01 N, a change in the course of the kinetic curve was found. The rate of hydrogenation of the triple bond increases to 16 ml/min, and after absorption of 60 ml of hydrogen a rapid drop in the hydrogenation rate to 5 ml/min begins. In 0.1 N cadmium sulfate the hydrogenation rate decreases to 9.6 ml/min; with a catalyst potential shift of 38 mV, in this case the reaction completely ceases after absorption of one mole of hydrogen. Analysis of the reaction mixture showed the presence of 99-100% dimethylvinylcarbinol. A further increase in the concentration of cadmium sulfate begins to greatly reduce the rate of the process.

Fig. 3. Hydrogenation of five successive portions of carbinol on one charge of Pd black in 0.1 N $CdSO_4$ at 20°.

To investigate the stability of the catalytic system, five successive portions of carbinol were hydrogenated on one charge of Pd black (Fig. 3). As can be seen from Fig. 3, the activity of the catalyst decreases during hydrogenation of the fifth charge, but the selectivity of the catalyst is fully retained.

From the charging curves it follows that adsorption of cadmium on the surface of palladium leads to a decrease in the amount of sorbed hydrogen. On Pd black (from 0.1 g PdO) the amount of sorbed hydrogen decreases from 9.3 ml in water to 8.2 and 7.8 ml in 10^{-3} and 10^{-1} N solutions of $CdSO_4$, respectively. This is also confirmed by direct measurement of the amount of sorbed hydrogen ([2,3]). However, despite the decrease in the amount

of hydrogen sorbed by palladium, the hydrogenation rate in 10^{-3} N $CdSO_4$ increases to 14.6 ml/min. The increase in the catalytic activity of Pd black with a simultaneous decrease in the amount of sorbed hydrogen unambiguously

shows the absence of a dependence between these two parameters. The independence of the catalyst activity from the amount of sorbed hydrogen can occur only when the rate of hydrogen replenishment in Pd black considerably exceeds the rate of its consumption, i.e., sorption $\gg$ desorption. Indeed, the nonequilibrium of these processes on Pd black in solutions of cadmium salts can be seen by comparing the anodic and cathodic charge curves: if in 1 N H_2SO_4 the forward and reverse branches of the curves do not coincide by 20 mV, then with increasing concentration of cadmium sulfate the hysteresis loop grows to 80 mV. The shift of the hydrogen diffusion potential in the negative direction indicates a significant facilitation of hydrogen penetration into the interior of palladium ([4]), whereas ionization and desorption of hydrogen are strongly hindered (anodic curve). Such a difference in the rates of hydrogen sorption and desorption indicates the impossibility of these processes proceeding at the same active centers, which is also confirmed by the inversely proportional dependence of the catalytic activity on the amount of sorbed hydrogen. Under conditions in which surface adsorption of hydrogen ([5–7]) on Pd black is absent, it must be assumed that its replenishment proceeds through a dissolution stage.

The course of the hydrogenation process of dimethylacetylenylcarbinol on Pd black in a 0.1 N solution of cadmium sulfate at small potential shifts ($\Delta\varphi = 38$ mV) shows that, according to the charge curve, the process proceeds in the region of the β-phase, where the amount of hydrogen dissolved in Pd black practically does not decrease during the hydrogenation of the carbinol (rate 9.6 ml/min). In this connection we assume that on palladium the processes of hydrogen sorption and desorption occur at different active centers. Adsorption and activation of the substance being hydrogenated apparently also take place near the centers of hydrogen desorption and ionization, as a result of which they do not hinder its diffusion into the interior of Pd black. Thus, the preservation of high rates of hydrogenation of the triple bond and the complete selectivity of the process are associated with an increase in the bond energy of adsorbed hydrogen, hindrance of the α–β transition, and a high rate of hydrogen diffusion into the metal. The question of the selective hydrogenation of dimethylacetylenylcarbinol to dimethylvinylcarbinol is of practical importance for the synthesis of isoprene by the Favorskii method.

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