ELECTROCATALYSIS ON MICRODEPOSITS OF PALLADIUM ON VITREOUS CARBON, DEPOSITED AT DIFFERENT POTENTIALS

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The potential at which Pd is deposited on vitreous carbon has a strong influence on the activity of the catalyst in the cathodic evolution of H_2 and the electrohydrogenation of acetophenone. The most effective catalyst is Pd deposited at E = 0.6 V.

Extensive use is made nowadays of metallic electrocatalysts deposited on a support at potentials close to or even greater than the equilibrium potentials of the system [1-3]. Such catalysts often exhibit an anomalously high activity or selectivity in the reactions of organic substances.

In the present study we have investigated the catalytic properties of Pd deposited on vitreous carbon at various potentials (E_{dep}) in the cathodic evolution of H_2 and the electrohydrogenation (EH) of acetophenone.

EXPERIMENTAL

The Pd was deposited electrolytically on plates of vitreous carbon of apparent area 100 cm^2 from solutions of $PdCl_2$ at constant potential.

The Pd catalysts were studied by means of a P-5827 potentiostat. All the measurements were carried out in 1 N H_2SO_4 or NaOH at about 20°C. The working and auxiliary electrodes were separated by a disphragm. The reference electrode was a reversible hydrogen electrode in the same solution. The freshly deposited palladized electrodes were subjected to anodic-cathodic polarization for 1 h in the potential range E = –0.2 to +0.6 V. The area of the metallic surface (S) in the deposited catalysts was defined by the quantity of adatoms adsorbed on the Pd from a solution of $CuSO_4$ (10^{-3} mole·dm^{-3}) at E = 0.4 V, and was determined from the anodic I, E curves obtained in the range E = 0.4-0.8 V as described in [4].

The electrohydrogenation of acetophenone was carried out in a 1 N aqueous-alcoholic solution of NaOH at about 20°C at constant current (I = –0.2 A) or at constant potential (E = –0.23 V). The products of EH were analyzed by using a Tesla BS-467 (60) NMR spectrometer.

RESULTS AND DISCUSSION

Table 1 shows the surface areas of the metallic phase of the Pd catalysts obtained with E = 0.25, 0.40, and 0.60 V and with various durations of deposition.

The electrocatalytic properties of the samples studied were characterized by the polarization curves in the hydrogen evolution region. All the samples obeyed the Tafel equation both in acid and in alkaline solution. The slopes of the curves for catalysts deposited at 0.40 and 0.60 V were 0.11-0.14 V (Fig. 1). For catalysts deposited at E = 0.25 V this slope was 0.07-0.10 V. For H_2SO_4 solutions Table 1 shows the exchange currents for the evolution of hydrogen (I_0), obtained by extrapolating the straight lines shown on Fig. 1 to E = 0.

The results in Table 1 show that for the sample with E_{dep} = 0.25 V an increase in the time of deposition causes the surface area of the Pd to increase sharply. For higher values

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TABLE 1. Dissolution and Cathodic Evolution of Hydrogen on Pd Deposits in H_2SO_4 Solution

E_{dep}, V	Time, min	I_0, A/m^2	S, cm^2	E_{dep}, V	Time, min	I_0, A/m^2	S, cm^2
0,60	5,0	25,0	100	0,40	7,0	36,0	700
0,60	60,0	56,0	520	0,25	0,2	10,0	60
0,40	1,0	0,6	200	0,25	0,8	45,0	510
0,40	3,0	8,1	700	0,25	1,2	63,0	1400

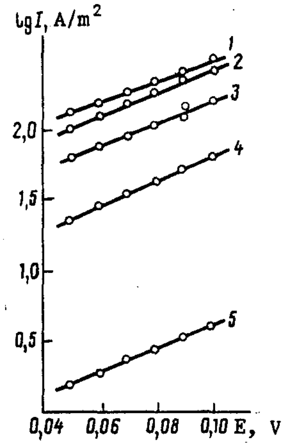

Fig. 1. Polarization curves for the cathodic evolution of hydrogen in H_2SO_4 solution on Pd/C catalysts deposited at 0.6 V (1, 3) and 0.4 V (2, 4, 5). Duration of deposition of Pd (min): 1) 60; 2) 7; 3) 5; 4) 3; 5) 1.

of E_{dep} the surface of the metallic phase increases considerably more slowly during deposition, which may indicate that the deposit of Pd becomes thicker with time when $E_{dep} = 0.4$ or 0.6 V. Comparison of the activity of deposits with similar values of S in the cathodic evolution of H_2 shows that I_0 is highest for the catalysts obtained with $E_{dep} = 0.6$ V. The relative activity of this catalyst appears even higher if comparison is made with deposits having lower values of S (60-200 cm^2).

The difference between catalysts obtained with different E_{dep} is specially marked in the EH of aetophenone. It has been shown [5, 6] that in acid media both the original substrate and the products of EH can undergo chemical changes, and EH was therefore carried out in alcoholic solution of alkali. It was found that under these conditions acetophenone undergoes conversion only in the presence of the catalyst obtained with $E_{dep} = 0.6$ V. The Pd deposits obtained at 0.25 and 0.40 V are inert in the EH of acetophenone. On the catalyst with $E_{dep} = 0.60$ V a single product, methylphenylcarbinol (MPC), is formed with an overall yield of 80-100%. The yield in terms of current is 35-50%. When EH is carried out at a constant potential of $E = -0.2$ V the overall current falls with time by 50%. For EH at a constant current the overpotential rises with time by 0.3 V. A rise in the reaction temperature somewhat decreases the current yield. Our results differ considerably from those of Fletcher et al. [5, 6], who carried out the EH of acetophenone on Pd and Ni. In the first case acetophenone was hydrogenated with high selectivity to ethylbenzene, while in the second case MPC and ethylbenzene were formed in the proportions 8:1. The Pd catalyst which we have described is therefore definitely to be preferred for the hydrogenation of acetophenone to MPC.

Thus our studies of Pd catalysts obtained by electrolytic deposition at different potentials have shown that the deposition of catalysts at high anodic potentials can give them a number of valuable catalytic properties.

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