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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Physical Chemistry

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THE EFFECT OF ADDITIONS OF ALKALI-METAL HALIDES ON THE AMOUNT OF HYDROGEN ADSORBED BY PLATINUM BLACK

Of great interest is the study of the effect of the medium on the amount of hydrogen adsorbed by platinum black. Study of the process of reduction of platinum oxide to platinum black (^1) makes it possible to determine directly the amount of adsorbed hydrogen. In the present work, the rate of reduction of platinum oxide to platinum black was studied, and the amount of hydrogen adsorbed on it was determined in the presence of potassium chloride, bromide, and iodide in 50% ethanol. Platinum oxide was reduced in a catalytic vessel. At definite time intervals the absorbed hydrogen was recorded and the potential of the catalyst was measured (relative to a 0.1 N calomel electrode).

Fig. 1. Effect of potassium bromide on the rate of reduction of platinum oxide to platinum black at 30°. 1 –50% alcohol, 2 –0.01 N KBr, 3 –0.1 N KBr, 4 –0.5 N KBr, 5 –1 N KBr

Figure 1 presents the curves obtained in the reduction of platinum oxide in 50% ethanol and in solutions of various concentrations of potassium bromide at 30°. From Fig. 1 it follows that in 50% C_2H_5OH and in (0.01 N; 0.1 N) solutions of potassium bromide, the reduction of platinum oxide proceeds at almost the same rate. With a further increase in the concentration of potassium bromide, the rate decreases somewhat. As the platinum oxide is reduced, the potential of the catalyst increases, approaching the reversible value.

Figure 2 gives the curves obtained in the reduction of platinum oxide in the presence of potassium iodide at 30°. From Fig. 2 it is seen that in solutions of potassium iodide the rate of reduction of platinum oxide is greatly slowed in comparison with the rate of reduction in 50% ethanol. This is already noticeable in 0.01 N potassium iodide. With a further increase in the concentration of

Fig. 2

Figure 2: Fig. 2

potassium iodide, an induction period arises, which in 0.1 N potassium iodide reaches 6 min, in 0.5 N 15 min, and in 1 N io-

with potassium iodide the reduction continues for 125-130 min. Moreover, upon reduction of platinum oxide in $1N$ potassium iodide, free iodine is liberated at the beginning of the experiment; the solution first acquires a red and then a brown tint, and the potential drops into the oxygen region (+20 mV).

Fig. 2. Effect of potassium iodide on the rate of reduction of platinum oxide to platinum black at 30°.
1 –50% alcohol, 2 –$0.01\,N$ KJ, 3 –$0.1\,N$ KJ, 4 –$0.5\,N$ KJ, 5 –$1\,N$ KJ

The platinum black reduced in $1N$ potassium iodide partially settles on the electrode and on the walls of the duck-shaped vessel; the platinum black remaining in solution is highly dispersed. Apparently, during this time the reduction of platinum oxide proceeds by an electron mechanism through oxidation of J' adsorbed on the Pt electrode to free iodine:

$$2J' \xrightarrow{-2e} J_2. \tag{1}$$

Then the free iodine again passes into the iodide ion, since after 30-35 min the color disappears instantaneously. It is interesting that this reaction proceeds in a stream of a strong reducing agent, namely hydrogen. From Figs. 1 and 2 it is evident that the reversible potential of the catalyst in the presence of potassium bromide and iodide is more positive than in 50% ethanol.

From the results obtained it follows that the nature of the solvent strongly affects both the rate and the mechanism of reduction of platinum oxide:

$$\mathrm{PtO_2 + 2H_2 \rightarrow Pt + 2H_2O}. \tag{2}$$

From reaction (2) it can be calculated that 19.7 ml of hydrogen are required for the reduction of 0.1 g of PtO_2. From the difference between the calculated amount (19.7) and the amount of hydrogen obtained experimentally, the amount of hydrogen adsorbed by one gram of platinum black was calculated. As can be seen from Table 1, the amount of hydrogen adsorbed on one gram of platinum black depends on the medium. Thus, for example, in 50% ethanol, 12.9 ml of hydrogen are adsorbed on one gram of platinum black. In solutions of potassium bromide and potassium chloride the amount of hydrogen decreases on average by 1.3 ml of hydrogen and is almost independent of concentration. In the presence-

in the presence of potassium iodide, the amount of adsorbed hydrogen decreases markedly with increasing electrolyte concentration. One gram of platinum black in the presence of 1 N potassium iodide adsorbs only 2.3 ml of hydrogen. Thus, adsorption of halides not only decreases

Table 1

Dependence of hydrogen adsorption on platinum black on the medium

Solvent	Electrolyte concentration, g-equiv.	Amount of hydrogen used for reduction and saturation of 0.1 g PtO_2, ml	Amount of adsorbed H_2 per 1 g Pt black, ml
50% C_2H_5OH	0	20.8	12.9
50% C_2H_5OH + KCl	0.1	20.8	12.9
50% C_2H_5OH + KCl	0.5	20.6	10.5
50% C_2H_5OH + KBr	0.01	20.7	11.64
50% C_2H_5OH + KBr	0.1	20.7	11.64
50% C_2H_5OH + KBr	0.5	20.6	10.5
50% C_2H_5OH + KBr	1	20.6	10.5
50% C_2H_5OH + KJ	0.01	20.6	10.5
50% C_2H_5OH + KJ	0.1	20.4	8.1
50% C_2H_5OH + KJ	0.5	20.2	5.8
50% C_2H_5OH + KJ	1	19.9	2.3

the energy of the hydrogen bond with the surface ([2]), but also to a considerable extent changes the amount of hydrogen adsorbed on the catalyst surface ([3]).

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