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Abstract

Full Text

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HYDROGENATION ON Pt AND Pd WITH UNIFORM FEED OF AN UNSATURATED COMPOUND

Uniform feeding of an unsaturated compound into the reaction mixture throughout the entire experiment makes it possible to conduct the process under conditions in which the removal of hydrogen from the catalyst surface is balanced by its replenishment, and to follow the formation of the catalyst surface.

We previously found that, in the hydrogenation of allyl alcohol, eugenol, and acrolein on Raney nickel, there is a shift of the potential (ΔE) into the anodic region by 240-300 mV, which indicates removal from the catalyst surface of all surface-adsorbed hydrogen. For Raney nickel, a lag of the establishment of adsorption equilibrium behind kinetic equilibrium is characteristic. In the present work we report the results of the hydrogenation of allyl alcohol, eugenol, acrolein, and heptene-3 at 5 and 30° in 96% ethanol on Pt black and $Pd/BaSO_4$, with simultaneous measurement of the catalyst potential. Platinum oxide was prepared as usual (5). Determination of the characteristics of PtO_2 was carried out by the reduction method (2), which gave results identical with electrochemical (6) and chemical (4) results. The amount of hydrogen sorbed by platinum was 13 ml/g. This agrees with some data (2,3) and disagrees with others (4). Assuming that all the hydrogen is on the platinum surface, we calculated the latter’ s area from the hydrogen: 1.0 g of Pt black has an area of 45 m^2; in the experiment—0.1 g of PtO_2 (0.0859 g Pt) $\sim$ 3.6 m^2. $Pd/BaSO_4$ ($PdO/BaSO_4$, containing 5% Pd) was prepared as usual (1). The discharge curve taken by us resembles the platinum discharge curve, as has been noted repeatedly (2–4).

Fig. 1. Hydrogenation of allyl alcohol on $Pd/BaSO_4$ at 5°; 25.0 ml of 96% ethanol). 1—2.3 ml H_2 in 1 min.; 2—6.2; 3—10.1; 4—16.0; 5—21.2; 6—40.0; 7—46.3

The total amount of hydrogen is 6.4 ml/g $Pd/BaSO_4$, surface hydrogen—2.6 ml (52 ml/g Pd), bulk hydrogen—3.8 ml/g (76.0 ml/g Pd); the surface of the active

Fig. 2. Hydrogenation of eugenol on Pd/$BaSO_4$.

Figure 2: Fig. 2. Hydrogenation of eugenol on Pd/$BaSO_4$.

phase (Pd) on the support is 9.1 m^2/g (180-182 m^2/g Pd), in the experiment 0.1 g PdO/$BaSO_4$ (0.9 m^2).

In the hydrogenation of allyl alcohol on Pt black (0.0059-0.0267 g/min), the specified hydrogenation rate is established (2.3; 6.3; 10.4 ml H_2 in 1 min.) at 30° within 2-3 min., and at 5° within 5-6 min. The anodic shift

potential from the reversible hydrogen potential is 50-120 mV, and after the specified constant rate has been established the potential continues to shift slowly. Such a lag of the establishment of adsorption equilibrium behind the kinetic equilibrium evidently indicates that all the necessary reaction sites of the catalyst surface have been brought into action, but the adsorption displacement of hydrogen by the reaction products or by the initial molecules of allyl alcohol continues ($^{9,\ 12}$).

Fig. 2. Hydrogenation of eugenol on Pd/$BaSO_4$ (at 30°; 0.1 g Pd/$BaSO_4$; 25.0 ml of 96% ethanol). 1—2.1 ml H_2 per 1 min.; 2—6.4; 3—10.7; 4—14.2; 5—18.2; 6—29.2; 7—32.0.

In the hydrogenation of allyl alcohol on Pd/$BaSO_4$, the optimum specified rate (0.1031 g/min; 40.0 ml H_2 in 1 min.) is the same at 5 and at 30°. With a further increase in the amount of allyl alcohol, the rate of hydrogenation increases but does not remain constant (Fig. 1). Kinetic equilibrium is established in the first minute; the potential shifts into the cathodic region, and the more so, the greater the specified reaction rate. At high rates (up to 10 ml H_2 in 1 min.) the potential of the catalyst relative to the potential of saturation of the catalyst with hydrogen remains more negative throughout the entire experiment, but with increasing concentration of allyl alcohol and with accumulation of reaction products the potential rapidly shifts into the anodic region. It is possible that at low concentrations of allyl alcohol its molecules are adsorbed horizontally by the donor mechanism ($^{7,\ 9}$).

After the feed of allyl alcohol is stopped, interaction of the catalyst surface with the aldehyde takes place. In this case ($^{7,\ 10}$) there is first observed a sharp shift of the potential in the cathodic direction (possibly withdrawal of electrons from the negative end of the dipole), and then in the anodic direction as a result of reorientation of the molecules. (The presence of aldehyde in the catalyst was established by a qualitative reaction (^{11}).)

In the hydrogenation of eugenol on Pt black, changing the amount from 0.0150 to 0.0436 g/min (from 2.1 to 6.0 ml H_2 in 1 min.) entails a shift of the potential into the anodic region from 50 to 140 mV. After the constant specified rates have been established, the potential still continues slowly to shift in the anodic direction. After the feed of eugenol is stopped, the hydrogenation rate falls; the

Fig. 3. Hydrogenation of acrolein on Pt black. (at 30°; 0.1 g PtO_2; 25.0 ml of 96% ethanol). 1 –2.5 ml H_2 per 1 min.; 2 –3.8; 3 –6.1; 4 –8.4

Figure 3: Fig. 3. Hydrogenation of acrolein on Pt black. (at 30°; 0.1 g PtO_2; 25.0 ml of 96% ethanol). 1 –2.5 ml H_2 per 1 min.; 2 –3.8; 3 –6.1; 4 –8.4

potential shifts in the cathodic direction, but does not reach the reversible value to a greater extent, the higher the concentration of eugenol (especially···

especially at 5°, which indicates an ever-increasing desorption of hydrogen from the catalyst surface.

Figure 2 presents the kinetic and potentiometric curves for hydrogenation of eugenol on $Pd/BaSO_4$. The constant imposed rate is established in 1-2 min. and, up to 29.2 ml H_2 per 1 min., remains constant; at rates greater than 10 ml H_2 per 1 min. there is a small ΔE, but with increasing concentration ΔE increases, reaching 140 mV at 5°.

The constant rate of hydrogenation of acrolein on Pt black is attained when the substance is supplied at only 0.0048 (at 5°) and 0.0062 g/min. (at 30°), which corresponds to 1.9 and 2.5 ml H_2 per 1 min. As is seen from Fig. 3, at an imposed rate of 8.4 ml/min. (curve 4) the rate of hydrogenation falls in the second half. After the supply of acrolein is stopped, hydrogenation proceeds at a low rate and after some time ceases, although an excess of it is present in the catalyst. The shift of the potential during the reaction can be explained by the ever-increasing adsorption of the aldehyde on the catalyst surface. With cessation of the supply of acrolein, dehydrogenation of the latter proceeds with a cathodic shift of the potential.

Fig. 3. Hydrogenation of acrolein on Pt black. (at 30°; 0.1 g PtO_2; 25.0 ml of 96% ethanol).
1 –2.5 ml H_2 per 1 min.; 2 –3.8; 3 –6.1; 4 –8.4

In the case of hydrogenation of acrolein on $Pd/BaSO_4$, kinetic equilibrium (2.0; 3.8; 6.0; 8.3 and 10.4 ml H_2 per 1 min. at 30°) is reached after 2-3 min., and the potential during the reaction shifts all the time into the anodic region, reaching 490 mV (at 5° $\Delta E = 200$ mV), i.e., probably, an oxidative process begins. In the hydrogenation of heptene-3 on Pt black, in the case of small amounts of heptene (0.0079 g/min.; 1.8 ml H_2 per 1 min.) the reaction rate is small and does not reach the imposed value, but with an increase in concentration to 0.0565 g/min. (12.4 ml H_2 per 1 min.) it increases sharply, exceeding the calculated value, then decreases and only after 45 min. assumes a constant value, almost corresponding to the rate of supply of heptene-3.

Table 1

Substance	Ni skeletal 5°	Ni skeletal 30°	Pt black 5°	Pt black 30°	$Pd/BaSO_4$ 5°	$Pd/BaSO_4$ 30°
Allyl alcohol	2.2	4.5	3.07	2.66	39.0	39.0
Eugenol	1.1	2.0	1.71	1.71	27.0	29.0
Acrolein	0.6	1.9	1.71	1.71	~10.0	10.0
Heptene-3	–	–	3.04	3.04	2.0	2.6

On $Pd/BaSO_4$ (0.3 g $PdO/BaSO_4$) at 30°, in the case of low concentrations (2.0-2.5 ml H_2 per 1 min.) the reaction rate reaches the imposed value after 3-4 min.; with increasing concentration the rate does not reach the imposed value, and this difference is the greater, the higher the concentration of heptene-3, while the rate slowly increases during the experiment. The maximum shift of the potential to the anodic side also increases (from 20 to 70 mV at 30°; from 80 to 210 mV at 5°), which indicates an ever-increasing desorption of hydrogen.

For comparison of the catalysts studied, we give data on the rate of hydrogen reproduction during hydrogenation of the compounds studied, calculated per 1 m^2 of the active phase of the catalyst (specific rates of hydrogen reproduction).

As can be seen from the data in Table 1, the rate of hydrogen reproduction on the surface of the given catalyst depends on the nature of the compound being hydrogenated; on Ni and Pt it is 5-15 times slower than on Pd.

Potentiometric hydrogenation with uniform feeding of the unsaturated compound into the reaction mixture makes it possible to follow the formation of the catalyst surface. It turned out that, in the presence of compounds with high adsorption capacity, the catalyst surface is formed much more rapidly than in the presence of substances with low adsorption capacity.

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