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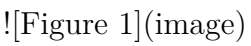

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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HYDROGENATION OF UNSATURATED COMPOUNDS UNDER EQUILIBRIUM CONDITIONS ON PLATINUM-GROUP CATALYSTS

Hydrogenation of unsaturated compounds with their slow and uniform feeding into the reaction vessel makes it possible to carry out the process under equilibrium conditions, at an almost zero concentration of the unsaturated substance and with a constant reaction rate from the moment a stationary regime is established. In the present work a comparison is made of the results obtained in the hydrogenation by this method of sodium maleate, sodium *o*-nitrophenolate, and dimethylacetylenylcarbinol in alkaline and alcoholic media. As was shown earlier (ˆ1), sodium maleate and sodium *o*-nitrophenolate are hydrogenated at a constant rate and at a constant ΔE, which increase to a certain maximum, characteristic for the given substance, as the concentration of the unsaturated compound in the solution being added is increased.

Fig. 1. Hydrogenation of sodium maleate in 0.1 N NaOH at 20° on skeletal nickel (1), platinum (2), and palladium on $CaCO_3$ (3).

Figure 1 presents curves showing the maximum hydrogenation rates of sodium maleate and the corresponding ΔE values in 0.1 N NaOH at 20° on skeletal Ni, Pt, and $Pd/CaCO_3$ (5%).

It is evident from Fig. 1 that, in the hydrogenation of sodium maleate on skeletal Ni, a constant reaction rate is established 5 min after the beginning of the addition. During this time the potential shifts into the anodic region by 66 mV and continues to fall. After 15 min from the beginning of the experiment ΔE reaches a value of 104 mV and no longer changes. This shift of the potential after the rate of reaction becomes constant indicates additional adsorption of the substance on such catalyst centers as do not participate in the reaction.

The kinetic and potential curves obtained in the hydrogenation of sodium maleate on $Pd/CaCO_3$ have a somewhat different form. A constant reaction rate is established after 2 min. During this time the potential shifts sharply into

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

the anodic region by 97 mV. After 5 min from the beginning of the experiment ΔE reaches 126 mV and remains constant. The rapid removal of hydrogen from Pd and the establishment of equilibrium conditions for hydrogenation are connected with the relative homogeneity of its surface and the approximately identical energy of bonding of hydrogen to it. On Pt the constant potential is established earlier than the constant rate of hydrogenation. Sodium maleate, which has a weak adsorption potential, cannot be adsorbed rapidly on Pt, with whose surface hydrogen is strongly bound. Therefore

hydrogenation of sodium maleate on Pt proceeds with a considerable coverage of the catalyst surface by hydrogen ([2]).

For sodium *o*-nitrophenolate, which has a high adsorption potential, the character of the curves changes somewhat (Fig. 2). On skeletal nickel, the constant reaction rate, as well as the constant $\Delta E = 110$ mV, is established simultaneously 7 min after the start of hydrogenation. The potential shift by 110 mV indicates that hydrogen does not have time to be activated on the catalyst surface and that part of the compound is hydrogenated at the expense of adsorbed hydrogen ([3]).

Fig. 2. Hydrogenation of sodium *o*-nitrophenolate in 0.1 N NaOH at 20° on skeletal nickel (1), platinum (2), and palladium on $CaCO_3$ (3).

Fig. 3. Hydrogenation of dimethylethynylcarbinol in 0.1 N NaOH at 20° on skeletal nickel (1), platinum (2), and palladium on $CaCO_3$ (3).

Adsorption and kinetic equilibria on Pd, as in the case of the hydrogenation of sodium maleate, are established in the first minute of hydrogenation.

Hydrogen strongly bound to the platinum surface is rapidly removed by sodium *o*-nitrophenolate: a constant potential is established in the first minute. However, the renewal of hydrogen on the catalyst surface occurs considerably more slowly than its removal. Owing to this, kinetic equilibrium is established not immediately, but 10 min after the start of the experiment.

Figure 3 presents the hydrogenation of dimethylethynylcarbinol under the same conditions and on the same catalysts. On the nickel surface, dimethylethynylcarbinol is hydrogenated with considerable coverage of the catalyst surface by hydrogen ($\Delta E = 34$ mV), and on palladium—with almost half coverage of the catalyst surface by the hydrogenated substance ($\Delta E = 180$ mV).

Comparing the potential shift during the hydrogenation of sodium maleate,

sodium *o*-nitrophenolate, and dimethylethynylcarbinol on skeletal nickel, platinum, and palladium on $CaCO_3$ in 0.1 N NaOH, we can immediately see how the character of adsorption of the substance changes on going from one catalyst to another, and what coverage of the catalyst surface by the hydrogenated substance is most favorable for the given process.

In the presence of an excess of any of the listed substances on any catalyst, an additional shift of the potential into the anodic region occurs. But the maximum hydrogenation rates do not increase in this case—

are observed. The shift of potential that we observe at a constant reaction rate is $\Delta E_{\text{react.}}$. The additional shift of the potential already indicates the presence on the catalyst surface of an unsaturated substance adsorbed on centers that do not participate in the hydrogenation process, $\Delta E_{\text{adsorb.}}$.

Hydrogenation of sodium maleate, sodium *o*-nitrophenolate, and dimethylethynylcarbinol in an alcoholic medium on skeletal nickel, platinum, and palladium on $CaCO_3$ leads to the same regularities. Only the constant reaction rate and the constant ΔE for any substance and on any catalyst are established more rapidly than in an aqueous medium. Owing to the weaker bond of a part of the hydrogen with the catalyst surface in the alcoholic medium, the rate of its removal increases and, simultaneously, so does its restoration on the catalyst surface. This leads to an increase in the hydrogenation rates of the substances and to a greater shift of the potential $\Delta E_{\text{react.}}$.

It is interesting to note that small amounts of dimethylethynylcarbinol on nickel and platinum in an alcoholic medium at 20° shift the potential into the cathodic region. Such shifts of the potential into the cathodic region may be caused by removal of positively charged hydrogen and by the different rate of restoration of the equilibrium between the forms of hydrogen on the surface ([3]).

Hydrogenation with slow and uniform feeding of the substance into the catalytic vessel promotes prolonged operation of the catalyst, since the removal of hydrogen by the substance being hydrogenated from the catalyst surface and its restoration on the surface are regulated by the rate of feeding of the unsaturated compound into the reaction vessel.

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