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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE ROLE OF HYDROGEN IN THE DEHYDROGENATION OF CYCLOHEXANE ON PLATINUM

H. Taylor was the first to suggest that the process of dehydrogenation both on metals and on oxides is limited by the desorption of hydrogen (^{1}). However, A. A. Balandin (^{2}) showed that the activation energy of the dehydrogenation process on metals is determined by the bond energies of the reacting atoms with the catalyst atoms. The available literature data give grounds to suppose that the kinetics and mechanism of the dehydrogenation process depend substantially on the nature of the catalyst. Thus, M. Ya. Kagan and N. A. Shcheglov (^{3}) showed that the kinetics and mechanism of dehydrogenation on platinized pumice (4%Pt) do not change appreciably upon dilution of cyclohexane with benzene, hydrogen, and nitrogen, and they concluded that the adsorption coefficients of all components of the reaction are close in value. Results close to these were obtained in work (^{4}) in the dehydrogenation of methylcyclohexane on Pt/C. On the other hand, in (^{3}) inhibition of the process by benzene is noted in dehydrogenation on Ni/Al_2O_3. Inhibition of the dehydrogenation of cyclohexane by benzene has been observed for Pd (^{5}) and Ni (^{6}) catalysts.

S. L. Kiperman considers the dissociative adsorption of cyclohexane to be the limiting stage for the $Pt \cdot HF \cdot Al_2O_3$ catalyst, while for the dehydrogenation process on nickel the concept is introduced of the presence of two slow stages (^{7}). In both cases it is especially emphasized that

Table 1

Dehydrogenation of cyclohexane on Pt foil at different initial potentials of the catalyst

Temperature of experiment, °C	Initial potential of catalyst, mV	Reaction rate, ml H_2/min NTP	Steady-state potential of catalyst, φ_{st}, mV	$\Delta\varphi^*$, mV	Degree of conversion, refractometric, %
I. Region of reversible hydrogen potential	**I. Region of reversible hydrogen potential**	**I. Region of reversible hydrogen potential**	**I. Region of reversible hydrogen potential**	**I. Region of reversible hydrogen potential**	**I. Region of reversible hydrogen potential**
200	1180	4.7	1040	200	0.9
215	1200	8.4	1100	140	1.4
230	1150	8.4	1130	110	2.0
250	1150	8.4	1120	120	2.0
275	1220	12.5	1090	130	2.5
300	1200	20.9	1220	20	3.5
II. Region of oxygen potential	**II. Region of oxygen potential**	**II. Region of oxygen potential**	**II. Region of oxygen potential**	**II. Region of oxygen potential**	**II. Region of oxygen potential**
200	70	4.7	1040	200	0.6
215	20	4.7	1040	200	0.9
230	20	8.4	1070	170	1.0
250	95	8.4	1080	160	1.8
275	40	8.4	1060	180	2.0
300	110	16.0	1160	80	3.5
III. Region of intermediate potential values	**III. Region of intermediate potential values**	**III. Region of intermediate potential values**	**III. Region of intermediate potential values**	**III. Region of intermediate potential values**	**III. Region of intermediate potential values**
200	840	4.7	910	–	–
230	980	4.7	1060	180	0.9
250	940	8.4	1070	170	2.0
275	980	8.4	1110	130	1.9
300	1030	12.5	1220	20	3.5

* $\Delta\varphi$ –shift of the potential during the reaction from the reversible hydrogen potential,
$\Delta\varphi = 1240 - \varphi_{st}$.

at high reaction temperatures neither cyclohexane nor hydrogen is practically adsorbed by the catalyst.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

P. Tetenyi and co-workers showed, using the example of the dehydrogenation of a series of hydroaromatic hydrocarbons on metallic nickel, that neither desorption of hydrogen nor desorption of the second reaction product can be the limiting stages (8). For metallic nickel it was shown by a kinetic method that the adsorption coefficient of hydrogen decreases linearly with temperature (9). It should be noted, however, that as the temperature increases, the rate of the dehydrogenation process increases and the partial pressure of hydrogen in the reaction mixture rises. This may lead to an increase in hydrogen adsorption even when its adsorption coefficient decreases.

Fig. 1. Effect of temperature on the reaction rate and change in the catalyst potential during the dehydrogenation of cyclohexane on platinum in a hydrogen atmosphere.
1 –275°, 2 –250°, 3 –230°, 4 –215°, 5 –200°. 1′, 2′, 3′, 4′, 5′ –corresponding changes in the catalyst potential.

In the present work, the previously described method and apparatus for measuring the catalyst potential in the gas phase (10) were used to study the process of cyclohexane dehydrogenation on a platinum film. In a preliminary series of experiments, the dehydrogenation of individual cyclohexane was studied at different initial catalyst potentials and different temperatures. Under steady-state conditions the reaction proceeded at a constant rate, which corresponded to a definite stationary catalyst potential. The results of these experiments are summarized in Table 1. The data in Table 1 make it possible to note a number of general regularities. The introduction of cyclohexane at the reversible hydrogen potential leads to a shift of the catalyst potential in the anodic direction by 20–200 mV, depending on the reaction temperature. The introduction of cyclohexane at an oxygen or intermediate potential causes a considerable cathodic shift of the potential. The magnitude of the stationary catalyst potential at a given temperature depends little on the initial value of the potential. Consequently, the magnitude of the stationary catalyst potential is a single-valued function of the reaction temperature or, correspondingly, of the amount of hydrogen evolved. With increasing temperature the reaction rate increases, and the partial pressure of hydrogen in the reaction mixture rises. In accordance with this, the value of the stationary catalyst potential becomes increasingly cathodic, and the coverage of the catalyst surface with hydrogen increases.

Fig. 2. Change in catalyst potential during the dehydrogenation of cyclohexane on platinum in a nitrogen atmosphere ($t = 300°$).

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1 —experiment begun at the reversible hydrogen potential; 2 —experiment begun at a potential in the oxygen region.

In the limit, at sufficiently high rates of the process, the dehydrogenation of cyclohexane proceeds with a shift of the potential of only 20-80 mV, i.e., it takes place on a surface almost completely filled with hydrogen. This evidently permits the assumption that adsorption of cyclohexane and of hydrogen on platinum occurs on different surface sites, without mutual adsorption displacement. This gave grounds for supposing that, when hydrogen is used as the carrier gas, the overall picture will not change substantially. Indeed, as can be seen from Fig. 1, in this case as well, with increasing temperature and increasing reaction rate the degree of filling of the catalyst surface with hydrogen increases, while the stationary potential of the catalyst becomes increasingly cathodic. The situation also does not change substantially when nitrogen is used as the carrier gas (Fig. 2). Thus, the dehydrogenation of cyclohexane on platinum is carried out at relatively high coverages of the surface with hydrogen. At the same time, adsorption of hydrogen does not suppress the process of cyclohexane dehydrogenation.

In contrast to this, the hydrogenation of benzene on platinum does not proceed at all at the reversible hydrogen potential ([10]). Only the forced removal of part of the adsorbed hydrogen leads to the reaction beginning to proceed at an appreciable rate. The maximum degree of benzene conversion in this case is observed with a preliminary shift of the catalyst potential by 250-300 mV, i.e., the reaction is carried out on a surface almost free of hydrogen. These facts make it possible to suppose that, both in the hydrogenation of benzene and in the dehydrogenation of cyclohexane on platinum, adsorption displacement of benzene by hydrogen takes place.

The peculiarity of the process of cyclohexane dehydrogenation on platinum is associated with the fact that the magnitude of the shift of the catalyst potential increases as the temperature is lowered. This is evidently due to the fact that the removal of part of the adsorbed hydrogen is caused by the reverse reaction—the hydrogenation of benzene. The lower the temperature, the greater the rate of the reverse reaction, and the greater the shift of the catalyst potential.

With increasing temperature, however, the partial pressure of hydrogen in the reaction mixture rises, the degree of filling of the surface with hydrogen increases, which leads to adsorption displacement of benzene by hydrogen and suppression of the reverse reaction.

Thus, the peculiar behavior of the platinum catalyst in the dehydrogenation process is due to the increase in hydrogen adsorption with increasing temperature. For the liquid phase an analogous phenomenon was noted by D. V. Sokol' skii and K. N. Kambarov ([11]).

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