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Abstract

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Dependence of the Catalytic Properties of Metals on the Degree to Which the State of Their Surface Approaches Equilibrium

(Presented by Academician A. A. Balandin, 17 IX 1960)

Metallic catalysts differ from all others in the simplicity of their chemical composition, which facilitates a thermodynamic analysis of the conditions of equilibrium between active centers and the crystal lattice of the catalyst. A study of the kinetics of allylbenzene isomerization on platinum films (⁀1), as well as on platinum, palladium, and tungsten wires (⁀2), showed that their catalytic activity is retained at temperatures that exceed not only the temperature at which mobility of the surface atoms of the metal appears ($T > 0.3T_{\mathrm{m}}$), but also the temperature at which appreciable crystal growth begins, T_R, which, as is known (see, for example, (⁀3)), for metals is close to $0.4T_{\mathrm{m}}$. On the basis of these data and of the abrupt increase in the experimental activation energy at temperatures 0.36—0.38 T_{m}, the suggestion was made (^{1,}2) that, when the surface atoms are sufficiently mobile, equilibrium is established between the catalyst lattice and the active centers.

Indeed, in the presence of such equilibrium the concentration of active centers will depend exponentially on the heat of their formation, which will enter into the experimental activation energy, sharply increasing it in comparison with the value found at lower temperatures and referring only to the catalytic reaction.

O. M. Poltorak (^{4,}5) analyzed the conditions of equilibrium

$$\text{nonequilibrium lattice} \rightleftarrows \text{active centers,}$$

characterizing the degree of nonequilibrium of crystals, which depends on their dispersity (or mosaic period) and on the presence in real crystals of other forms of faceting than in equilibrium crystals, by the quantity $\Delta\lambda_r = \lambda_\infty - \lambda_r$, where λ_∞ is the heat of sublimation of large, regularly faceted crystals and λ_r is the mean energy of detachment (per mole) of atoms from the surface of crystal faces of a given type. Proceeding from these ideas, he considered various types of dependence of the number of active centers on the calcination temperature of the catalyst. However, in any case, at temperatures above T_R, $\Delta\lambda_r \to 0$, and the concentration of active centers should approach the extremely small value that follows from defect theory for ideal crystals.

The experimental data cited above on the presence of catalytic activity at temperatures above T_R cannot be associated with $\Delta\lambda_r$ differing substantially from zero, since the catalysts had undergone too severe a heat treatment. To explain these results, the hypothesis was advanced ($^\frown$2) that the active centers, being in equilibrium with the catalyst lattice, possess two translational degrees of freedom. As is known, adsorbed atoms and molecules in some cases may be regarded as a two-dimensional gas possessing ent-

the entropy of two-dimensional translational motion. However, in works on the theory of evaporation processes of metallic crystals (for example, ((1))) the entropy of translational motion is neglected. O. M. Poltorak (4) likewise did not consider the entropy of translational motion of atoms over the crystal surface. Taking this quantity into account, however, makes it possible to explain the presence of catalytic activity at high temperatures. The pre-exponential factors of the rate constants for the isomerization of allylbenzene on platinum films, as well as on platinum and palladium wires, calculated on the basis of the indicated hypothesis, agree satisfactorily with experiment (2).

If the study of the kinetics of a catalytic reaction over a sufficiently broad temperature range makes it possible to judge the degree to which the active centers approach equilibrium with the catalyst lattice, then this method can be used to elucidate the influence of temperature and of the conditions of preliminary heat treatment on the catalytic properties of a metal. In particular, at temperatures that do not ensure attainment of the equilibrium concentration of active centers, the degree of approach to it must depend mainly on the cooling rate of the catalyst that has been held at a higher temperature. After rapid cooling of the catalyst, the concentration of active centers will differ more strongly from the equilibrium value than after slow cooling.

In the case of catalytic activity of atomic structures consisting of different numbers of atoms, the rates at which their equilibrium concentrations are established will be unequal. Apparently, the activation energy of the process by which equilibrium is established will increase from simple centers to complex ones. Therefore, with increasing temperature, other conditions being equal, the equilibrium concentrations will be reached first for simple centers and then for more complex centers. A change in the ratio of the concentrations of different active centers will lead to a change in the selectivity of the catalyst action.

The expected effects were observed in a study of the transformations of cyclohexene on a platinum film. When the platinum film was heated to no higher than 500°, dehydrogenation of cyclohexene to benzene was observed. At temperatures of 290–485° the experimental activation energy of this reaction is equal to 23.7 ± 0.5 kcal/mole. After heating the film in high vacuum at 700°, cyclohexene begins to be converted on it at an appreciable rate only at temperatures above 450°, with cyclohexadiene-1,3 being formed. According to what was set forth above, this makes it possible to regard the active centers on which dehydrogenation to benzene occurs as more complex and, at temperatures up to 700°, thermodynamically less stable than the centers responsible for the formation of cyclohexadiene from cyclohexene. The preservation of these more complex centers at 500° indicates a high activation energy for the process of their destruction.

For two series of experiments with an increase in temperature to 600°, the experimental activation energy of cyclohexadiene formation at 520-600° is the same and equal to 60 kcal/mole. At lower temperatures the catalyst activity decreased, and in a third series of experiments the experimental activation energy was 60 kcal/mole over the entire temperature range from 450 to 600°. This points to the establishment of the equilibrium concentration of active centers, which is confirmed by the agreement of the results obtained at 544° before and after the experiment at 600° in the third series. When, however, the activity of the catalyst at 544° was determined by nonequilibrium centers, it decreased, approaching the level that was found in the third series of experiments.

After "quenching" the film (cooling from 700 to 460° over the course of 4 min), the activation energy of cyclohexadiene formation at temperatures below 530° decreased to 26 kcal/mole and the activity of the film increased sharply, whereas in the region of higher temperatures these parameters remained as before. It should be noted that the difference between the experimental activation energies, $60 - 26 = 34$ kcal/mole, proved to be the same as for the isomerization of allylbenzene on

films of platinum (⁀1). This makes it possible to assume that both reactions proceed on equilibrium active centers of the same type. If the nonequilibrium active centers that appear after quenching or in the course of synthesis of the catalyst have the same nature as those in equilibrium with the catalyst lattice, then the heat of formation of the latter can be determined by means of formula (8) of paper (⁀2) from the difference in experimental activation energies on equilibrium and nonequilibrium active centers.

To elucidate the mechanism of formation from cyclohexene either of benzene or of cyclohexadiene, depending on the conditions of preparation and heat treatment of the metallic catalyst, a special investigation is necessary. The data given above, as well as their comparison with the results of experiments on films of palladium and platinum that were not heated above 200°, indicate the existence of such a dependence. Thus, on palladium films (⁀7) at temperatures from 50 to 150° cyclohexene is not dehydrogenated, but is converted according to the equation:

$$3C_6H_{10} = C_6H_6 + 2C_6H_{12}. \tag{1}$$

This is in complete agreement with the results obtained by N. D. Zelinskii and G. S. Pavlov (⁀8) with an active palladium catalyst, on which dehydrogenation was observed at higher temperatures. The degree of conversion of cyclohexene according to the equation

$$C_6H_{10} = C_6H_6 + 2H_2 \tag{2}$$

increased from 1% at 164° to 89% at 320°. No unsaturated hydrocarbons were found in the catalyzates; therefore the sum of the percentages of conversion of cyclohexene according to equations (1) and (2) must be close to 100 at a given temperature. Comparison of the percentages of conversion according to reaction (1), calculated from the refractive indices of the catalyzates given in paper (^8), with the percentages of dehydrogenation reported there confirmed this. An analogous result was obtained by B. V. Erofeev and N. V. Nikiforova (^9) in studying the conversion of cyclohexene on copper catalysts: with an increase in temperature from 249 to 350° the percentage of conversion according to equation (1) decreases, while the percentage of dehydrogenation increases. Assuming, in accordance with A. A. Balandin’ s multiplet theory (^10), that process (1) takes place on triplets and process (2) on doublets, the authors explain these results by a decrease in the number of triplets as compared with the number of doublets when the temperature is raised. Taking into account data (^11) on the considerable mobility of atoms on the copper surface at the temperatures of catalytic experiments, B. V. Erofeev and N. V. Nikiforova (^9) regard multiplets as unstable atomic aggregates, the number of which can be determined by the conditions of equilibrium between the multiplets and the crystal.

However, the opposite dependence of the percentages of conversion of cyclohexene according to equations (1) and (2) on temperature was observed by N. D. Zelinskii and G. S. Pavlov (^8) at temperatures much lower than those at which the mobility of palladium atoms over the surface of its crystals can become manifest. The change in the ratio of the rates of reactions (1) and (2) with increasing temperature found in works (^{8,}9) may be due to a difference in their activation energies. The degree of inhibition of these reactions by the adsorbed conversion products may also be different. Therefore the explanation proposed by B. V. Erofeev and N. V. Nikiforova (^9) is not the only possible one.

The assumption that, at the temperatures used in work (^9), 249-350° (0.39-0.46 T_m of copper), the crystals of the copper catalysts are in equilibrium with the active centers is consistent with the data given above, which indicate the establishment of an equilibrium concentration of active centers carrying out reaction (2) at temperatures above 0.38

T_m of platinum. In the interval $0.36 \div 0.38\,T_\mathrm{m}$, equilibrium was established between the active centers for the isomerization of allylbenzene and the platinum film (1). It may be expected that this regularity will also hold for other metals.

The foregoing shows that studying the kinetics of catalytic reactions over a broad temperature range makes it possible to judge the degree to which equilibrium is attained between the active centers and the catalyst lattice, on the basis of which the influence of heat treatment on the activity and selectivity of the catalyst can be explained.

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CITED LITERATURE

[1] V. I. Shimulis, V. M. Gryaznov, A. E. Cherkashin, *Kinetics and Catalysis*, **1**, No. 3 (1960).
[2] V. I. Shimulis, V. M. Gryaznov, A. E. Cherkashin, Reports at the Conference on Organic Catalysis, Moscow, 1959; *Kinetics and Catalysis*, in press.
[3] V. Zait, *Diffusion in Metals*, Moscow, 1958.
[4] O. M. Poltorak, *ZhFKh*, **29**, 1650 (1955); **33**, 2524 (1959).
[5] O. M. Poltorak, *Kinetics and Catalysis*, Moscow, 1960, p. 187.
[6] J. Hirth, G. Pound, *J. Chem. Phys.*, **26**, 1216 (1957).
[7] V. M. Gryaznov, V. D. Yagodovskii, M. K. Charkviani, *Bulletin of Moscow University*, Ser. II, Chemistry, No. 1, 11 (1960).
[8] N. D. Zelinsky, G. S. Pavlov, *Ber.*, **57**, 1066 (1924).
[9] B. V. Erofeev, N. V. Nikiforova, Reports at the 11th International Congress on Catalysis, Paris, 1960.
[10] A. A. Balandin, *ZhRKhO*, **61**, 909 (1929).
[11] A. T. Gwathmey, R. E. Cunningham, *Advances in Catalysis*, **10**, 57 (1958).

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

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