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Abstract

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THE ACTION OF A REACTION MIXTURE ON A CATALYST UNDER CATALYSIS CONDITIONS

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In recent years a considerable number of works have appeared indicating changes in the properties of a catalyst in the course of catalysis, connected with the action of the reaction mixture on the catalyst ([1]). Changes in the composition and properties of a catalyst due to the action of the reaction mixture were considered in general form by G. K. Boreskov ([2]). In ([3]) it was found that the interaction of fused iron catalysts with the components of the reaction mixture in synthesis from CO and H_2 proceeds differently in the presence and in the absence of the catalytic reaction. Further consideration of this question showed that the occurrence of the catalytic reaction in most cases substantially affects the interaction of the catalyst with the components of the reaction mixture, and the catalyst—reacting-mixture system may acquire fundamentally new properties. Some of the results obtained are set forth in the present communication.

Let a catalytic reaction proceed in a flow system

$$a_1 A_1 + a_2 A_2 + \cdots = b_1 B_1 + b_2 B_2 + \cdots \tag{I}$$

and let the catalyst (K) be capable of existing in several different states, one of which, K_a, is active, while K_c is thermodynamically stable under the given conditions in the absence of catalysis

$$\mathrm{K}_1 \to \mathrm{K}_2 \to \cdots \to \mathrm{K}_a \to \mathrm{K}_{a+1} \to \cdots \to \mathrm{K}_c. \tag{II}$$

Let us further suppose that at least one of the stages of catalyst transformation, namely the stage $\mathrm{K}_a \to \mathrm{K}_{a+1}$ (we shall call it deactivation), proceeds with participation of components of the reaction mixture. This general model has the limitation that only one of the states of the catalyst is assumed to be active. However, this latter assumption is not essential and is introduced to make the discussion more transparent. What is essential is only that K_a is not identical with K_c. Since, apart from those indicated, no other assumptions or suppositions have been introduced,* the subsequent arguments are general in character and apply both to heterogeneous and to homogeneous catalysis, although for definiteness we shall speak of a solid catalyst.

According to the laws of behavior of the catalyst—reaction-mixture system, three types of systems may be distinguished:

Systems of type A, in which the deactivation stage proceeds with participation of the products of the catalytic reaction.

Systems of type B, in which the deactivation stage proceeds with participation of the initial components of the catalytic reaction, and the reverse transition $\mathrm{K}_c \to \mathrm{K}_a$ is impossible under the given conditions.

Systems of type C, in which the deactivation stage proceeds with participation of the initial components of the catalytic reaction, and under the given conditions the reverse transition $\mathrm{K}_c \to \mathrm{K}_a$ is possible with a finite, even if extremely small, rate.

Systems of type A in pure form are uncommon. The stationary composition of the catalyst for systems of this type does not depend on the rate of catalysis; for its characterization the method developed in (^{2}) is applicable. An estimate of the rate of attain— ···of the stationary composition can be carried out on the basis of the method[^4]. Systems of type B are less widespread than systems of type V. In such systems there must be no possibility for competing or reversible reactions of the catalyst with the components of the reaction mixture to occur. As an example one may cite the polymerization of olefins on chromium oxide catalysts, accompanied by reduction of the catalyst (oxidation of the catalyst is excluded in this case).

In systems of type B, the interaction of the reacting molecule A_i with K_a may lead both to the occurrence of the stage $K_a \to K_{a+1}$ and to the catalytic reaction, which is expressed in simplified form by the scheme

$$\begin{array}{c} K_{a+1} \\ \uparrow \\ K_a + A_i \\ \downarrow \\ \text{product of catalysis} + K_a \end{array}$$

Since some of the molecules A_i interacting with the catalyst will be consumed in the catalytic reaction, the rate of the stage $K_a \to K_{a+1}$ during the catalytic reaction will be lower than in its absence. Consequently, when the catalytic reaction proceeds in systems of type B, the lifetime of the catalytically active state of the catalyst surface increases; in other words, other conditions being

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* The assumption of several states of the catalyst surface possessing different activities is justified, for example, by the different activity of different crystal faces. In addition, it is necessary that deactivation and the catalytic reaction have at least one common stage (for example, impact of A_i on the surface).

equal, the stability of the catalytically active state of the surface increases. To characterize the increase in this stability one may introduce the concept of the stability factor (η), expressing the number of acts of catalysis occurring at the active center K_a before its deactivation. The quantity η may be estimated approximately from the formula

$$\eta = W_{\mathrm{ud}}/V_{\mathrm{ud}}, \tag{1}$$

where W_{ud} and V_{ud} are the specific rates of the catalytic reaction and of the stage $K_a \to K_{a+1}$,* respectively (referred to a unit amount of K_a). When $W_{\mathrm{ud}} \ll V_{\mathrm{ud}}$, $\eta \to 0$; the state K_a is practically not catalytically active, and no increase in the stability of active centers occurs; the catalyst rapidly loses activity. In the opposite limiting case, when $W_{\mathrm{ud}} \gg V_{\mathrm{ud}}$ and $\eta \to \infty$, the deactivation stage is practically completely suppressed by the catalytic reaction; the concentration of K_a is pseudostationary and close to the maximum possible; the catalyst operates for a long time without loss of activity. In the general case, the stability of the active state of the catalyst surface increases with increasing η.

Thus, the stability of catalysts in systems of type B can be increased by increasing the value of the factor η through changes in the reaction conditions, promotion, etc.; in principle, one can thereby obtain a practically stationarily operating catalyst. Another way of increasing the stability of catalysts in systems of type B is to introduce into the reaction mixture components that interact with the catalyst in the direction opposite to the deactivation stage. In this way we essentially pass to systems of type V, which will be considered below. Let us only note that such a transition may also be achieved by changing the experimental conditions, promotion of the catalyst, etc.

Systems of type V are widely encountered in catalysis (oxidation on metals and oxides, syntheses from CO and H_2 on iron catalysts, etc.). In systems of this type, the stage $K_a \to K_{a+1}$, as in systems of type B, is suppressed by the catalytic reaction; the rate of this stage decreases during the catalytic process. At the same time, the rate of the competing reaction (V'_{ud}), leading to regeneration of active states, does not change during catalysis. Therefore, in systems of type V, during the catalytic reaction, the concentration of the states active for the given reaction

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* The stage $K_a \to K_{a+1}$ may proceed with participation of the solid phase. The method for determining the specific rates of reactions of this type is set forth in[^4].

of the surface is always higher than in the absence of catalysis, and for any initial state of the catalyst (not identical with K_a) increases to one and the same steady-state concentration.

Systems of this type are thus self-adjusting systems, the role of feedback being played by the dependence of the rate of transformation of active centers on their activity. The catalytic reaction as it were selects the most active states of the catalyst surface and stabilizes them. At sufficiently large values of the factor η, the active centers in the steady state will predominate on the catalyst surface, although in the absence of the catalytic reaction their steady-state concentration may be close to zero.

The steady-state concentration of active states (C_a) in systems of type B can be determined from kinetic data. Thus, for a system with one active state, when the specific reaction rate is independent of C_a, it is determined in the first approximation by the formula

$$C_a = \frac{1}{1 + V_{\mathrm{ud}}^2 / V_{\mathrm{ud}}^{\mathrm{ud}} W_{\mathrm{ud}}}\,. \tag{2}$$

The quantities entering into equation (2) depend on the experimental conditions (concentration, temperature), and the observed kinetics of the catalytic reaction in the general case includes these dependences. In the presence of several active states of different activity, two cases are possible: either the concentration of different centers (all other conditions being equal) is approximately proportional to their activity, or the more active state practically completely displaces all the others. The steady-state concentrations of active states can also in this case be determined from kinetic data.

Enrichment of the reaction mixture with components participating in the stage of regeneration of active states makes it possible, within known limits, to increase the steady-state activity of the catalyst.

Among other features of these systems we note that there exist at least three regions characterized by different kinetics, the transition between which may occur upon changing the experimental conditions (temperature, concentration, etc.).

On the basis of the foregoing discussion, the properties of particular systems can be predicted. The formal assignment of a system to one of the types considered, or to a mixed type, is as a rule easily determined.

It should also be noted that consideration of the mechanism of heterogeneous catalytic reactions with allowance for developed concepts makes it possible to expect, in a number of cases, quite simple true equations for the reaction rate and for the prevalence, in heterogeneous catalysis, of active states of the type of solid solutions.

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

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