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NATURE OF THE ACTIVE SURFACE OF METALLIC CATALYZERS

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Generally a sharp boundary is drawn between mixed and simple catalyzers. The catalytic action of the latter is considered to be their basic property which requires, however, for its clearer manifestation, special «active structures». As far back as 1935 our observations showed for the first time the essential importance of the gases entrapped by metallic nickel, in producing active preparations. These observations disclosed a new, theretofore neglected, source of promotion of simple pure catalyzers, and so put to doubt the veracity of the above standpoint (1).

Further experiments were started in our laboratory along two lines: checking the possibility of retaining catalytic activity in degasified massive metals and studying the influence of dosed admixtures of gases on the activity. These experiments showed that for all the metals studied, degasification results in total loss of catalytic activity at low temperatures (2,3). The objects of study in the latter case were transitional elements, mainly metals of the VIII group, which are the most typical catalyzers in oxidation and hydrogenation reactions. The following metals were studied in relation to the hydration of ethylene and partly in relation to the oxidation of hydrogen: platinum, palladium, iron, nickel and tungsten. Activation due to the presence of gases and disactivation by degasification is especially clearly manifest in the case of platinum. According to Rosnig's experiments degasification of a platinum wire for a short time is sufficient to cause almost total loss of its capacity to accelerate the combination of hydrogen and oxygen at room temperature. Heating in oxygen revives high activity in the inactive metal. The more completely the sample was degasified, the more difficult it is to revive its activity with oxygen.

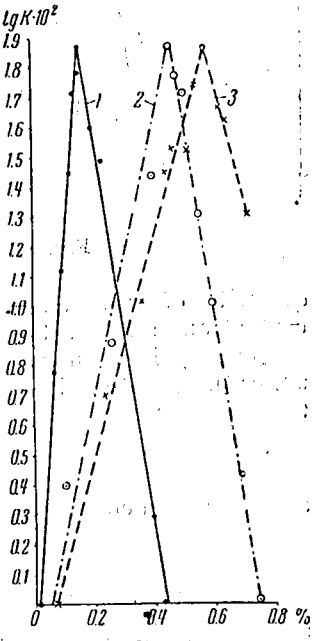

Fig. 1.

Data on catalysis by metallic films, produced by condensation from vapours, are in full conformance with the data on massive metals just mentioned. As has already been noted, if these experiments are performed under sufficiently pure conditions, the metallic films studied are always totally

inactive. If gaseous molecules are introduced in doses into the layer at the moment of condensation of the latter, there appear well-expressed promotion curves, examples of which are given below (Figs. 1 and 2). These data show that in two simple and typical catalytic reactions pure metals that have been well degasified do not possess high catalytic activity at all. Their activity is closely connected with the presence of small promoting admixtures (gases in this case) which act as latent promoters.

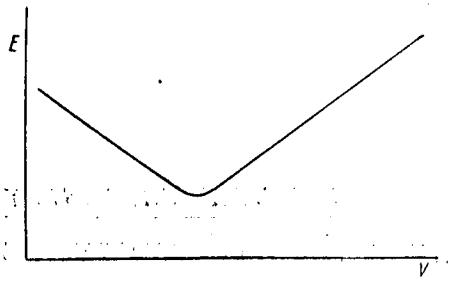

Fig. 2.

This erases the boundary between simple and mixed catalyzers and puts under question the actuality of the empirically established selection laws and activity series. As a matter of fact, such «professional» catalyzers as platinum and palladium are totally inactive when degasified. On the other hand, metallic tungsten which heretofore has not been considered a low-temperature catalyzer in hydrogenation, becomes highly active as catalyzer, if nitrogen, hydrogen, oxygen, or faucet lubricant vapour are introduced into the metal in dosed quantities. It may be expected that similar phenomena would be observed in other solid bodies, oxides, sulphides, etc.

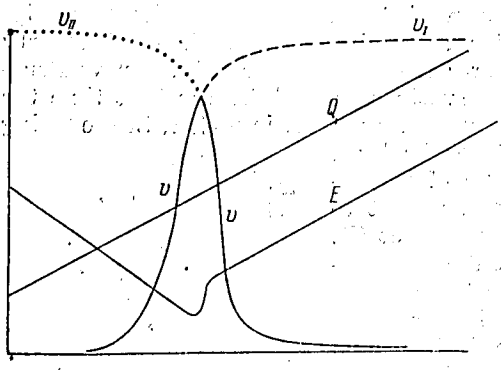

Fig. 3.

If promoted evenly, the activity depends strongly on the quantity of promoter entrained. Within the interval of admixture concentrations studied, the activity changes hundreds of times its initial value.

As may be seen from Fig. 1, the relation between the activity and the admixture content is exponential. The activity increases exponentially up to a certain value of γ, according to the law

$$k = k_0 e^{+\alpha\gamma}$$

and then it decreases according to the law

$$k = k_\infty e^{-\alpha_1\gamma} \text{ (when } \gamma > \gamma_{max}).$$

The value of α_1 is close to that of α. Such a violent law of activity change means that the heat of activation of the catalytic process should be under the direct influence of γ. At γ_{max} this heat should pass through its minimum (Fig. 2), since there would be no exponential relation in the schematic equation

$$v = Ze^{-E/RT}$$

if the preexponential coefficient varied (Fig. 2). This statement is confirmed by experiments in which the velocity of activized adsorption was measured. The absolute surface areas, on the other hand, do not change practically upon promotion.

It may be considered that in the most typical cases variations in activity are connected with variations in adsorption heats and activation, as functions of the quantity of admixtures. There is a certain value of these heats which is optimal for catalysis and is attained at $\gamma=\gamma_{max}$. Up to this point the velocity of the process as a whole is limited to the velocity of one of the first stages of the process (e. g. the velocity of activized adsorption), while the average activation energy of this process decreases linearly during catalysis as γ increases. When $\gamma=\gamma_{max}$ the velocity of the limited initial stage becomes equal to the velocity of one of the subsequent stages, e. g. to the velocity of desorption of the reaction product. As γ continues to rise, this latter stage becomes the limiting one. Its velocity falls as γ increases (Fig. 3). This scheme explains all the most important features of the promotion observed. A more elaborate account will be given elsewhere.

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