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Abstract

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ON THE QUESTION OF THE MECHANISM OF OXIDATION OF ORGANIC COMPOUNDS ON SOLID NONMETALLIC CATALYSTS

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Since any reaction of oxidation of organic compounds is associated with the transfer of electrons from the organic molecule to oxygen, it must include the following stages: 1) Transfer of electrons from the reactant molecule to the catalyst (chemisorption of the reactant). 2) Transfer by the catalyst of the donor electrons (of the reactant) to the acceptor (oxygen). 3) Addition of electrons by the oxygen molecule (chemisorption of oxygen), with formation of an oxygen ion. 4) Interaction of the organic ion formed in stage (1) (radical, ion-radical) with the oxygen ion, with the emergence of a new molecule—the oxidation product.

It follows from the foregoing that an oxidation catalyst must possess two functions: 1) the ability to form an acceptor-donor bond with the organic reactant and oxygen, and 2) the ability, by some means, to transfer electrons from one molecule participating in the reaction to another.

With respect to the successive stages of oxidation reactions, the general principle of the rate-limiting stage is applicable. It follows from this that, depending on the magnitudes of the rates of the component stages, correlations between the activity of a catalyst and such of its properties as the ability to form complexes, electrical conductivity, and the ability to chemisorb oxygen may either be observed or be absent. Because of this, the seeming ambiguity arises in the connection between the catalytic activity of a solid in oxidation reactions and the above-listed properties. It is also obvious that theories which regard each of the named properties as the only one determining the catalytic capacity of a solid are limited and do not encompass the full breadth of the phenomenon.

The first stage of the contact oxidation reaction—the transfer of electrons from the organic molecule to the solid catalyst—is in essence a particular case of the process of complex formation. This question has been considered in detail by Dowden and Wells ([1]), who put forward a number of assumptions concerning the relation between catalytic activity and the filling of the *d*-orbitals of the cations participating in the construction of the catalyst lattice. It is necessary to dwell on certain other aspects of the first stage of the reaction. The transfer of electrons from an organic molecule to a solid catalyst may proceed by several

Fig. 1

Figure 1: Fig. 1

paths. There may occur the usual reduction reaction of a variable-valence cation that is part of the catalyst.

Such a mechanism is quite probable if the cations of the catalyst lattice can be regarded as independent of one another. Morin ([2]) showed that in the right-hand members of the series of $3d$ oxides (Mn_2O_3, Fe_2O_3, Co_2O_3, Ni_2O_3) there is corresponding mutual overlap of the electronic levels of the lattice cations and the formation of band conduction, so that electrical conductivity in this case proceeds only according to the ion-recharging mechanism proposed by Verwey ([3]), with a tunneling mechanism of electron transfer. For the above-listed oxides, and for other oxides of elements with unfilled d- and f-electron shells with a probably similar mechanism of electrical conductivity, capture of electrons from an organic molecule must presumably proceed by an oxidation–reduction mechanism. According to–

···mechanism in the case of homogeneous catalysis, primarily the rupture of C –H bonds occurs, and not the rupture of the double bond. In oxidation on catalysts with isolated lattice cations, the mechanism is apparently analogous to the mechanism of homogeneous catalytic oxidation, and the C–H bond is likewise ruptured first. We shall hereafter call catalysts of this type σ-activating.

Fig. 1

Electron transfer from an organic molecule to a catalyst, in compounds possessing double and triple bonds, may proceed by the withdrawal of the molecule' s electrons into the catalyst lattice. In this case, a complex will form on the surface, which we shall call a surface π-complex. In simplified form, the formation of a surface π-complex can be represented by the scheme (Fig. 1), which includes rupture of the double bond.

The ability of the crystalline lattice of a catalyst to form surface π-complexes is the greater, the greater the probability of "smearing out" the withdrawn π-electrons among all the cations of the lattice. This, in turn, is directly dependent on the ability of the electrons of the cation on which adsorption of the reactant has occurred to interact with the electrons of other cations of the lattice. Such a probability is high in cases of electron delocalization, i.e., when band electrical conductivity is present in the solid, and also in the case of sufficiently high electrical conductivity by the ion-recharging mechanism. Catalysts possessing the property of forming surface π-complexes we shall call π-activating. The relationship in the conductivity region for σ- and π-activating catalysts is clearly illustrated by the scheme in Fig. 2.

Fig. 2

The measure of the oxidizing ability of ions in solutions is known to be the

Fig. 2

Figure 2: Fig. 2

value of the oxidation-reduction potential. By analogy with the equations of Brønsted and Voevodskii-Semenov ([4]), it may be assumed that the rate of the stage of electron transfer from the organic molecule to the catalyst is expressed by the equation

$$\lg K = A + \lg P,$$

where P is the redox potential of the cations with the opposite sign, K is the rate constant of the transfer, and A is a constant.

In this case, at a sufficient rate of oxidation of the cation, the activity of the catalyst will be determined by the value of P. Indeed, we know that the most active homogeneous catalysts are ions of manganese and cobalt, which have the most negative redox potential. Evidently, this principle can also be extended to σ-activating catalysts. As is known, cobalt-containing catalysts, including vanadium-free ones, possess high activity in processes of oxidative cleavage of the C—H bond ([5]).

The formation of a surface π-complex should proceed the more readily, the higher the acceptor ability of the catalyst. Hence, for a series of π-activating catalysts with the same support but modified differently, one should expect a correlation between changes in activity and work function. Indeed, in a number of cases this was observed by us jointly with L. Ya. Margolis.

The stage in which the catalyst transfers electrons from the donor to the acceptor may, in principle, proceed in the following ways: by direct interaction of the electron that has joined the catalyst cation (the reduced cation) with oxygen; by conduction through ion exchange (the Verwey mechanism); and by band conduction.

All three methods are, in principle, equivalent, and their practical realization depends only on the ratio of their rates. The assertion that only conducting substances (metals and semiconductors) can be oxidation catalysts is fully valid only for elements of constant valence. For elements of variable valence, compounds that have almost no conductivity—for example, nickel protoxide and cobalt oxides—may be effective catalysts, which is evidently associated with a sufficiently rapid transfer of electrons by the oxidation-reduction mechanism. This is confirmed by Winter' s data [(6)] on the high rate of isotopic exchange of oxygen on oxide nickel and cobalt catalysts.

There are experimental data, for example, on the oxidation reaction of maleic anhydride [(7)], which are satisfactorily interpreted only on the basis of a mechanism of electron transfer through oxidation-reduction of the crystal lattice of

the catalyst. It is obvious that, for σ-activating catalysts, the mechanism of electron transfer depends on which pair—the organic molecule and the catalyst —takes part in the interaction. If the rates of reduction of the catalyst by the organic substance and of its oxidation by oxygen are high, the catalytic process may proceed by an oxidation-reduction mechanism. If the rates of oxidation-reduction of the catalyst are low, then electron transfer proceeds by the mechanism of ion exchange, and in the catalytic process the catalyst lattice is not affected.

In π-activating catalysts, electron transfer, owing to their high electrical conductivity, should as a rule proceed either by band conduction or by conduction through ion exchange with a low activation energy. In this case the crystal lattice of the catalyst is not affected during the catalytic process, and the process takes place entirely in the adsorption layer, as was shown by V. A. Roiter [8] for the oxidation reaction of naphthalene on vanadium oxides.

We shall not touch in this article upon the questions of chemisorption of oxygen and the interaction, on the catalyst surface, of organic radicals or ion-radicals with oxygen ions.

As an illustration of the propositions advanced, one may consider the question of the synthesis of oxide catalysts for the oxidation of hydrocarbons. The synthesis of selective σ-activating catalysts, on which cleavage of the double C=C bond does not occur in oxidation processes, should presumably be carried out by one of two routes.

In the first case, one should start from oxides with isolated lattice cations, a sufficiently high oxidizing potential, and a high rate of oxidation-reduction of the lattice, i.e., with sufficiently mobile oxygen. At the same time, the catalysts should have low electrical conductivity determined by the ion-exchange mechanism. When it is necessary to increase the rate of electron transfer so that it does not become the limiting stage, either ions of transition metals that promote the formation of band conduction (vanadium, titanium, molybdenum, etc.) or compounds that are phase modifiers—i.e., catalysts accelerating the oxidation-reduction reaction of the catalyst itself—must be added to the catalyst.

In the second route for the synthesis of σ-activating catalysts, one should start from oxides of elements with a sufficiently high oxidizing potential, possessing high conductivity, and add to them cations of nontransition elements, for example P, Bi, Mg, etc., in order to reduce the electro-

conductivity and the rupture of the conduction band. To improve the selectivity of π-activating catalysts, the conductivity of the catalyst should be increased while simultaneously increasing its acceptor properties.

It should be emphasized that the propositions set forth concerning the synthesis of catalysts are directly applicable in cases where additions to the basic oxide do not lead to the formation of a new phase. Otherwise, at the point of phase transition, abrupt changes in the properties of the solid may occur. This should

have an especially strong effect on the properties of π-activating catalysts, which possess a band mechanism of conductivity. Phase transitions apparently may have no effect on σ-activating catalysts with isolated cations. Indeed, a direct influence of the phase transformation of a catalyst on its activity was observed earlier ([9]).

Experimental confirmation of the propositions developed in the present communication is given in work ([10]).

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