PRINCIPLE OF BIVALENT CATALYTIC SITES
IN THE REACTION OF HYDROGEN PEROXIDE DECOMPOSITION

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Principle of bivalent catalytic sites is presented, by means of which some physico-chemical and catalytic properties of a series of one- and two-component semiconductive catalysts involved in the decomposition of hydrogen peroxide can be explained. Using the principle, a general model of elementary reactions of the hydrogen peroxide decomposition, which allows to describe all the systems studied hitherto, has been suggested.

Some papers dealing with questions of oxide catalysts show that their catalytic activity is closely related to the quantity of superstoichiometric oxygen on their surface[1,2]. This has been confirmed also in papers which are associated with irradiation of some catalysts[3,4]. These findings lead to a conclusion that catalytic activity is exhibited by those oxides in which the metal occurs in two different oxidation states, this fact being also experimentally confirmed[5,6].
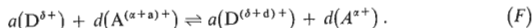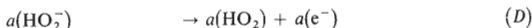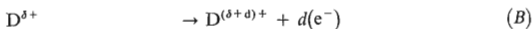
These findings as well as a series of studies on the decomposition of hydrogen peroxide on oxide catalysts[7-13], studied by us, yield the possibility of formulating new principle of bivalent catalytic sites, by means of which a series of observed properties of a catalytic system can be explained. From the viewpoint of the formulated principle, properties of nickel(II) (ref.[10]) and copper(II) (ref.[11]) oxides as well as those of the two-component catalysts of the NiO–ZnO (ref.[7]), NiO–CuO (ref.[8]), and CuO–ZnO (ref.[13]) types can be described.

THEORETICAL

The electron theory of catalysis[14] and several papers[1-13] anticipate that on the catalyst surface there are under given conditions two kinds of catalytic sites in equilibrium: donor and acceptor sites which may be formed by catalyst metal ions in various valency states, or by charge defects stabilized on the catalyst surface. The surface concentration of both kinds of sites and possibility of their influence between one another can vary according to conditions of preparing the catalyst especially by affecting dispersity of the catalyst particles and by conditions of the catalytic reaction. Character of the proceeding reaction is determined by sites of smaller surface concentration (minority sites) which are under given conditions

thermodynamic less stable: if the donor sites are involved, the reaction will proceed as an acceptor process and *vice versa*. The surface concentration of these sites will specify catalytic activity of the catalyst (probably by means of the frequency factor of the reaction). In addition, the catalytic activity of a specimen will be function of the charge difference of both kinds of sites, *i.e.* a function of number of electrons which are during the elementary reaction transferred from the substrate into the catalyst or *vice versa*, this fact likely appearing in the value of apparent activation energy of the catalytic reaction. The catalytic activity of a catalyst will be the greater, the higher surface concentration of the minority catalytic sites and greater charge difference of both types of sites will be involved. The first of the given conditions can be fulfilled by preparing the catalyst by various methods (doping, heat treatment, *etc.*); the second condition, however, is difficult to fulfill. The great charge difference of metal ions present next to each other leads to redox processes which balance this difference.

On the basis of these conception the catalytic decomposition of hydrogen peroxide can be generally written in the following way:
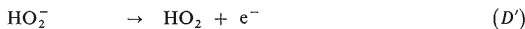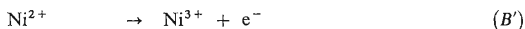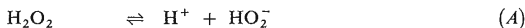
$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \tag{A}$$

$$D^{\delta+} \rightarrow D^{(\delta+d)+} + d(e^-) \tag{B}$$

$$d(H^+) + d(e^-) \rightarrow d(H) \tag{C}$$

$$a(HO_2^-) \rightarrow a(HO_2) + a(e^-) \tag{D}$$

$$A^{(\alpha+a)+} + a(e^-) \rightarrow A^{\alpha+} \tag{E}$$

$$a(D^{\delta+}) + d(A^{(\alpha+a)+}) \rightleftharpoons a(D^{(\delta+d)+}) + d(A^{\alpha+}). \tag{F}$$

Meaning of symbols: D, A element acting as donor or acceptor catalytic site; d, a number of electrons transferred in one elementary step by the donor and acceptor site; δ, α the lowest valency state of the element having function as the donor and acceptor catalytic site.

In this general scheme, reactions (B) and (C) express an acceptor process which takes place on the minority donor sites of catalyst $D^{\delta+}$, reactions (D) and (E) specify a donor process occurring on minority acceptor sites of catalyst $A^{(\alpha+a)+}$, and reaction (F) provides equilibrium between both kinds of catalytic sites (for the one-component catalyst, the equilibrium is, of course, given by equations (B) and (E)).

DISCUSSION

Examination of catalytic properties of nickel oxide proved[10] the donor sites of Ni^{2+} to act here as majority catalytic sites, and the minority sites to be produced by acceptor sites formed by Ni^{3+} ions whose surface concentration (in accordance with the principle of bivalent catalytic sites) is responsible for the catalytic activity of the specimen. This is demonstrated by the following facts: *1*) the catalytic activity of oxide is proportional to oxygen chemisorbed on its surface; *2*) the test reaction has been described as a donor reaction type[3,5,15,16]; *3*) the heat treatment of oxide leads to an adequate decrease in specific catalytic activity of the specimen as well as of the amount of oxygen chemisorbed on the surface unit; *4*) during the reaction, autocatalytic effect due to an increase in the surface concentration of minority catalytic sites Ni^{3+}, caused by chemisorption of the oxygen produced.

Hence, decomposition of hydrogen peroxide on nickel oxide can be described by equations $(A)-(F)$ using constants summarized in Table I. To ellucidate this, we present elementary steps of the hydrogen peroxide decomposition on the one-component catalyst in question:

$$H_2O_2 \quad \rightleftharpoons \quad H^+ + HO_2^- \qquad (A)$$

$$Ni^{2+} \quad \rightarrow \quad Ni^{3+} + e^- \qquad (B')$$

$$H^+ + e^- \quad \rightarrow \quad H \qquad (C')$$

$$HO_2^- \quad \rightarrow \quad HO_2 + e^- \qquad (D')$$

$$Ni^{3+} + e^- \quad \rightarrow \quad Ni^{2+}. \qquad (E')$$

The catalytic activity if nickel oxide with finely dispersed metallic nickel[10] has been shown to be proportional to the amount of metallic nickel, and to be independent of the quantity of chemisorbed oxygen. Thus the minority reaction sites can be assumed to be donor sites formed by Ni atoms, which are in equilibrium with the majority acceptor Ni^{2+} sites. Mechanism of the reaction can be described by a general scheme. When using characteristic constants from Table I it can be seen that 2 electrons are exchanged in one elementary process; this fact should be according to the principle of bivalent catalytic sites demonstrated by a lower value of the apparent activation energy of the process, or by a higher catalytic activity of the specimen. This has been confirmed experimentally.

From a detailed analysis of results of the study of catalytic copper(II) oxide properties it has been found[11] that Cu^+ ions (donor), which are in equilibrium with the majority acceptor sites Cu^{2+}, function here as the minority catalytic sites. This is con-

firmed, among other things, by the finding that the catalytic activity of oxide is not proportional to the amount of chemisorbed oxygen, and furthermore by the earlier statement that process of the acceptor character[16] is here concerned. Validity of the principle of bivalent catalytic sites is in this case supported by the finding that heat treatment of the specimen in the air or at higher temperatures provides a decrease in its catalytic activity, since the equilibrium of catalytic sites is thus shifted towards higher oxidation states of copper, this fact leading to a concentration decrease in the minority catalytic sites. Analogously, irradiation of the specimen with gama radiation, which provides increased chemisorption of oxygen, lowers for the same reason catalytic activity of the oxide. On the basis of these findings copper(II)oxide may be characterized by constants summarized in Table I, and the model reaction may be described by general scheme $(A)-(F)$.

Copper(II)oxide with finely dispersed metallic copper can be considered a case analogous to the NiO + Ni system, where, owing to 2 electrons exchanged in one elementary process, lower value of the apparent activation energy of the reaction[11] was observed. Consequently, the system can be characterized by constants presented in Table I.

For zinc oxide, its substoichiometry for oxygen allows to assume the Zn^+ ions, which have a function of donor sites[17] in the decomposition of hydrogen peroxide, to be the minority catalytic sites. They are obviously in equilibrium with the majority Zn^{2+} sites and the decomposition of hydrogen peroxide can be described by a general scheme using characteristic constants (Table I). Validity of the established principle is in this case supported by the finding that the reaction slows down within its course (for the most part with the specimen of the highest catalytic activity), because the
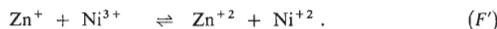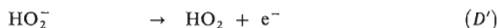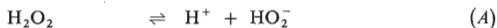
TABLE I

Values of Constants for Reactions (A) to (F) Involving Various Catalysts

Catalyst	D	A	d	a	δ	α
NiO	Ni	Ni	1	1	2	2
NiO + Ni	Ni	Ni	2	2	0	0
CuO	Cu	Cu	1	1	1	1
CuO + Cu	Cu	Cu	2	2	0	0
ZnO	Zn	Zn	1	1	1	1
ZnO + Zn	Zn	Zn	2	2	0	0
NiO–ZnO	Zn	Ni	1	1	1	2
NiO–CuO	Cu	Ni	1	1	1	2
CuO–ZnO	Zn	Cu	1	1	1	2

Zn^+ ions are oxidized during the reaction and the surface concentration of the minority catalytic sites thus decreases[12].

Zinc oxide with finely dispersed zinc shows considerably higher initial catalytic activity than pure oxide. This allows to anticipate equilibrium of $Zn-Zn^{2+}$ sites — consequently an analogous case as in systems $NiO + Ni$ and $CuO + Cu$ (Table I). Its catalytic activity rapidly decreases by the heat treatment, evidently due to rapid oxidation of the zinc metal[12].

For the two-component $NiO-ZnO$ catalyst, the Ni^{3+} ions can be regarded as the minority acceptor sites and the Zn^+ ions as the minority donor sites, which are in equilibrium with majority Ni^{2+} and Zn^{2+} sites, respectively.[7] Mechanism of the decomposition of hydrogen peroxide can be in this case described by a general scheme, using constants summarized in Table I. To make the whole thing more clear we schematically present elementary processes of the test reaction on this two-component catalyst:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad (A)$$

$$Zn^+ \rightarrow Zn^{2+} + e^- \qquad (B'')$$

$$H^+ + e^- \rightarrow H \qquad (C')$$

$$HO_2^- \rightarrow HO_2 + e^- \qquad (D')$$

$$Ni^{3+} + e^- \rightarrow Ni^{2+} \qquad (E')$$

$$Zn^+ + Ni^{3+} \rightleftharpoons Zn^{+2} + Ni^{+2} . \qquad (F')$$

The validity of the principle of bivalent catalytic sites is for this system supported by the following facts found experimentally[7]: 1) Nonmonotonic dependence of the catalytic activity on composition of the catalyst, which can be accounted for the charge interaction of both kinds of catalytic sites (if suitable dispersity of both oxides is involved); 2) the first order of the test reaction with respect to hydrogen peroxide, due to reaction (F'); 3) observed change in the catalyst colour in the first stage of the reaction, caused by "stoichiometrization" of both oxides (reactions (B''), (E'); 4 observed change in the catalytic activity of the system, due to irradiation of the latter by gama radiation, which can be explained on the basis of general mechanism of the reaction by a change, evocated by radiation, in the adsorption equilibrium of oxygen on the specimen surface[18].

The study of the two-component $NiO-CuO$ catalyst has shown[8,9] that the minority acceptor and donor sites produced by the Ni^{3+} and Cu^+ ions, which are in equilibrium with the majority sites $Ni^{2+}(d)$ and $Cu^{2+}(a)$, are here most probably applied.

The decomposition of hydrogen peroxide occurs then according to the general mechanism, the constants given in Table I being applied. This model makes it possible to explain the observed effect of dispersity on catalytic properties of the system, as well as the fact that deviation from the first reaction order is smaller than in the one-component systems.

As has been shown[13], the $Cu^{3+}(a)$ and $Zn^+(d)$ ions in the CuO–ZnO system function as minority catalytic sites, which are in equilibrium with majority sites $Cu^{2+}(d)$ and $Zn^{2+}(a)$. The reaction course as a whole can be then described schematically with use of characteristic constants (Table I). On the basis of this scheme the decrease in catalytic activity of this system with the increasing amount of zinc oxide may be explained by a shift of equilibrium F towards the right side (stoichiometric form of both oxides).

A conclusion can be made that examination of various catalytic systems, made up to now, confirms general validity of the principle suggested. It is necessary to verify its validity for other catalytic systems and reactions in another studies.

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