

DECOMPOSITION OF HYDROGEN PEROXIDE ON COPPER(II) OXIDE

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In studying the catalytic decomposition of hydrogen peroxide in aqueous solution of copper(II) oxides, prepared from different starting materials, it was demonstrated that the surface concentration of chemisorbed oxygen is not decisive for their activity. With most of the prepared oxides, Cu^+ ions present in the oxides seem to play an important role, which serve as catalytic donor centers for the testing reaction and whose surface distribution is homogeneous. With some of the copper oxides perhaps metallic copper may be supposed to form these donor centers. On the basis of this assumption a model was suggested of the elementary processes of decomposition which made it possible to explain the observed properties of the oxides. Irradiation of oxide by γ rays or by neutrons results in a change of its catalytic activity. The observed effects allow to draw some conclusions concerning the nature of oxygen adsorption on the oxide surface.

The study of decomposition of hydrogen peroxide on oxide catalysts has been given a relatively great attention^{1,2}. Some papers, dealing with this subject, prove that the amount of superstoichiometric oxygen on the surface of the oxide³⁻⁷ plays an important role in this process. These conclusions were basically verified in our studies of decomposition of hydrogen peroxide on two-component catalysts of the NiO—ZnO and NiO—CuO type^{8,9} where a model of elementary processes of the studied reaction was proposed. As has been further shown, the same model can be used to explain the catalytic properties of the mentioned catalysts either after their irradiation by an ionizing radiation¹⁰ or with an incorporated radionuclide¹¹. From this point of view, a very detailed study was accomplished of nickel(II) oxide¹² where the proposed model allowed to explain all observed properties of this oxide including the extremely high activity of the oxide prepared from nickel(II) oxalate. The interpretation was based on the assumption that with nickel(II) oxide which is a semiconductor of the *p*-type, the reaction proceeds *via* a donor mechanism on catalytic centers formed by Ni^{3+} ions.

Taking into account the fact that copper(II) oxide, too, is a semiconductor of the *p*-type and further because the acceptor mechanism has been found in the decomposition of hydrogen peroxide¹³, it seemed of interest to study in more detail the course of decomposition of hydrogen peroxide on copper(II) oxide concerning the way of its preparation and eventually to find the possible effect of ionizing radiation on its catalytic activity.

EXPERIMENTAL

Five samples differing in their initial substances were employed to study the decomposition of hydrogen peroxide on copper(II) oxide. Copper(II) oxide of carbonate origin was prepared by calcination of commercially obtainable copper(II) carbonate (Lachema), in an electric oven at 400°C for 3 hours. A part of the sample was calcinated on air (sample C_A), another part in nitrogen atmosphere (sample C_N), Copper(II) oxide of nitrate origin (sample N) was prepared analogously by calcination of copper(II) nitrate (Lachema) at 300°C for 3 hours on air. Copper(II) oxide from oxalate was prepared by precipitating the solution of copper(II) nitrate (1 mol/l) by a solution of potassium oxalate of the same concentration. After washing and drying of the precipitate one part of it was calcinated on air (sample O_A) and another part in nitrogen atmosphere (sample O_N) at 350°C for 3 hours. Copper(II) oxide of hydroxide origin was prepared by precipitation of saturated solution of copper(II) nitrate by solution of sodium hydroxide (1 mol/l), at 0°C. The precipitated hydroxide was, after thorough washing, calcinated on air at 250°C for 2 hours (sample H_A). Another sample of copper(II) oxide (sample H_L) was prepared by decomposition of aqueous suspension of the freshly precipitated copper(II) hydroxide by boiling for 1 hour. The formed oxide was decanted, washed with ethanol and dried at laboratory temperature. Some of the experiments were performed also using the commercially available copper(II) oxide, product of Lachema (sample K). All samples prepared were triturated in an agate mortar and the fraction of grain size *c.* 0.1 mm was selected for further experiments.

Chemical analysis of the prepared oxides was carried out electrolytically, using the current of 1.5–2 A, at 2–2.5 V and at 70°C. Fine structure of the prepared samples was determined by X-ray spectroscopy¹⁴.

Specific surface areas of the samples were measured by low temperature adsorption and subsequent desorption of nitrogen from the gaseous mixture hydrogen–nitrogen (3 : 2)¹⁵. The amount of superstoichiometric chemisorbed oxygen on the surface of oxides was determined by titration¹². To determine the semiconductivity characteristics of the prepared catalysts, their samples were pressed into tablets without binder by 49–98 MPa. The measurement was carried out in the system metal–semiconductor–metal, where the temperature gradient between the tungsten tips was 30–50°C. Indication was provided by a mirror galvanometer.

Part of the prepared samples was, prior to use, irradiated by ionizing radiation. Irradiation by ⁶⁰Co γ rays was carried out in glass ampoules at atmospheric pressure and at laboratory temperature, at a dose rate 2.31 W/kg, so that, using exposure times 168–1656 h the total absorbed dose varied within the interval 1.40 · 10⁶ J/kg to 1.38 · 10⁷ J/kg. Irradiation

TABLE I

Specific Surface Area, S (m²/g) and Amounts of Chemisorbed Oxygen A (% O²⁻); B (g_{O₂}-/m²) on Copper(II) Oxide of Different Origin

Sample	C _A	C _N	N	O _A	O _N	H _A	H _L	K
S	9.40	8.35	0.29	2.07	0.67	8.63	18.10	29.61
$A \cdot 10^2$	6.1	0.8	1.7	2.0	2.0	29.0	1.5	10.0
$B \cdot 10^4$	0.65	0.10	5.86	0.97	2.99	3.36	0.08	0.34

of samples by fast neutrons (4–6 MeV) was carried out by an ^{241}Am -Be source. Samples were placed in polyethylene covers screened by lead sheet. Dosimetric measurements showed that the fraction of thermal neutrons does not exceed 5% and that the total flow density of fast neutrons ranges in the interval $2.06 \cdot 10^{16}$ neutrons/m² – $4.45 \cdot 10^{16}$ neutrons/m², which corresponds to doses 36.9 J/kg – 79.8 J/kg.

The catalytic activity of individual samples was measured by means of a testing reaction, in our case the decomposition of hydrogen peroxide in aqueous solution of the initial concentration 1.2 mol/l. The measurement was carried out using the apparatus as described earlier⁸ which made it possible to measure the rate of oxygen evolution within the accuracy 0.5–2%. All measurements were carried out at four different temperatures.

RESULTS

Physico-chemical characteristics. According to chemical analysis, all samples can be looked upon as copper(II) oxide. The only exception is the oxide of oxalate origin which was found to contain a greater than stoichiometric amount of metal (Sample O_A contains 33% of free copper, sample O_N 8.4%). The way of preparation of copper(II) oxide affects significantly (Table I) both its specific surface area and the amount of chemisorbed oxygen (expressed in weight % (A) or in the amount per unit of surface (B)). In general, the value of specific surface area of samples prepared on air is higher than that of analogous samples prepared in nitrogen atmosphere.

Debyegramms of all samples revealed only selective reflexions belonging to copper(II) oxide. Here also, the only exception was the oxide prepared by decomposition of copper(II) oxalate where also reflexions of metallic copper could be detected.

The results of measurement of semiconductive characteristics showed a relatively low value of *p*-semiconductivity in all samples.

Catalytic activity. Preliminary experiments were performed to find conditions under which the testing reaction proceeds in the kinetic region. Using these conditions, the decomposition of hydrogen peroxide can be considered to be a 1st order reaction wherein the measurable deviation towards autocatalytic course is of course well reproducible with all samples. For this reason the reaction was in all experiments

TABLE II
Specific Catalytic Activity k_s (l/m² min) and Apparent Activation Energy of Reaction, E (J/mol) of Copper (II) Oxide Samples

Sample	O _N	O _A	C _N	C _A	N _{300°}	N _{400°}	H _A	H _L	K
$k_s \cdot 10^4$	6.040	2.398	5.185	3.955	3.198	1.355	3.050	1.927	1.255
$E \cdot 10^{-4}$	9.9	10.9	9.5	10.1	8.6	8.9	9.9	6.7	6.7

carried out only to 4% conversion and its kinetics was evaluated as for a 1st order process. With increasing specific surface area the catalytic activity of samples first increases and later it does not change considerably any more. The dependence of catalytic activity on the amount of chemisorbed oxygen is strongly non-monotonous (Fig. 1).

The values of specific catalytic activity k_s (catalytic activity standardized for a unit surface) of individual samples differ very significantly (Table II). Samples calcinated in nitrogen atmosphere show a higher activity than the same samples prepared on air. Higher calcination temperature affects the catalytic activity of the respective oxide negatively (*cf.* samples N_{300°} and N_{400°}). Considerable differences in catalytic activity are also found with samples prepared from hydroxide by different routes (samples H_A, H_L). Further it can be stated that the reaction proceeds with the same value of the apparent activation energy practically on all studied catalysts. Only the sample prepared from hydroxide in the wet way (H_L) and commercial copper(II) oxide (K) have a lower value of this quantity.

The specific surface area of samples is not affected by the applied radiation. Therefore, the catalytic activity of irradiated samples can be characterized by the rate constant k . Measurement of the catalytic activity of samples irradiated by γ rays has shown that only a radiation dose as high as $1.38 \cdot 10^7$ J/kg can affect both the catalytic activity of the catalysts and the amount of chemisorbed oxygen (Table III). The amount of chemisorbed oxygen increases about four times upon irradiation, whereas the catalytic activity of sample C_A decreases to about 75% and of samples O_A to c. 88% of the initial value of non-irradiated sample. At the same time the value of apparent activation energy of the reaction does not practically change. The observed decrease in catalytic activity is unstable, varying both with time and with temperature, (Table IV), whereas the value of the apparent activation energy remains practically unchanged. Irradiation by neutrons results in a multiple increase

TABLE III

Effect of γ Radiation (dose D , J/kg) on the Values of the Rate Constant of Reaction at 30°C k (l/g min), on the Value of Apparent Activation Energy, E (J/mol) and on the Amount of Chemisorbed Oxygen A (% O²⁻)

Sample	$D \cdot 10^{-7}$	$k \cdot 10^3$	$E \cdot 10^{-4}$	$A \cdot 10^2$
C _A	0.00	3.892	10.3	6.1
	1.38	2.910	9.8	24.2
O _A	0.00	0.497	10.9	2.0
	1.38	0.437	10.1	8.0

of the amount of chemisorbed oxygen which differs for different samples of oxides (Table V). This kind of radiation affects the catalytic activity of individual samples in a different way, both as to its quantity and also to its sense. A positive effect can be found only with samples C_N and O_N , whereas with the other samples the effect of irradiation is negative or practically zero. No change in the value of the apparent activation energy has been found in this kind of irradiation.

TABLE IV

Rate Constant k (l/g . min) and Apparent Activation Energy of Reaction, E (J/mol) for Sample C_A Non-irradiated (a), Irradiated by a Dose $1.38 \cdot 10^7$ J/kg (b), Sample 23 Days after Irradiation (c) and for Irradiated Sample after Thermal Treatment for 2 h at 90°C (d)

Sample	a	b	c	d
$k \cdot 10^3$	3.892	2.910	3.530	3.578
$E \cdot 10^{-4}$	10.3	9.8	10.2	9.6

TABLE V

Effect of Irradiation by Neutrons (D , neutrons/ m^2) on the Catalytic Activity k (l/g min), Apparent Activation Energy of Reaction E (J/mol) and on the Amount of Chemisorbed Oxygen A (% O_2) of Copper(II) Oxides of Different Origin

Sample	$D \cdot 10^{-16}$	0.00	2.39	4.45	Sample	$D \cdot 10^{-16}$	0.00	2.39	4.45
C_N	$k \cdot 10^3$	4.330	3.690	5.662	K	$k \cdot 10^3$	3.720	3.835	3.320
	$E \cdot 10^{-4}$	9.6	10.2	9.2		$E \cdot 10^{-4}$	6.7	6.3	6.8
	$A \cdot 10^2$	0.8	0.9	8.1		$A \cdot 10^2$	1.0	—	10.6
C_A	$k \cdot 10^3$	3.892	—	3.628	N	$k \cdot 10^3$	0.093	0.101	0.068
	$E \cdot 10^{-4}$	10.3	—	12.8		$E \cdot 10^{-4}$	8.6	8.3	7.7
	$A \cdot 10^2$	6.1	—	9.8		$A \cdot 10^2$	1.7	2.3	5.2
H_L	$k \cdot 10^3$	3.490	3.616	3.469	O_N	$k \cdot 10^3$	0.045	0.334	0.501
	$E \cdot 10^{-4}$	6.7	5.9	5.9		$E \cdot 10^{-4}$	9.9	11.7	11.1
	$A \cdot 10^2$	1.5	0.9	7.3		$A \cdot 10^2$	2.0	3.2	—
H_A	$k \cdot 10^3$	2.631	—	2.290					
	$E \cdot 10^{-4}$	9.8	—	9.2					
	$A \cdot 10^2$	1.1	—	9.0					

DISCUSSION

Physical-chemical properties of catalysts. According to the finding that copper(II) oxide prepared from oxalate contains a certain amount of metallic copper it can be assumed that, under the given conditions, copper oxalate is decomposed to metallic copper which in the course of further calcination is oxidized to oxide, similarly as it was in the case of nickel(II) oxide prepared from oxalate¹². The fact that the amount of metal is higher with samples prepared on air than in samples prepared in nitrogen atmosphere can be explained so that metallic copper formed by decomposition is very fastly oxidized on air and the thus formed surface layer of oxide inhibits further process of oxidation in deeper layers of the nucleus. The concept is also supported by the results that specific surface areas of samples prepared in nitrogen atmosphere are less than those of analogous samples prepared on air (Table I). The slower process of metal oxidation in nitrogen atmosphere probably makes possible the formation of a more regular surface structure which leads to a lower value of the specific surface area. In this way also the fact can be explained that the discussed difference in the surface areas is greater with samples O than with samples C, because the amount of metallic copper formed in samples O during calcination is high.

The way of oxide preparation has also an important effect on the amount of chemisorbed oxygen per unit surface area (Table I). This amount is higher in sample C in oxide prepared on air, evidently owing to the higher partial pressure of oxygen in the calcination atmosphere. The fact that with sample O the situation is just reversed, can probably be explained so that a sample prepared on air contains a considerable amount of metallic copper which participates in decreasing the concentration of superstoichiometric oxygen in the sample.

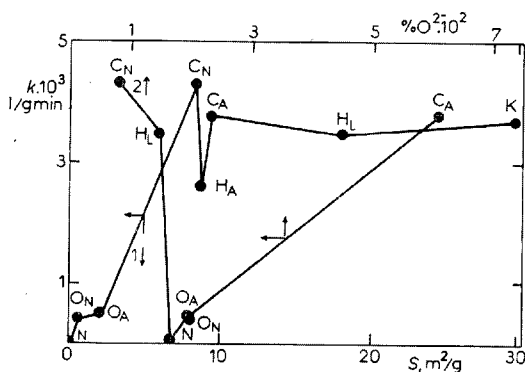


FIG. 1

Dependence of Catalytic Activity k at 30°C on the Specific Surface Area S (1) and on the Amount of Chemisorbed Oxygen (2) for Different Samples of Copper(II) Oxide

The amount of chemisorbed oxygen is also markedly affected by irradiation of samples by ionizing radiation. (Tables III, V). The observed increase of surface concentration of chemisorbed oxygen upon irradiation can be explained in terms of electron theory of adsorption processes on semiconductive catalysts. This explanation is possible, provided that owing to the *p*-semiconductive character of the studied samples the irradiation leads to the transition of the loosely bound form of oxygen into a strongly bound, chemisorbed form which can be chemically detected by the described procedure. Copper(II) oxide behaves, from this point of view, analogously to nickel(II) oxide^{10,12}.

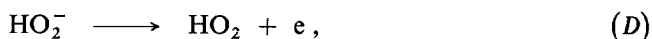
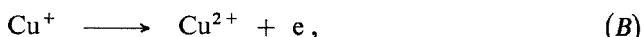
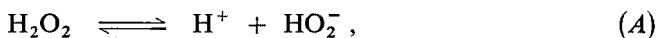
Catalytic activity. The experimental finding that catalytic activity of copper(II) oxide is not proportional to the amount of chemisorbed oxygen (Fig. 1) indicates that in this case ions Cu^{3+} (whose presence in the oxide cannot be excluded) cannot be taken as catalytic centers of the testing reaction, determining the catalytic activity of the catalyst, as it was in the case of nickel(II) oxide (Ni^{3+} ions)¹². This is in accord with the already mentioned fact that the decomposition of hydrogen peroxide proceeds on copper(II) oxide as an acceptor process¹³.

Let us now try, on the basis of the already obtained results, to find a scheme of the decomposition of hydrogen peroxide on copper(II) oxide, which would, similarly as with other semiconductor systems⁸⁻¹², be based on the concept that the reaction proceeds both on donor and on acceptor catalytic centers and that the catalytic activity of the catalyst is determined by the surface concentration of centers in minority concentration and by the charge differences of the two kinds of centers which, under the given conditions, are in equilibrium on the catalysts surface (principle of bivalent centers).

In addition to Cu^{3+} ions, also Cu^{2+} ions are present in copper(II) oxide and, in view of the rather high affinity of Cu^{2+} ions to electrons, also the presence of Cu^+ ions or even of metallic copper (experimentally found in sample O) may be assumed. Cu^{2+} ions can, because of their content in oxide, participate in the catalytic process, however, as major centers, *i.e.* their concentration cannot be decisive for the catalytic activity of the sample. Provided that the minority centers are represented by free copper atoms, the case would be similar to that of nickel(II) oxide prepared from oxalate which showed an extremely high catalytic activity and a lower value of the apparent activation energy of the studied reaction, as compared with other oxide samples¹². Since we did not find the mentioned effect it is hardly probable that atoms of free copper might be effective in this sense. This could only be possible with samples H_L and K, characterized by a lower value of apparent activation energy of the testing reaction (Table II). Accordingly, in these samples the reaction may proceed on donor centers formed by free copper which are the minority centers and thus determine the catalytic activity of the catalyst. As the majority centers can the Cu^{2+} ions action. The mechanism of elementary processes of the studied

reaction is then quite analogous to those found with nickel(II) oxide of the oxalate origin¹². The fact that these samples did not show a high catalytic activity can be explained so that in this case the surface concentration of minority centers is probably relatively low. This supports a low probability of the occurrence of free copper in these samples.

As for the remaining samples of copper(II) oxide studied, it can be assumed according to the above mentioned facts that the reaction proceeds on acceptor centers Cu^{2+} and on donor centers formed by Cu^+ ions which are in minority population. Mechanism of elementary processes proceeding during the decomposition of hydrogen peroxide, can accordingly be described by the following scheme

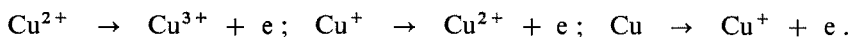


Processes (B) to (E) provide an equilibrium of both kinds of centers on the catalysts surface and thus also its relatively stable catalytic activity. According to our assumption, the minority centers (Cu^+ ions) determining the catalytic activity of the catalyst, are donor centers, *i.e.* the decomposition of hydrogen peroxide must be in general an acceptor reaction, as has been experimentally proved earlier¹³. This supports the validity of the suggested reaction mechanism.

The finding that catalytic activity of all samples under study (except samples H_L and K) related to 1 g of the catalyst increases approximately linearly with increasing specific surface area of the catalyst (Fig. 1) suggests that the coverage of the surface of these samples by catalytic centers is homogeneous. The value of the apparent activation energy of the reaction is the same with all these oxides within the limits of experimental error (Table II), and therefore it can be assumed that it is the same kind of catalytic centers, most probably the pair of $\text{Cu}^+ - \text{Cu}^{2+}$ centers.

The fact that the samples prepared in nitrogen atmosphere or at a lower calcination temperature have a higher catalytic activity than analogous samples prepared on air or at higher temperature (Table II) also supports the proposed model of the mechanism of the studied reaction. Evidently, the equilibrium between different forms of copper in the oxide is shifted on air or at higher calcination temperatures to higher valency forms, which leads to a decrease in concentration of the minority catalytic centers and thus to a decrease in the catalytic activity of the sample.

Also the deviation of the reaction order from unity can be explained in terms of the proposed mechanism, quite similarly, as it was with nickel(II) oxide¹². Oxygen, evolved during the reaction, can be assumed to be partially chemisorbed on the oxide surface. Having in mind the acceptor character of this sorption it can be assumed that it is accompanied by the following processes



Provided that the suggested mechanism is correct, only the first of these processes could lead to the observed autocatalytic character of the studied kinetics (of course in this case the reaction would proceed *via* a donor mechanism), whereas the further two processes would have a retarding effect, or would not cause any deviation (decrease or no change in the concentration of minority centers). The probable priority of chemisorption of the evolved oxygen on adsorption centers formed by Cu^{2+} ions is evidently caused by their relatively high surface concentration.

Table III indicates that irradiation by γ rays leads to a simultaneous increase of the amount of chemisorbed oxygen and to a decrease of the catalytic activity of the oxide. If, however, the chemisorption induced by radiation, took place on centers formed by Cu^{2+} ions, then, according to assumptions, increased activity of the samples would have been observed. However, experimental results indicate that chemisorption occurs on other centers than in the course of the reaction proper. In our case, chemisorption of oxygen probably takes place just on Cu^+ ions which causes the decrease of concentration of the minority catalytic centers. This concept is justified by the finding that irradiation leads only to a shift of the equilibrium from the weakly bound form of oxygen to the chemisorbed one³.

Weakly sorbed oxygen is concentrated on the surface in the region of charge perturbations of various kinds (*i.e.* also in the vicinity of Cu^+ ions) and therefore this kind of oxygen chemisorption will be connected with "blocking" of these perturbations (and thus also with a decrease of the actual concentration of catalytic centers formed by Cu^+ ions). However, in this it must be borne in mind that radiation-induced chemisorption proceeds evidently also on further charge perturbations on the sample surface which is demonstrated by the fact that the increase in the amount of chemisorbed oxygen after irradiation is considerably higher than the corresponding decrease in its catalytic activity (Table III). The fact that the changes of catalytic activity induced by irradiation are relatively poorly stable (Table IV) only supports the assumption that these changes must be considered as connected with the charge perturbations caused in the sample by the applied radiation.

The finding that irradiation of copper(II) oxide by neutrons leads to various changes of catalytic activity, both as to its sense and to its magnitude (Table V) proves the complexity of the effect of irradiation on the studied process. The fact that in all samples irradiation causes an increase in the amount of chemisorbed oxygen indi-

cates that this irradiation leads to the formation of charge perturbations, resulting in an equilibrium shift towards strongly bound form of oxygen which is accompanied by both above-mentioned reactions ($\text{Cu}^+ \rightarrow \text{Cu}^{2+} + e$; $\text{Cu}^{2+} \rightarrow \text{Cu}^{3+} + e$), one of them leading to a decrease and the second to an increase in the concentration of catalytic centers which determine the catalytic activity of the sample. Final equilibrium, resulting from these changes, determines the character of the observed changes in catalytic properties of the oxide. However, the change is probably also affected by other parameters of the catalyst, depending on the way of its preparation. To elucidate these problems in more detail will need to study this system from wider aspects and thus to make the assumptions suggested here more precise.

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