

DECOMPOSITION OF HYDROGEN PEROXIDE ON ZINC(II) OXIDE

V. MÚČKA

*Department of Nuclear and Physical Engineering,
Czech Technical University, 115 19 Prague 1*

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Decomposition of hydrogen peroxide has been studied on samples of zinc(II) oxide of different "origin". The way of preparation of the oxide affects significantly both its specific surface area and its specific catalytic activity. The observed catalytic properties of the oxide can be explained under the assumption that the reaction proceeds *via* an acceptor mechanism on donor centers, represented by Zn^{+} ions provided that the principle of bivalent catalytic centers is valid.

Several of our recent publications were devoted to the study of decomposition of hydrogen peroxide on nickel(II) oxide^{1,2} and copper(II) oxide³. Since both these catalysts are of the *p*-semiconductor type, it seemed of interest to investigate the catalytic properties of a typical *n*-semiconductor. To this purpose we have chosen zinc(II) oxide, prepared from different starting substances. In addition, the aim of the present publication was also to verify the validity of the principle of bivalent catalytic centers³, which could also be successfully applied to some two-component catalytic systems, consisting of the mixture of nickel(II) oxide with zinc(II) oxide⁴⁻⁶ or copper(II) oxide⁷.

EXPERIMENTAL

Different samples of zinc(II) oxide were prepared by the following routes: Sample F: Zinc oxide was dissolved in formic acid, affording zinc(II) formate which was, after crystallization, calcinated to oxide. Sample O: Zinc(II) oxalate was prepared from a saturated solution of zinc(II) nitrate by precipitation with a saturated solution of potassium oxalate and the obtained product was calcinated to oxide. Sample C: Zinc(II) nitrate was analogously precipitated by primary potassium carbonate to form a mixture of basic zinc carbonates which, after washing, was calcinated to oxide. Sample N: Zinc(II) oxide was prepared by calcination of recrystallized zinc(II) nitrate. For comparison, also the commercial sample of zinc(II) oxide, product of Lachema, reagent grade purity, was investigated (sample K).

Calcination of all samples was carried out in an electric oven, on air, at 350°C for 4 hours. After trituration and sieving the fraction of average grain size 0.1 mm was selected for further experiments.

All samples were analysed by complexometric titration. According to the results, all catalysts contain only oxides of the respective metals. The only exception was sample O in which a certain

TABLE I
Specific Surface Area S of Zinc(II) Oxide of Different Origin

Sample	F	O	O'	C	N	K
$S, \text{m}^2/\text{g}$	1.80	37.70	10.20	26.60	0.04	4.40

amount of undecomposed oxalate could be found both by chemical analysis and by X -ray spectroscopy (tube with copper anode). Further calcination of this sample at 500°C for 1 hour afforded already pure zinc(II) oxide (sample O).

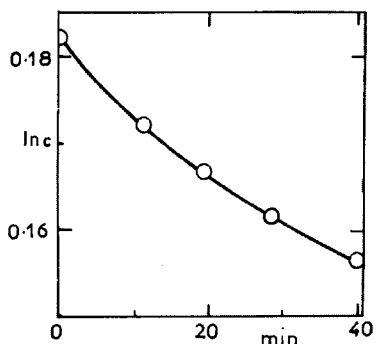
Specific surface area of the catalysts was measured by low-temperature adsorption of nitrogen and its subsequent desorption⁸. A part of the prepared samples was, prior to examination, irradiated by ^{60}Co γ -rays (0.8 MeV) and by fast neutrons from an Am-Be source (4–6 MeV) on air at laboratory temperature. In the former case the absorbed dose was $8.3 \cdot 10^6 \text{ J/kg}$, in the latter case the density of passed neutrons was $1.09 \cdot 10^{16} \text{ neutrons/m}^2$.

Catalytic activity of both irradiated and non-irradiated samples was measured under identical conditions at four different temperatures in the interval from 50° to 80°C , using the method described earlier⁴, whereby it was guaranteed that the measurement was carried out in the kinetic region of the reaction. Since, at the highest temperature used, a slight spontaneous decomposition of hydrogen peroxide occurred, all further measurements were corrected accordingly.

RESULTS AND DISCUSSION

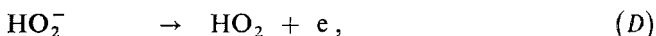
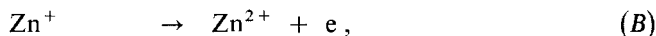
The way of zinc(II) oxide preparation has an important effect on the value of its specific surface area (Table I), analogously as it was found in the case of nickel(II) oxide¹ or copper(II) oxide³. As could be demonstrated by electron microscopy, this effect is connected with different roughness of the surface of various samples. At the same time, the way of preparation of the oxide has no effect on the size of its lattice parameters, as it was shown by X -ray diffraction using the method of reflected beam.

FIG. 1
Kinetics of Decomposition of Hydrogen Peroxide on Zinc(II) Oxide Prepared from Nitrate (Sample N)



Investigation of the kinetics of hydrogen peroxide decomposition on all samples of zinc(II) oxide showed (Fig. 1) that the order of the reaction approaches unity, however, the deviation from this value in the sense of reaction rate decrease is reproducible in all samples. This finding is just opposite to what was found in the case of nickel(II) oxide¹ and copper(II) oxide³ where a positive autocatalytic effect was observed.

This fact can be explained in terms of the above-mentioned principle of bivalent catalytic centers. Zinc(II) oxide is a typical *n*-semiconductor in which also Zn⁺ ions may be present in addition to Zn²⁺ ions (substoichiometry with respect to oxygen) and consequently Zn⁺ ions may be assumed to represent the catalytic donor centers^{4,9} of the reaction which have the minority population in the catalyst. Accordingly, the decomposition of hydrogen peroxide on zinc(II) oxide can be described by the following scheme



In this reactions (B) and (E) assure the equilibrium concentration of donor and acceptor centers. Since the donor centers (Zn⁺ ions) are the minority species, their surface concentration will be decisive for the catalytic activity of the sample. Since oxygen is released from the system in the course of the reaction and can be later on partially chemisorbed on the oxide and since this chemisorption is an acceptor reaction, it will be evidently accompanied by the process: $\text{Zn}^+ + \text{O} \rightarrow \text{Zn}^{2+} + \text{O}_{(\text{ads})}^-$. This of course leads to a decrease in the concentration of minority catalytic centers and to the finally observed decrease in the catalytic activity of the oxide during the reaction itself.

Verification of the proposed model was carried out in the following way: According to the model we can assume that the greatest deviation from the reaction order 1 will be found in the sample with the greatest content concentration of Zn⁺ ions, *i.e.* with the greatest catalytic activity. This deviation (*a*, mm) was graphically evaluated and its values for individual samples are: F 3.0, O 5.0, O' 3.0, C 3.0, N 6.9. As can be seen, the greatest deviation is found with the oxide prepared from nitrate. From the results of measurements of the catalytic activity (Table II) it follows that sample N also displays the greatest specific activity, characterized by the rate constant of a 1st order reaction as related to unit surface of the catalyst. This supports the correctness of the proposed mechanism and also of the explanation of the discussed

deviation. The fact that the increase in the specific catalytic activity of the sample is higher than the corresponding increase in quantity a characterizing the deviation from 1st order can be explained so that chemisorption can take place even on other perturbations of donor character. This is evidently also the cause why with the other samples the dependence of deviation a on the catalytic activity, which is rather low, cannot be detected.

Table II also shows clearly the important difference of the catalytic activity of differently calcinated samples prepared from oxalate (samples O and O'). In order to investigate this phenomenon in more detail some samples were thermally treated in an electric oven at 300°C for 3 h. Denoting the specific catalytic activity of thermally treated samples k_s^0 and that of non-treated samples k_s we can describe the effect of thermal treating by the ratio $(k_s^0 - k_s)/k_s$ in per cent. The found values of this ratio are: O 4470, O' -8.5, N -13.2, O⁺ (12 days after treating) 22.6. It is evident that whereas in sample O' and N thermal treating has no significant effect on their catalytic activity, in sample O (uncompletely decomposed zinc(II) oxalate) it is manifested by manifold increase in its activity. This increase, however, is unstable and disappears practically after a few days' standing at laboratory temperature (sample O⁺). The thermal treating may probably cause a partial decomposition of the present oxalate to metallic zinc which virtually increases the catalytic activity (in addition to the pair of centers Zn⁺-Zn²⁺ also pairs Zn-Zn²⁺ are effective). This is a case analogous to that of nickel(II) oxide prepared from oxalate¹. In this case, however, the formed zinc is very fastly oxidized and thus the catalytic activity decreases.

TABLE II

Specific Catalytic Activity k_s (l/m² min) of Zinc(II) Oxide of Different Origin at 60°C, Apparent Activation Energy of the Reaction E (J/mol) and Values of These Quantities after Irradiation

X Non-irradiated samples, Y samples irradiated by gamma rays, Z samples irradiated by neutrons.

Sample	X		Y		Z		
	$k_s \cdot 10^5$	E	$k_s \cdot 10^5$	$\Delta k_s/k_s$ [%]	$k_s \cdot 10^5$	$\Delta k_s/k_s$ [%]	E
F	1.82	32.6	1.79	- 1.7	1.95	7.2	28.0
O	0.45	51.9	0.44	- 2.2	0.35	-22.2	47.7
O'	4.05	61.2	3.95	- 2.5	3.95	- 2.5	60.3
C	1.41	58.2	1.50	6.4	1.47	4.3	56.9
N	71.20	61.0	54.50	-23.4	57.00	-20.0	49.7
K	1.18	13.4	—	—	1.23	4.2	—

$\Delta k_s = k_s^+ - k_s$; k_s^+ catalytic activity of irradiated sample.

The study of irradiated catalysts revealed (Table II) that in most of them the applied radiation has no substantial effect on their catalytic activity. This finding supports the earlier reported fact that the effect of ionizing radiation is more marked in the case of multicomponent catalyst than in a catalyst of a simple type^{1,2,5}. A more significant (negative) effect of γ radiation and of neutrons can only be found with sample N which can be connected with the fact that this sample, as has already been demonstrated, has the greatest concentration of perturbations formed by Zn^+ ions. The new perturbations, of the charge character, formed by irradiation, can recombine with the former ones which is then manifested by the decrease in the catalytic activity of the sample. The finding that also irradiation by neutrons results in a decrease in the catalytic activity also in sample O (this was not observed in sample O' nor in any of these samples after γ irradiation) can be considered as the proof that in this case, in view of the rather great roughness of the surface, the so-called polishing effect of radiation comes into action, leading to the destruction of catalytic centers. This explanation is also supported by the fact that irradiation of sample by neutrons does not cause any change in the apparent activation energy of the test reaction.

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