

## DECOMPOSITION OF HYDROGEN PEROXIDE ON A TWO-COMPONENT CATALYST OF THE TYPE CuO-ZnO

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Decomposition of hydrogen peroxide on a two-component CuO-ZnO catalyst has been studied over the whole concentration range of 0–100% of one component. It was found that a mutual charge interaction of both components of the catalyst takes place which is manifested by the non-monotonous character of the dependence of specific surface areas of the samples and of their specific catalytic activity on composition. A model of elementary reactions was proposed to elucidate this dependence, based on the earlier published principle of bivalent catalytic centers. Irradiation of samples by  $\gamma$  rays leads to small both negative and positive changes in catalytic activity (in dependence on composition), whereas irradiation by neutrons results in a slight decrease in the catalytic activity of the samples. These observed changes can be qualitatively interpreted in terms of the electron theory of catalysis.

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In our earlier works we have studied, besides some one-component catalysts, also the properties of two-component systems of the type NiO-ZnO (see<sup>1-3</sup>) and NiO-CuO (see<sup>4</sup>). In both cases a mutual interaction was found of both components of the catalyst, manifested by the non-monotonous course of the dependence of catalytic activity on the composition of the catalyst. Moreover, in the case of the system NiO-ZnO it was found that its catalytic properties are significantly modified by irradiation of the sample by  $\gamma$  rays and neutrons (Ra-Be source) and by incorporation of a radioisotope into the catalyst. Therefore it was interesting to investigate, from this point of view, also the behaviour of a further two-component system, CuO-ZnO, where one of the components is a weak *p*-semiconductor, while the other one represents a typical *n*-semiconductor. At the same time, our aim was to verify, whether also for this system a model could be found, based on the earlier introduced principle of bivalent catalytic centers, which had been successfully applied to a number of one- and two-component catalysts.

Decomposition of hydrogen peroxide was chosen as the test reaction (like in the studies of other catalytic systems<sup>1-4</sup>) especially with respect to the fact that this reaction is a relatively simple one and proceeds at a measurable rate already at laboratory temperature. This reaction had been employed for testing in a number of different catalytic systems of the oxide type<sup>5-10</sup> and it was found that the catalytic activity of two-component oxide catalysts was not additive.

## EXPERIMENTAL

*Mixed catalysts* were prepared from saturated solutions of nitrates of both respective metals (analytical reagent grade) which were mixed in various ratios in the interval 0–100% of one component. After crystallization the mixed nitrates were calcinated in an electric oven at 350°C on air for 4 h. The formed oxides were triturated and the fraction of the grain size c. 0.1 mm was selected for further measurements.

All samples were analyzed complexometrically. Determination of the fine structure of oxides by X-ray spectroscopy (copper anode) showed that, as far as structure is concerned, no interaction of the components takes place. Specific surface area was measured by low-temperature adsorption and subsequent desorption of nitrogen<sup>1–4</sup>.

A part of the prepared samples was irradiated by <sup>60</sup>Co  $\gamma$  rays and by fast neutrons from an Am-Be source on air at laboratory temperature so that the absorbed dose of  $\gamma$  radiation was  $8.3 \cdot 10^6$  J/kg and the density of passed neutrons was  $1.09 \cdot 10^{16}$  neutrons/m<sup>2</sup>.

*Determination of catalytic activity* was carried out by measuring the rate of evolution of oxygen in the decomposition of hydrogen peroxide at constant temperature and pressure<sup>1</sup>. 25 ml of aqueous solution of hydrogen peroxide (reagent grade purity) of the concentration 1.2 mol/l and 0.200 g of the catalyst were used for testing; the measurement was carried out at four different temperatures in the interval 50°–80°C. Preliminary measurements performed with various weighings of the catalyst, various initial concentrations of hydrogen peroxide, various rates of mixing of the system and at different reaction temperatures showed that under these conditions the reaction proceeds in kinetic region and is not governed by transport processes.

## RESULTS AND DISCUSSION

The results of chemical analysis of individual samples together with their specific surface areas are summarized in Table I. From it can be seen that the studied system contains only copper and zinc oxides. (This was confirmed, within the limits of experimental error, also by X-ray spectroscopy of the samples which revealed the presence of selective reflexions of monoclinic (CuO) and hexagonal (ZnO) structure with lattice parameters identical with the tabellated values). The dependence of the specific surface area on the catalyst composition indicates the interaction of both oxides, which characterizes also other mixed catalysts<sup>1–4,11</sup>. From this finding it follows that samples with excess copper(II) oxide have a greater specific surface area than those with excess zinc(II) oxide. All mixed catalysts have greater specific surface areas than would correspond to a mechanical mixture of the respective composition.

On the basis of the measurement of catalytic activity to a higher degree of decomposition of hydrogen peroxide (40%) it could be demonstrated that the decomposition of hydrogen peroxide proceeds on all mixed catalysts as a 1st order reaction. This supports the earlier finding that the deviation from integer reaction order is only very small in mixed oxides<sup>1–4</sup>, whereas in one-component catalysts it is significant and well reproducible<sup>12–14</sup>.

The dependence of specific catalytic activity (defined as the rate constant of a 1st order reaction referred to a unit surface area of the catalyst) on the composition of

samples is shown in Fig. 1, curve 1. Its markedly non-monotonous character proves again mutual interaction of both components of the catalyst. Like with other two-component systems<sup>4,11</sup>, also in this case there is the maximum catalytic activity in both limit regions of the composition and in the region where the percentage of both components is approximately the same. An explanation can be given, similarly as in the above cited publications, in terms of the electron theory of catalysis assuming the validity of the principle of bivalent catalytic centers.

TABLE I

Composition and Specific Surface Area  $S$  ( $\text{m}^2/\text{g}$ ) of Catalysts

| Sample | Weight % |       |       |       | Mol % |       | $S$  |
|--------|----------|-------|-------|-------|-------|-------|------|
|        | Cu       | Zn    | CuO   | ZnO   | CuO   | ZnO   |      |
| 1      | 79.55    | —     | 99.54 | —     | 100.0 | —     | 0.32 |
| 2      | 79.13    | 0.78  | 98.91 | 0.94  | 99.0  | 1.0   | 0.26 |
| 3      | 70.94    | 8.69  | 88.67 | 10.77 | 89.4  | 10.6  | 0.34 |
| 4      | 63.21    | 16.63 | 79.01 | 20.62 | 79.7  | 20.3  | 0.32 |
| 5      | 55.40    | 24.52 | 69.25 | 30.40 | 69.9  | 30.1  | 0.36 |
| 6      | 47.12    | 32.82 | 58.90 | 40.69 | 59.7  | 40.3  | 0.22 |
| 7      | 40.79    | 39.21 | 50.98 | 48.62 | 51.7  | 48.3  | 0.13 |
| 8      | 31.11    | 48.06 | 38.88 | 59.59 | 40.0  | 60.0  | 0.17 |
| 9      | 22.72    | 53.78 | 28.40 | 66.70 | 30.3  | 69.7  | 0.17 |
| 10     | 15.25    | 64.85 | 19.06 | 80.39 | 19.5  | 80.5  | 0.15 |
| 11     | 6.39     | 73.77 | 7.98  | 91.47 | 8.2   | 91.8  | 0.10 |
| 12     | 0.76     | 79.48 | 0.95  | 98.56 | 1.0   | 99.0  | 0.08 |
| 13     | —        | 80.15 | —     | 99.78 | —     | 100.0 | 0.02 |

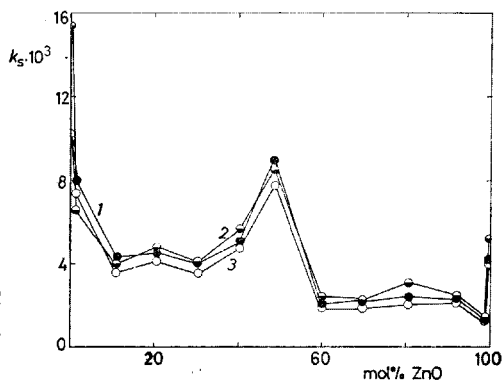
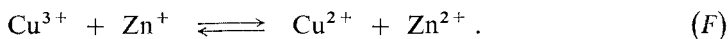
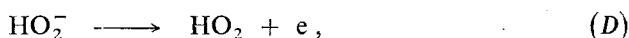
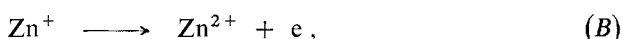
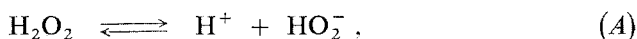


FIG. 1

Dependence of Specific Catalytic Activity of Catalysts on Their Composition at  $65^\circ\text{C}$

Samples: 1 non-irradiated 2 irradiated by  $\gamma$  rays, 3 irradiated by neutrons.

In our earlier papers we have shown that decomposition of hydrogen peroxide proceeds in the case of pure zinc(II) oxide on catalytic centers formed by ion pairs  $Zn^+ - Zn^{2+}$  (ref.<sup>14</sup>) and in the case of pure copper(II) oxide the pairs  $Cu^+ - Cu^{2+}$  take most probably part in the reaction (ref.<sup>13</sup>). In the latter case, however, also the influence of free copper or even of ion  $Cu^{3+}$  (ref.<sup>13</sup>) cannot be excluded. Thus, if we assume that on zinc(II) oxide the reaction proceeds as an acceptor mechanism on  $Zn^+$  donor centers, the observed mutual interaction of both oxides can be accounted for by a donor process on acceptor centers of copper oxide in minority population which are in equilibrium with the majority centers formed by  $Cu^{2+}$  ions. This requirement is met only with centers formed by  $Cu^{3+}$  ions. Consequently, in accordance with the above-cited works on hydrogen peroxide decomposition on a semiconductor type catalyst, the following scheme can be proposed for this reaction and for the studied mixed catalyst:



Reactions (B) and (C) represent an acceptor process, reactions (D) and (E) a donor process. Reaction (F) affords both kinds of centers in equilibrium concentration. According to the above mechanism we can suppose that in the case of mutual interaction of oxides equilibrium (F) will be shifted to the right-hand side (towards ionic forms without potential difference). This leads to a decrease in the concentration of minority catalytic centers on the catalyst surface and to a decrease of its catalytic activity. Since, in our case, the increasing concentration of the second component in the sample is accompanied by a decrease of its dispersity, there must exist in both marginal regions a sample with the maximum degree of interaction of both oxides. Therefore, the dependence of catalytic activity on composition, when measured from pure components, has first a decreasing and then an increasing course, attaining a maximum in the region of approximately the same concentration of both oxides. However, since in this region the catalytic activity is higher than the value obtained by adding the weighted activities of pure components, we can admit that even in this case, analogously to other systems, we have to do with a region with a maximum

interfacial surface on which further kinds of catalytic centers may be stabilized, contributing to a higher catalytic activity of the respective samples.

As can be seen from Fig. 1, curve 2, irradiation by  $\gamma$  rays under the given conditions causes no substantial change in the character of the dependence of specific catalytic activity on composition. This means that basic parameters of the system remain unchanged even after irradiation. In spite of this, relatively small changes of catalytic activity occur due to irradiation, both negative and positive in dependence on composition (Fig. 2). This fact, together with the finding that the effect of irradiation practically disappears after thermal treatment at 300°C for 1 h, proves that the observed changes are probably caused by changes in the quasiequilibrium concentration of free charge carriers due to irradiation. These changes lie, of course, on the limit of detectability (with the exception of pure copper(II) oxide) and therefore no unambiguous conclusions can be drawn.

As further follows from Fig. 1, curve 3, even irradiation of samples by neutrons does not change, under the given conditions, the overall character of the dependence of catalytic activity on composition. In contradiction to the effect of  $\gamma$  radiation, irradiation by neutrons has under the given conditions approximately the same negative effect on the catalytic activity over the whole composition range (Fig. 3). The only exception are one-component catalysts. Considering these results and also the results of our earlier studies on irradiated catalysts, we can assume that the

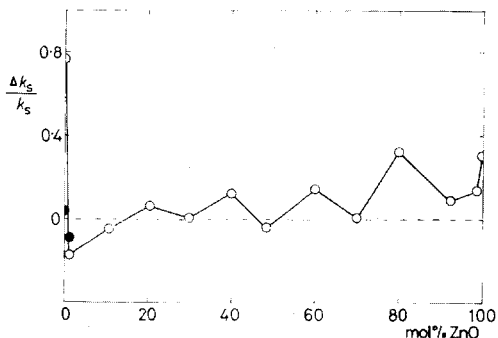


FIG. 2

Relative Change of Catalytic Activity after Irradiation of Samples by  $\gamma$  Rays in Dependence on Their Composition

$\Delta k_s = k_s^+ - k_s^-$ ;  $k_s^+$  specific catalytic activity of the irradiated sample. ● Irradiated sample which had been thermally treated for 1 h at 300°C.

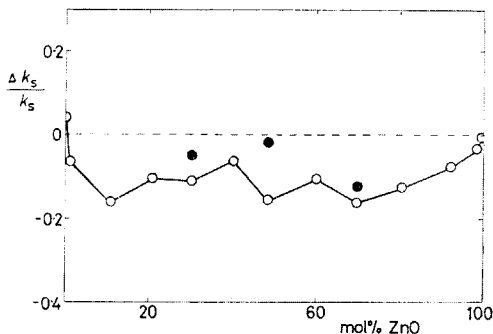


FIG. 3

Relative Change of Catalytic Activity after Irradiation of Samples by Neutrons in Dependence on Their Composition

Symbols the same as in Fig. 2.

cause of the found relatively small effect of irradiation is the formation of new perturbations in the crystalline structure, which are of such a kind that they can recombine with the existing perturbations functioning as catalytic centers for the reaction. Because of recombination the concentration of catalytic centers and accordingly also the catalytic activity of the catalyst decreases. This process is evidently possible only in the case of mixed catalysts where the concentration of original perturbations ready to recombine is high enough.

This explanation is also confirmed by the fact, that after a thermal treatment of the irradiated samples at 300°C for one hour the radiation effect has practically disappeared (Fig. 3). With this phenomenon the fact is connected that neither an irradiation of the catalysts, nor their thermal treatment lead to a change in the apparent activation energy value of the test reaction. Even in this case the observed changes are relatively small. Therefore the mentioned interpretation represents a mere hint concerning the possible mechanism of interaction of neutrons with the surface of the catalyst.

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