

DECOMPOSITION OF HYDROGEN PEROXIDE ON TWO-COMPONENT CATALYSTS NiO-ZnO AND NiO-CuO

V. MÚČKA, J. CABICAR and A. MOTL

*Faculty of Nuclear and Engineering Physics,
Czech Technical University, 115 19 Prague 1*

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The paper describes decomposition of hydrogen peroxide catalysed by two-component catalysts NiO-ZnO and NiO-CuO, prepared by calcination of nitrates with different proportions of the two components covering the whole range of 0 to 100% of one of them. In either system the components affects each other, which is represented by non-additivity of the specific surfaces of the samples and by a strongly non-monotone dependence of the specific catalytic activity on the composition. The way of preparation of the catalysts has been found strongly to influence the properties of the systems studied. From the results of the study it can be deduced that the formation of a solid solution is not a prerequisite for interaction of the individual components of the catalyst; this interaction is supposed to be the cause of non-additivity of the properties studied. These properties can be qualitatively interpreted by the electron theory of catalysis.

Some papers dealing with the decomposition of hydrogen peroxide on two-component catalysts suggest that the catalytic activity is influenced by interaction of the two components¹, which may give rise to a solid solution²⁻⁴ or to a surface compound⁵.

Our previous paper⁴ treated the catalytic properties of the system NiO-ZnO, prepared by decomposition of co-precipitated carbonates of the two metals. The interaction of the two components manifested itself by an increased catalytic activity of the system at about 6 mol % of ZnO. This could be explained qualitatively on the basis of the electron theory of catalysis, provided that the catalytic process proceeds by a donor mechanism on NiO and acceptor mechanism on ZnO, since the system is a mixed crystal of a typical *p*- and a typical *n*- semiconductor.

It was of interest to compare the properties of this system with those of the system NiO-CuO, where either component is a *p*-semiconductor with a different value of semiconductivity. We also considered it worth while to study again the system NiO-ZnO, but this time prepared by decomposition of nitrates of the two metals, so that the possible effect of the preparation way on the catalytic properties would be revealed.

EXPERIMENTAL

The two series of catalysts were prepared by crystallization of solutions of nitrates of the two metals (A.G.), mixed in calculated ratios so that the resulting samples would cover the whole composition range, 0-100%. The nitrates were then calcinated in the air in an electric oven for

6 h at 400°C. The samples thus prepared were ground in an agate mortar to fine-grained catalysts. Further details concerning the preparation procedure are described elsewhere⁶.

The *specific surfaces* of the individual samples were measured by low-temperature adsorption of nitrogen.

Chemical analysis of the system NiO–ZnO was carried out complexometrically⁴. The system NiO–CuO was determined electroanalytically.

The *microstructure* of the catalysts was investigated by X-ray diffraction, a copper mode being used. Details of the method and evaluation of the results are described elsewhere³.

To test the *catalytic activities* of the samples a 2.5% aqueous solution of hydrogen peroxide, A. G., was employed. The apparatus and procedure were described previously⁴. With all samples the measurements were carried out at four temperatures in a range of 20 to 35°C.

RESULTS AND DISCUSSION

The chemical compositions of the samples of the series NiO–ZnO and NiO–CuO are given in Table I. In Fig. 1 the specific surface of the samples is plotted *vs* their composition. The function is monotone with neither system and exhibits a peak around 4 mol% of the second components. The character of the function was not changed even by heating the samples under nitrogen at 500°C for 1 h. Its course suggests that in either system the components of the catalysts affect each other. This course was identical with the two systems, but qualitatively differed from that observed with the NiO–ZnO system prepared from carbonates⁴. From this fact it can be inferred that the preparation procedure of the samples has a strong effect on their specific surface.

TABLE I
Chemical Compositions of the Catalysts

Sample	mol %		mol %		Sample	mol %		mol %	
	NiO	ZnO	NiO	CuO		NiO	ZnO	NiO	CuO
1	100.0	0.0	100.0	0.0	8	43.6	56.4	36.7	63.3
2	97.8	2.2	98.7	1.3	9	32.7	67.3	27.7	72.3
3	90.8	9.2	92.3	7.7	10	22.7	77.3	17.9	82.1
4	81.4	18.6	84.6	15.4	11	11.4	88.6	9.6	90.4
5	72.3	27.7	74.2	25.8	12	2.8	97.2	5.4	94.6
6	64.2	35.8	56.6	43.4	13	0.0	100.0	2.0	98.0
7	53.9	46.1	47.7	52.3	14	—	—	0.0	100.0

As became apparent from microstructures of the samples in the system NiO–ZnO (prepared both from carbonates and from nitrates), in the region 0 to 30 mol % of ZnO a solid solution of this oxide in NiO was formed, which was accompanied by a change of the lattice parameter of the cubic structure³ by +0.6%. By contrast, the system NiO–CuO was shown by X-ray analysis to have a structure corresponding only to the two oxides, and no change in lattice parameter of one or the other component was observed, within the accuracy range of the method, at any composition of the samples. Hence we deduce that in all probability no solid solution gets formed under the given conditions. This, in turn, suggests that the above-mentioned non-monotone dependence of the specific surface on composition demonstrates mutual influencing of the two components, which probably is not caused by the formation of a solid solution in the system.

Measurements of catalytic activities of the samples showed that under the given conditions the decomposition was a first-order reaction in respect to hydrogen peroxide, in agreement with the results reported for similar systems^{4,7}. In all experiments the reaction was not allowed to exceed a 5% decomposition of hydrogen peroxide and the rate constant of the reaction thus obtained (zero order) related to a unit surface of the catalyst (specific catalytic activity) was used as a measure of catalytic activity for all samples. The dependence of this quantity on composition of the catalysts for the NiO–ZnO system is shown in Fig.2 and for the NiO–CuO system in Fig. 3. It is evident that in either case the specific catalytic activity is a non-

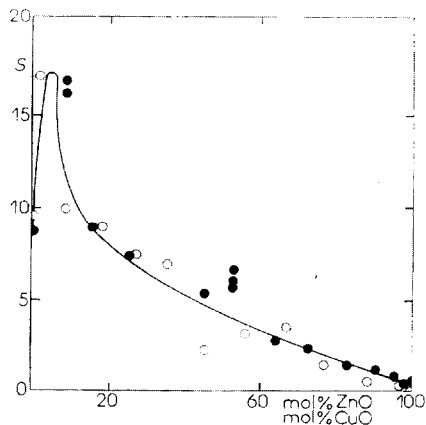


FIG. 1

Specific Surface, S [m^2/g], as a Function of Composition; \circ System NiO–ZnO, \bullet System NiO–CuO

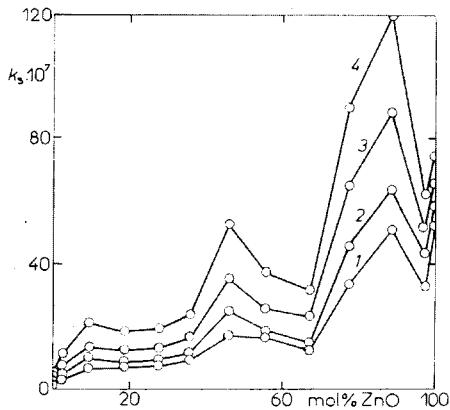


FIG. 2

Specific Catalytic Activity, k_s [$\text{mol}/\text{s} \cdot \text{m}^2$] as a Function of Composition of the System NiO–ZnO at 20°C (1), 25°C (2), 30°C (3) and 35°C (4)

monotone function of the composition of the catalysts, which again can be regarded as demonstration of the mutual influence (interaction) of the two components. With either system three peaks are typical: for the system NiO–ZnO at 10, 50 and 90 mol % of ZnO; for the system NiO–CuO at 20, 60 and 95 mol % of CuO. The fact that in the latter system the peaks are shifted to lower contents of NiO may be due to the possibility that the difference in composition between the surface and the interior of a catalyst is not the same in the two systems. With this function, however, in contrast to that relating the specific surface to composition (Fig. 1), qualitative composition of the catalysts has a considerable effect on its character; this shows itself in the extent of interaction of the two components (represented by the maximum specific catalytic activity) at a given composition of the catalyst and in the fact that the system NiO–ZnO is generally a more efficient catalyst than the system NiO–CuO. The preparation procedure of the catalysts also has a considerable effect on this function, since, as was found earlier⁴, with the system NiO–ZnO prepared from carbonates the function exhibits only one peak, at 6 mol % of ZnO.

Consequently, both systems have maxima of the specific catalytic activity in the marginal regions of their composition. Hence it can be assumed that the cause of the increased catalytic activity is an effect of one of the components on the other, which is only possible if the amount of the former is relatively small and its dispersity considerable. This idea is supported by other papers, reporting direct proportion of dispersity of a catalytic component to its catalytic activity⁸. In this connexion it should be noted that, as our measurements show, the interaction of the catalyst components is not conditioned by the formation of a solid solution in the system. Also the structural studies afford evidence that in the discussed marginal regions of the two systems, characterized by increased catalytic activities, the dispersity of the minor component is relatively great; in the system NiO–ZnO in the region of excess

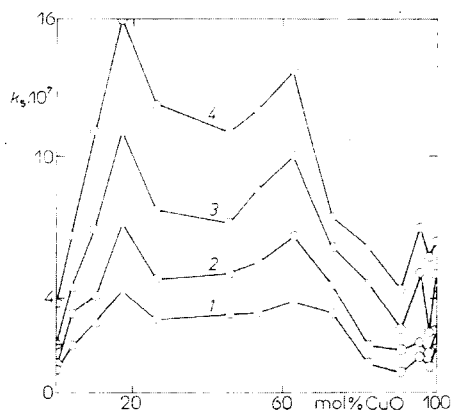
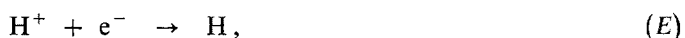


FIG. 3

The Same Function as in Fig. 2 for the System NiO–CuO

of NiO a solid solution was observed, whereas in a sample containing ~ 70 mol % of ZnO we detected only the two most intense reflexions of NiO, which completely disappeared with further decrease in the content of NiO. It is characteristic of the system NiO–CuO that only in samples containing at least ~ 30 mol % of CuO the first selective reflexions of CuO appear. In the other marginal region of this system the strongest reflexion of NiO was observed in a sample containing 95% of CuO.

The discussed peaks of specific catalytic activity in the marginal regions of the two systems can be interpreted on the basis of our hypothesis in terms of the electron theory of catalysis (in analogy to the system NiO–ZnO prepared from carbonates⁴). The decomposition of hydrogen peroxide on a system NiO–ZnO can schematically be described by the following elementary reactions



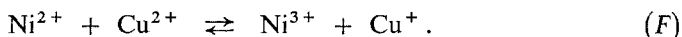
Reactions (B) and (C) express a donor process, proceeding on the acceptor sites of the catalyst (ions Ni^{3+}), reactions (D) and (E) express the acceptor mechanism on the donor sites (Zn^+). Reaction (F) maintains a constant concentration of the catalytic sites (and thus a constant catalytic activity) on the surface of the catalyst. Similarly to what was shown with the system NiO–ZnO prepared from carbonates⁴, the maximum catalytic activities should be observed with samples having the maximum concentrations of the pairs of ions Ni^{3+} and Zn^+ in a state where either ion can affect the other. With an increase in the content of ZnO in the sample the concentration of these ion pairs will be greater, since the minor reaction sites are the donor sites, *i.e.* Zn^+ ions. As, however, an increase in the content of ZnO is accompanied by a decrease in dispersity of this oxide in the sample, the concentration of the ion pairs Ni^{3+} – Zn^+ with a possible interaction of the two partners will reach a maximum value in the marginal region of the excess of nickel oxide (around 10 mol % of ZnO), as was the case in the system NiO–ZnO prepared from carbonates.

Quite analogously can be explained the maximum catalytic activity in the other marginal region, with the excess of ZnO, where the minority reaction sites are the

acceptor sites (Ni^{3+}), whose surface concentration controls the catalytic activity of the sample.

The considerable "sharpness" of the maxima discussed can be ascribed to the fact that the introduction of the minority component into the catalyst is associated with the establishment of an equilibrium expressed by reaction (F). The circumstance that in this system the maximum specific catalytic activity is higher in samples with an excess of ZnO than in those representing the other margin can be accounted for by the assumption that in the latter region the solid solution shifts equilibrium (F) to the left side, *i.e.* the free electrons of ZnO (*n*-semiconductor) fill the positively charged holes of NiO (*p*-semiconductor), by which the two oxides are "stoichiometrized".

The peaks in the marginal regions of the system NiO–CuO can be explained analogously. The analogy is justified by measurements of semiconductivity types of the two oxides. These showed that in contrast to NiO, as a typical *p*-semiconductor with a high *p*-semiconductivity, the CuO oxide prepared by ourselves had a very low value of *p*-semiconductivity. Hence we can infer that the acceptor sites will be the ions Ni^{3+} and the donor sites the ions Cu^+ . The course of the reaction can be described by the following steps:



From the course of the specific catalytic activity of this system measured in relation to its composition and from the structural analysis it seems that in the region of NiO excess the interaction of the two components is stronger (probably as a consequence of a higher dispersity of CuO) than in the other marginal region.

In addition to the catalytic maxima discussed above, either system exhibited a maximum at about 50 to 60 mol % of one of the components. This maximum cannot be explained by interaction of the two components since here, as appears from a structural analysis, the dispersities of the two components in the catalyst were low. It seems likely, however, that just in this region of about equal content of the two components the interphase surface of the two-component system is largest, which stabilizes catalytic sites at the interphase and promotes the catalytic

activity of the system. Our observations⁹ substantiate this view; it was ascertained that a system NiO-ZnO prepared by calcination of carbonates and irradiated by neutrons and γ -rays had its greatest catalytic activity just in the region of equal contents of the two oxides, which suggests stabilization of the defects caused by the irradiation in the interphase of the system.

Measurements of catalytic activities of the samples at different temperatures revealed that the apparent activation energy of the reaction ranged with composition from the value corresponding to pure NiO (15 kcal/mol) to that corresponding to pure ZnO (4.1 kcal/mol) or CuO (22.4 kcal/mol). This demonstrates that the measured value is an average of the apparent activation energies of the reaction proceeding at the catalytic sites of the pure components and at the sites formed by their interaction. Since the apparent activation energy was found to be unchanged after heating the samples to 500°C for 1 h under nitrogen the heating seems to have had no effect on the character of the catalytic sites.

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