DECOMPOSITION OF HYDROGEN PEROXIDE ON A TWO-COMPONENT NiO-ZnO CATALYST

V. MÚČKA and J. CABICAR

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

Catalytic activity of two-component catalysts consisting of nickel and zinc oxides having different contents of both oxides within $0-100\%$ has been studied in the decomposition of hydrogen peroxide. In this system, influence of both basic components between each other takes place, which becomes evident not only in the specific surface areas of samples of various composition, but also in their catalytic activity which attains its maximum value for a sample containing 6 mol% of ZnO. The nonmonotonic dependence of catalytic activity upon composition of samples, as well as other properties of the catalysts under investigation, can be explained taking the electronic mechanism of catalysis into account, provided that this reaction proceeds on nickel oxide as a donor process, while on zinc oxide an acceptor process is involved.

It follows from some papers dealing with decomposition of hydrogen peroxide on two-component semiconductor catalysts that specific catalytic activity of these systems is as a rule not an additive function of the catalyst composition[1]. This may be explained by influence of both catalyst components between each other. The influence can be in some cases demonstrated by formation of a solid solution in the system[2,3], or by formation even of a compound[4]. The surface "compound" with oxygen[5-8] seems to play an important role for the catalytic activity of oxide catalysts in the decomposition of hydrogen peroxide.

In this paper, the catalytic activity of a two-component catalyst composed from nickel oxide and zinc oxide of varying content of a pure component within $0-100$ mol% has been studied. It is of interest to study this system, particularly because of the fact that decomposition of hydrogen peroxide proceeds on nickel oxide as a donor reaction[9], whereas decomposition on zinc oxide may be classified as an acceptor process[10]. Owing to the fact that it was proved in our another paper[3] that influence of basic components between each other takes place in the preparation of these catalysts, represented by formation of a solid solution, it may be expected that also catalytic properties of this system will be markedly affected.

EXPERIMENTAL

Preparation of samples. All the samples were prepared by calcination of freshly precipitated carbonates of both metals for 6 hours at 400°C. Some of them were calcinated at temperatures

of 300 and 600°C. The reagents used were of A.R. purity. Detailed description of the preparation, analysis and measurements of specific surface areas have been presented in paper[11].

Measurement of catalytic activity. As testing reaction to measure catalytic activity of the samples, decomposition of a 2·5% aqueous solution of hydrogen peroxide (A. R. purity) was employed. Catalytic activity of the samples was examined using apparatus designed in Fig. 1. Volume quantity of oxygen released from the system by the reaction was measured with a gas burette 3. The reaction system was uniformly stirred by a magnetic stirrer 2 during the measurement, and thermostated by a flow mantle connected to the thermostat (temperature was maintained at the given value within ± 0.1°C). Constant pressure could be in the system maintained within ± 1 mm of the manometer column 5 filled with dibutyl phthalate, this making it possible to carry out measurements with an error less than $0.5 - 2\%$. A levelling bottle 6 served to compensate pressure alterations, due to external effects, on both sides of the manometer. After tempering the given volume (20 ml), of the hydrogen peroxide solution to the temperature desired, the reaction vessel 1 was given an accurately weighed amount of the catalyst (20 to 80 mg). The increasing pressure of the system was compensated by letting water flow from the gas burette, whose amount was measured at suitable time intervals. The measured volume amount of released gas was transformed to standard conditions of the ambient. Catalytic activity of each sample was measured at four different temperatures (20·0; 25·0; 30·0, and 35·0°C). Decomposition of hydrogen peroxide without a catalyst was proved not to take place under these conditions.

RESULTS

Composition of the catalysts and their specific surface areas are summarized in Table I. It shows that specific surface areas of samples are a distinct nonmonotonic function of their composition. Practically with all the samples having excess of nickel oxide a change in colour of the catalyst takes place at first moments of the course of the catalytic reaction; the colour changes from grey to green. The reaction kinetics was thus examined on the catalyst surface modified by the reaction itself.

Prior to the study of the catalytic activity of samples it was demonstrated that speed of stirring the system has no effect on the rate of the reaction and for at least up to a 5% conversion of peroxide, the reaction may be considered a zero-order process. In this region, the catalytic activity of a catalyst can be therefore characterized by the rate of reaction measured, *i.e.* by the amount of oxygen released within a time unit. This rate was then evaluated in the amount of hydrogen peroxide decomposed in one second, thus the catalytic activity of all the samples being characterized. It has been further found that under given conditions the rate of the reaction is for all the samples proportional to the amount of the catalyst used as well as to initial concentration of hydrogen peroxide; this gives evidence that a 1st order reaction is concerned, similarly as has been found also by other authors[4,9,12].

Results of a systematic study of the catalytic activity of samples at four different temperatures are graphically presented in Fig. 2. Here, the catalytic activity of samples relates to the weight amount unity of the catalyst. It is evident from this Figure that nonmonotonic course of the catalytic activity of the samples as dependent on their composition takes place, which is similar for all the temperatures employed. The

catalytic activity of pure nickel oxide is here higher than that of zinc oxide. Owing to a distinct dependence of the specific surface areas of the samples upon their composition, this catalytic activity was standardized for the surface. Dependence of the specific catalytic activity thus achieved upon composition of the samples is presented in Fig. 3, curve *1*.

It follows that even specific catalytic activity of pure nickel oxide is higher than
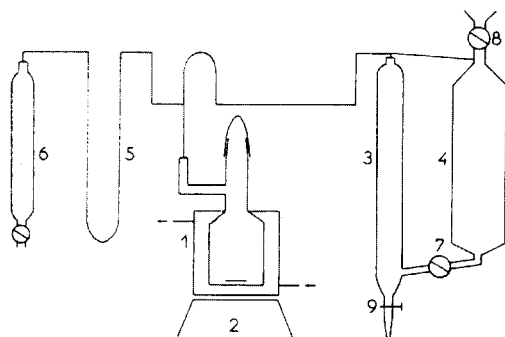

FIG. 1

Apparatus for Measuring Kinetics of Decomposition of Hydrogen Peroxide

1 Reaction vessel, 2 magnetic stirrer, 3 gas burette, 4 water reservoir, 5 pressure gauge, 6 compensation volume, 7—9 stopcocks.
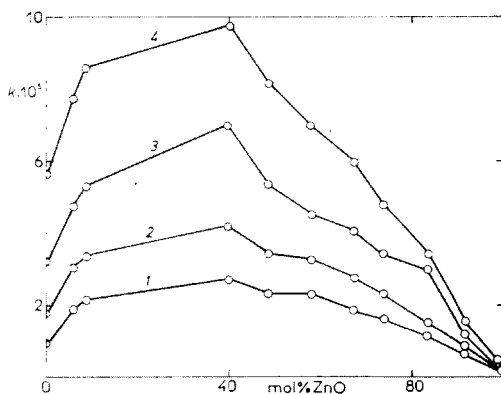

FIG. 2

Dependence of Catalytic Activity k (mol/s.g) upon Composition of Samples for Reaction Temperatures of 20·0 *1*; 25·0 *2*; 30·0 *3*; 35·0 *4* °C

that of zinc oxide. This is in accordance with the fact described earlier that in the decomposition of hydrogen peroxide the p-type semiconductor becomes evident as a more effective catalyst than the n-type semiconductor[12,13]. With the increasing content of zinc oxide the specific catalytic activity increases at the beginning, attains maximum for 6 mol % of ZnO and afterwards, it linearly decreases down to a value belonging to pure zinc oxide. Unlike this, an analogous dependence measured for samples obtained by mechanical mixing of pure oxides at different ratios is monotonic and linearly decreases with the increasing content of zinc oxide in the sample. As was further found, composition of the catalyst affects also value of apparent activation energy of the process studied (Table II).

The measurement of catalytic activity and apparent activation energy of the reaction for a sample having 30 weight % of nickel, which was calcinated at various temperatures, results in a finding that specific catalytic activity of the sample prepared at 400°C is higher $(12 \cdot 7 \cdot 10^{-7} \text{ mol/s.m}^2)$ than that of the same sample obtained at 300°C $(8 \cdot 0 \cdot 10^{-7} \text{ mol/s.m}^2)$. At the same time value of the apparent activation energy of decomposition is independent of the temperature of calcination $(13 \cdot 0 \text{ and } 12 \cdot 9 \text{ kcal/mol, respectively})$.

Furthermore, effect of heat treatment of the catalysts on their catalytic properties has been studied. To achieve this, the samples of various compositions were heated in a nitrogen atmosphere at 150, 300, and 500°C for 1 hour. It was shown on these
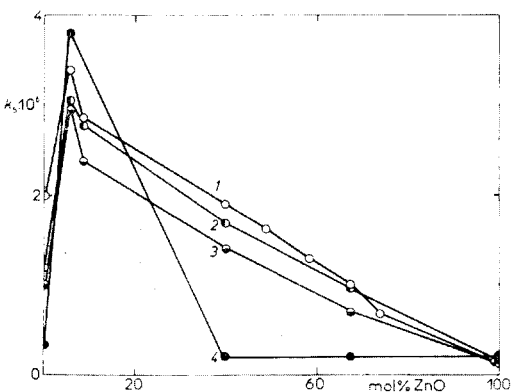

FIG. 3

Dependence of Specific Catalytic Activity k_s (mol/s.m^2) upon Composition of Catalysts Heat-Treated in Different Ways

Temperature of reaction 35·0°C; Heat treatment: 1 —; 2 150; 3 300; 4 500 °C.
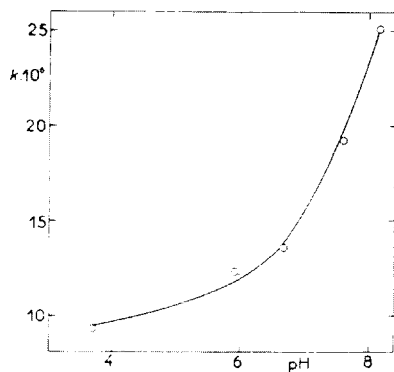
FIG. 4

Dependence of Catalytic Activity of Nickel Oxide k (mol/s.g) at 20·0°C upon pH Value of the Hydrogen Peroxide Solution

samples that only heating up to a temperature of 500°C has a measurable effect on size of their specific surface area. After treating the samples at this temperature, their specific surface area was again measured and the catalytic activity measured was standardized for this value. Fig. 3 shows that temperatures of 150 and 300°C (curves *2*, *3*) become evident only by a moderate decrease of specific catalytic activity of the samples. In contrast to this, the temperature of 500°C provides distinct changes in catalytic properties of the samples (curve *4*), which become evident by a great decrease of their catalytic activity (except for the sample having approx. 6 mol% of ZnO, and pure zinc oxide).

TABLE I

Composition and Size of Specific Surface Areas of Catalysts

No	Weight %		Weight %		mol %		Spec. surface area m^2/g
	Ni	Zn	NiO	ZnO	NiO	ZnO	
1	74·98	—	95·4	0·0	100·0	0·0	28·3
2	70·64	6·08	89·8	7·6	94·3	5·7	22·7
3	68·25	6·84	86·8	8·5	91·5	8·5	30·1
4	60·61	13·78	77·1	17·1	83·1	16·9	45·7
5	52·94	22·14	67·3	27·6	72·8	27·2	48·4
6	43·07	31·56	54·8	39·3	60·4	39·6	51·3
7	36·53	38·23	46·5	47·6	51·5	48·5	50·7
8	29·12	45·64	37·1	56·8	42·2	57·8	55·0
9	22·70	51·43	28·9	64·0	33·0	67·0	59·9
10	18·61	54·83	23·7	68·2	27·5	73·5	72·9
11	11·44	63·19	14·6	78·6	16·8	83·2	66·8
12	6·07	69·17	7·7	86·0	8·9	91·1	51·2
13	0·98	75·09	1·3	93·5	1·1	98·9	37·7
14	—	78·54	0·0	97·7	0·0	100·0	19·3

TABLE II

Apparent Activation Energy Values of H_2O_2 Decomposition (kcal/mol) on Catalysts of Various Composition

mol% ZnO	0·0	12·4	50·2	91·6	100·0
E	21·1	16·2	15·0	10·0	9·2

The fact that heating the catalysts changes considerably their catalytic properties is also proved by the dependence of the value of apparent activation energy of the process upon temperature of treating the samples of various compositions (Table III). It can be seen from this Table that with the samples thermally treated at higher temperature, the reaction with a lower apparent activation energy takes place. An exception is made with samples of an approximate content of 6 mol% of ZnO (samples No 2 and 3) and with pure zinc oxide (sample No 14).
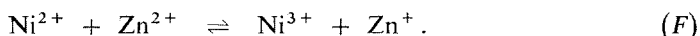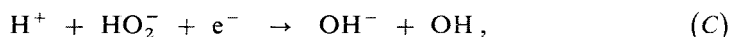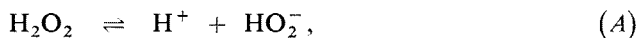
Further experiments proved that catalytic activity of pure nickel oxide considerably depends upon pH value of the solution employed (Fig. 4). From this Figure it follows that catalytic activity of the oxide rises approximately exponentially with the increasing pH value of the medium. For the case, when the reaction proceeds on a pure zinc oxide, an increase of pH value of the medium can be found. After a several-hours decomposition of peroxide at 35°C, the pH value of the solution increased from 3·68 to 6·48.

DISCUSSION

It follows from the experiments presented that in the studied NiO–ZnO system, an influence of both components between each other becomes evident not only in structural properties[3], but also in sizes of specific surface areas of the samples of different composition. Influence of the catalytic properties manifests itself in the nonmonotonic dependence of specific catalytic activity of the samples upon their position (Fig. 3, curve 1).

A proof of that this dependence is really a result of influence of the oxides between one another, is the fact that for a mechanical mixture, the specific catalytic activity is an additive function of catalytic activities of pure components. The found dependence of the specific catalytic activity is typical for a modified surface of the catalyst[14] and is analogous to the dependence found for the magnesium oxide–tin(IV)oxide system[4], where the authors explain the obtained course by the presence of the surface compound suggested. In our case, X-ray analysis of the samples[3] did not prove formation of the compound and the observed dependence seems then little probable to be explained in this way.

The phenomenon observed can be explained by the influence of both oxides between one another. As has been said at the beginning of this paper, presence of superstoichiometric oxygen on the surface of nickel oxide is important for catalytic activity of the latter. This means that the Ni^{3+} ions are primarily responsible for the catalytic activity of nickel oxide. On the other hand, the Zn^+ ions are responsible for the catalytic activity of zinc oxide[15]. The Ni^{3+} ions and Zn^+ ions may be then regarded as acceptor and donor centres of the reaction, respectively. On the basis of these assumptions the decomposition of hydrogen peroxide may be depicted by the following elementary steps:

$$H_2O_2 \quad \rightleftharpoons \quad H^+ + HO_2^-, \tag{A}$$

$$Zn^+ \quad \rightarrow \quad Zn^{2+} + e^-, \tag{B}$$

$$H^+ + HO_2^- + e^- \quad \rightarrow \quad OH^- + OH, \tag{C}$$

$$HO_2^- \quad \rightarrow \quad HO_2 + e^-, \tag{D}$$

$$Ni^{3+} + e^- \quad \rightarrow \quad Ni^{2+}, \tag{E}$$

$$Ni^{2+} + Zn^{2+} \quad \rightleftharpoons \quad Ni^{3+} + Zn^+. \tag{F}$$

The dissociated molecule of hydrogen peroxide accepts one electron (reaction (C)) released by the donor centre of zinc oxide (reaction (B)). The ionic radical HO_2^- produced by dissociation of hydrogen peroxide (reaction (A)) gives over an electron (reaction (D)) to the acceptor centre of Ni^{3+} (reaction (E)). At the same time, the equilibrium of acceptor and donor centres (reaction (F) is maintained in the catalyst, due to the influence of both oxides between each other. Both processes (B, C) and (D, E) lead to the decomposition of hydrogen peroxide. The sample of the highest concentration of the Ni^{3+} and Zn^+ ions couple on its surface may be then assumed to exhibit the highest catalytic activity. An analogous finding has been presented for manganese oxide[8]. This concentration increases with the increasing content of zinc oxide in the sample. Owing to the assumed charge, interaction of the oxides having an increasing content of ZnO in the sample, the holes of NiO are filled with electrons of ZnO (both oxides are approaching a stoichiometric com-

TABLE III

Apparent Activation Energy of Reaction Taking Place on Catalysts of Various Composition and Heat Treatment

No	E, kcal/mol			
	—	150°C	300°C	500°C
1	21·1	19·0	14·7	9·1
2	16·7	16·3	15·3	18·1
3	16·4	16·0	15·4	—
6	14·8	15·0	11·9	8·2
9	13·6	12·3	9·9	—
14	9·2	12·1	11·3	12·2

position). A maximum concentration of the couples quoted must be then in the region of the nickel oxide excess. In this region (probably at 6 mol% of ZnO), the catalytic activity of the system is therefore the highest one.

It follows from reaction (C) that the acceptor mechanism leads to an increasing concentration of hydroxyl ions in the solution. As has been presented, this fact can be observed in the decomposition of peroxide on pure zinc oxide. On the other hand, relation

$$r = k^0[K_c/c(H^+)]\, c(H_2O_2) \tag{1}$$

can be derived for the rate of reaction on acceptor centres (IV); k^0 denotes the constant, K_c is the dissociation constant of peroxide, $c(H^+)$ the concentration of H^+ ions in the solution, and $c(H_2O_2)$ concentration of hydrogen peroxide. The relation shows that with the increasing pH value of the solution the rate of the donor reaction must increase exponentially. This fact was likewise experimentally confirmed with pure nickel oxide (Fig. 4).

It follows from relation (1) that decomposition of hydrogen peroxide is a 1st order reaction with respect to hydrogen peroxide. Since for the rate of decomposition on donor centres an analogous relationship can be derived, which evidently suggests also a 1st order reaction, it may be expected that also the reaction on mixed catalyst will be the 1st order one. This was likewise confirmed experimentally.

On the basis of the reaction model suggested, even the observed colour change of the catalyst at first stages of the decomposition can be explained. In accordance with other papers it may be assumed[16,17] that the dark colour of the catalysts is due to superstoichiometric oxygen present in nickel oxide, because of the stoichiometric oxide being of green colour. As can be seen from processes (B) and (E), the decomposition of hydrogen peroxide leads to "stoichiometrization" of both oxides. This process stops at a certain value given by reversible reaction (F) which secures steady catalytic activity to the catalyst. This is demonstrated on the outside by a relatively speedy change in colour of the catalyst in the first stage of the reaction, while further course of decomposition does not provide any change of the catalyst.

It seems from the results of the measurements made on samples beforehand thermally treated that system with a maximum catalytic activity (6 mol% of ZnO), for which maximum concentration of donor as well as acceptor centres of the reaction can be assumed, is markedly thermally stable and even after a heat treatment at 500°C, its catalytic activity and apparent activation energy of the reaction do not change. Zinc oxide exhibits a similar stability. This can be associated with the fact that oxygen-defficient places serve here as catalytic centres, and the heat treatment in an inert atmosphere cannot obviously influence concentration of these places considerably.

A particular attention from the viewpoint of the reaction mechanism suggested has been paid to the study of the reaction on pure components. Reaction on pure nickel oxide was examined by Schwab and Múčka[18]. Here it was possible to state that even in this case the kinetics of decomposition can be explained according to the mechanism suggested, provided that the Ni^{2+} ions are here donor centres of the reaction and the Ni^{3+} ions serve as acceptor centres. More attention will be paid to the study of the reaction on pure zinc oxide in another paper, where possibility to assume equilibrium of the $Zn^{2+} - Zn^{+}$ centres will be discussed.

REFERENCES

1. Múčka V.: Chem. listy *62*, 709 (1968).
2. Rubinštejn A. M., Slinkin A. A., Fedorskaja E. A., Šaškin D. P., Kljačko-Gurevič A. L., Sagalovič A. V., Melnikova I. V.: Kinetika i Kataliz *9*, 87 (1968).
3. Múčka V., Cabicar J.: This Journal *40,* 245 (1975).
4. Žabrova G. M., Fobina E. A.: Izv. Akad. Nauk, Otd. Chim. Nauk *6*, 963 (1955).
5. Voltz S. E., Weller S. W.: J. Am. Chem. Soc. *76*, 1586 (1954).
6. Matsunaga Y.: Bull. Chem. Soc. Japan *30*, 984 (1957).
7. Maxim I., Braun T.: J. Phys. Chem. Solids *24*, 537 (1965).
8. Mooi J., Selwood P. W.: J. Am. Chem. Soc. *72*, 4333 (1950).
9. Žuravlev V. A., Kozak M. I., Kuželjuk A. A.: Kinetika i Kataliz *4*, 312 (1965).
10. Schwab G. M.: *Properties of Solid Surfaces.* University of Chicago, 1952.
11. Pospíšil M., Cabicar J.: This Journal *38*, 2016 (1973).
12. Venkateswarlu K. S., Virmani Y. P., Shankar J.: Indian J. Chem. *6*, 495 (1968).
13. Hart A. B., Ross R. A.: J. Catalysis *2*, 251 (1963).
14. Bliznakov G., Lazarov D.: Kinetika i Kataliz *2*, 920 (1961).
15. Mach G. W., Schwab G. M., Sizmann R.: J. Catal. *14*, 261 (1969).
16. Klier K.: Kinetika i Kataliz *3*, 65 (1962).
17. Kuznecov A. N.: Ž. Neorg. Chim. *13*, 2027 (1968).
18. Schwab G. M., Múčka V.: Z. Physik. Chem., Neue Folge *93*, 77 (1974).

Translated by J. Hejduk.