

DECOMPOSITION OF HYDROGEN PEROXIDE ON A TWO-COMPONENT NiO-CdO CATALYST AND THE EFFECT OF IONIZING RADIATION ON ITS CATALYTIC PROPERTIES

Viliam MÚČKA

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

Received September 5th, 1977

The catalytic properties of two-component catalyst nickel oxide-cadmium oxide with the proportions of the components covering the whole composition region 0-100% were examined by studying the decomposition of hydrogen peroxide in aqueous solution on it. In the range 0-25 mol.% CdO, cadmium oxide is found to affect unfavourably the ability of nickel oxide to chemisorb oxygen. The amount of the chemisorbed oxygen increases several times on gamma irradiation of the samples. The effect of cadmium oxide on the catalytic activity of the system shows up in fresh samples only indirectly *via* the changed amount of the oxygen chemisorbed. In older samples the initial catalytic activity of the system is changed, which can be explained based on the concept of bivalent catalytic centres in terms of the co-action of the catalytic centres of the two oxides, which are in equilibrium. The irradiation of the system under study speeds up the processes leading to the establishing of this equilibrium which is thermally very stable, and results in a substantial increase of the catalytic activity of the samples investigated.

The catalytic decomposition of hydrogen peroxide has been studied in several works on various types of catalysts. Although the mechanism of this rather simple reaction has not yet been made fully clear, some qualitative general conclusions can be drawn from the results. According to one of them the catalytic reaction centres are in a way associated with the valency state of the active catalyst component. This applies to metal type catalysts, where a metal can occur in nonzero valency on the metal surface^{1,2}, as well as to oxide catalysts. It has been shown that the catalytic activity of an oxide catalyst is related to the amount of oxygen chemisorbed on its surface³⁻⁵; we were able to confirm this fact for several one-component and two-component catalytic systems, which led us to formulate the concept of bivalent catalytic centres⁶.

The present work deals with the catalytic properties of another two-component catalyst - a nickel oxide-cadmium oxide one - which has not yet been studied from this point of view. This is a system composed of typical *p*- and *n*-semiconductive oxides similarly as the nickel oxide-zinc oxide catalyst studied previously⁷⁻⁹, which offers the possibility to compare analogous catalytic systems.

EXPERIMENTAL

The nickel oxide-cadmium oxide catalysts with the content of the components covering the whole concentration region 0–100% were prepared from nitrates of the two metals (in different ratios) by calcination in an electric furnace on air at 400°C for 4 h; the starting chemicals were reagent grade purity, the concentration of the nitrate solutions was 1 mol/l. The oxides formed were ground and the fraction of the mean grain size 0.1 mm was selected for the study. The samples were analyzed chelatometrically. The amount of the over-stoichiometric chemisorbed oxygen was determined by iodometric titration. The fine structure was studied by X-ray diffraction (Cu anode) both by the Debye-Scherrer method and by the method of back reflections. The lattice parameters of the two oxides were determined from the positions of the selective reflections, and from their half widths the size of the coherent ranges of the two cubic structures was quantitatively estimated. The specific surface of the oxides was determined by means of nitrogen desorption from a mixture nitrogen-hydrogen after the prior low-temperature adsorption. The catalytic activity of the samples was tested by measuring the kinetics of the decomposition of hydrogen peroxide in an aqueous solution of the starting concentration 1.2 mol/l. The kinetics was investigated by measuring the rate of releasing of oxygen from the reacting system at constant temperature and pressure⁷; four different temperatures were applied in the range 40–65°C, the conditions used ensured that the reaction proceeded in the kinetic region. In all cases the reaction was only conducted up to the 5% degree of decomposition, and the catalytic activity of the samples was characterized by the rate constant of the 1st order reaction. In the same manner was tested the catalytic activity of the prior irradiated samples, prepared by irradiating by the ⁶⁰Co γ -radiation so that the total dose was $4.02 \cdot 10^6$ J/kg. Prior to the testing, some of the samples were heat treated in an electric furnace in nitrogen atmosphere at 300, 400, and 500°C for 1h.

RESULTS AND DISCUSSION

Physicochemical properties. The principal physicochemical characteristics of the system under study are given in Table I. As evidenced by the chemical analysis, the conversion of the nitrates to the oxides proceeded quantitatively in the calcination conditions applied. The system can be thus regarded as composed of nickel oxide and cadmium oxide only, which has been also confirmed by the X-ray diffraction analysis. The lattice parameters of the two oxides are in a satisfactory agreement with the tabulated values¹⁰ and do not vary with the sample composition. This indicates that in no composition range a solid solution is formed, in contrast to the NiO-ZnO system where the occurrence of a solid solution of zinc oxide in nickel oxide was found in the range of 0–30 mol % zinc oxide¹¹. It is furthermore apparent from Table I that the specific surface of the samples increases with the increasing content of nickel oxide; the increase is monotonic but not linear, which shows that the catalysts prepared do not represent a mere mechanical mixture of the two oxides. The amount of chemisorbed oxygen rises analogously with the increasing nickel oxide content monotonically and nonlinearly, too, the amount sorbed on samples with high contents of cadmium oxide being practically not measurable by this technique (Table I). This is in agreement with the concept of the

electronic mechanism of oxygen chemisorption on semiconductors. Assuming the chemisorption of oxygen to occur only on nickel oxide, the nonlinearity of the dependence in question may be due to the nonlinear dependences of the specific surface and of the content of nickel oxide (Table I) on the sample composition. For a verification of this hypothesis, the amount of chemisorbed oxygen was normalized to the catalyst's specific surface and to the amount of nickel present in 1 g of the catalyst. This value (α) decreases with the increasing content of cadmium oxide (Fig. 1) up to 25 mol % CdO and does not vary with the additional increase of the cadmium oxide content. This indicates that in the range 0–25 mol % cadmium oxide the amount of the chemisorbed oxygen is not governed uniquely by the specific surface and the content of nickel oxide in the sample (assuming its homogeneous distribution on the surface and in the bulk of the grain). It is thus reasonable to suppose that the oxygen chemisorption is in this range of the catalyst composition affected by the mutual interaction of the two oxides. Since the α value decreases in this range with the increasing content of cadmium oxide, recombination of the nickel oxide holes with the cadmium oxide electrons is likely to occur here, whereupon the concentration of the Ni^{3+} ions in the nickel oxide lowers, as detected by the iodometric titration.

TABLE I

Composition, Specific Surface (S), Amount of Oxygen Chemisorbed on Unirradiated (O^{2-}) and Irradiated ($\text{O}^{2-\prime}$) Catalysts, the Effects of Irradiation on this Quantity ($A_{\text{O}^{2-}}$) and the Size of the Coherent Regions (L) of the Samples

| Sample No | NiO | CdO | NiO | CdO | S m^2/g | O^{2-} | $\text{O}^{2-\prime}$ | $A_{\text{O}^{2-}}$ % | L , nm | |
|-----------|-------|------|-------|-------|------------------------------|-----------------|-----------------------|--------------------------|----------|------|
| | wt. % | | mol % | | | 10^4 | wt. % | | NiO | CdO |
| 1 | 0.0 | 98.8 | 0.0 | 100.0 | 0.2 | 0 | 0 | — | — | 63.6 |
| 2 | 0.9 | 98.4 | 1.4 | 98.6 | 0.2 | 0 | 0 | — | — | — |
| 3 | 16.1 | 83.8 | 24.9 | 75.1 | 2.9 | 10 | 0 | — | — | 48.4 |
| 4 | 30.6 | 69.2 | 43.3 | 56.7 | 2.6 | 15 | 0 | — | — | — |
| 5 | 42.2 | 57.7 | 55.7 | 44.3 | 2.3 | 19 | 128 | 660 | — | 76.9 |
| 6 | 53.5 | 46.5 | 66.4 | 33.6 | 2.9 | 35 | 1 400 | 3 955 | — | 54.9 |
| 7 | 63.7 | 36.2 | 75.2 | 24.8 | 4.6 | 61 | 640 | 1 056 | 69.6 | 63.6 |
| 8 | 70.1 | 29.3 | 81.5 | 18.5 | 5.1 | 173 | 214 | 124 | 86.9 | 83.0 |
| 9 | 79.0 | 21.1 | 86.6 | 13.4 | 5.6 | 331 | 1 500 | 453 | 50.0 | 45.0 |
| 10 | 85.4 | 14.5 | 91.0 | 9.0 | 6.3 | 319 | 2 010 | 630 | 62.2 | 34.4 |
| 11 | 91.2 | 8.6 | 94.8 | 5.2 | 9.3 | 399 | 1 020 | 341 | 27.5 | — |
| 12 | 96.1 | 3.8 | 97.7 | 2.3 | 10.3 | 500 | 646 | 129 | — | 29.4 |
| 13 | 99.9 | 0.0 | 100.0 | 0.0 | 8.9 | 753 | 761 | 101 | 69.6 | — |

In the region of cadmium oxide contents exceeding 25 mol % the α value is constant; the aforesaid interaction of the oxides probably does not occur any more. This may be due to the low dispersity of the two oxides in this range, not changing with the catalyst composition, in contrast to the relatively high dispersity of the oxides in the region of low cadmium oxide contents, exhibiting a decreasing tendency with the increasing cadmium oxide content (Table I).

The gamma irradiation of the oxides brings about a multiple increase of the amount of chemisorbed oxygen (except for pure nickel oxide), which is no more a monotonic function of their composition; this effect of irradiation, expressed through the quantity $\Delta_{O^{2-}} = (O^{2-}/O^{2-}) \cdot 100$ (%) (Table I), exhibits in dependence on the composition a maximum at approximately 9 mol % CdO (a six-fold increase of chemisorption on the irradiation) and another, very pronounced maximum at approximately 34 mol % CdO (a forty-fold increase). It can be assumed that the irradiation results in the formation of nonequilibrium charge carriers, which in the region below 25 mol % CdO (region of mutual influencing of the oxides) can affect partly the charge equilibrium of the two oxides and after the stabilization serve partly as adsorption centres for oxygen; in the region of higher cadmium oxide contents, where the mutual charge interactions of the oxides do not appear, these charge defects can serve as the centres for the chemisorption of oxygen. In the case of samples containing excess cadmium oxide, no overstoichiometric chemisorbed oxygen was found even after the irradiation.

Catalytic activity. The testing reaction of hydrogen peroxide decomposition was studied up to a high degree (40%) and was found to proceed as a first order process, save the two pure components, where a departure from the first order was observed in the sense of an autocatalytic process.

The catalytic activity of the system under study, characterized by the rate constant of the first order reaction, decreases monotonically nonlinearly with the increasing content of cadmium oxide (Fig. 2, curve 1). The shape of this dependence is the same

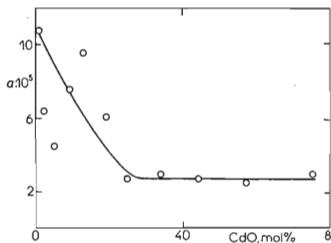


FIG. 1

Dependence of the Amount of Chemisorbed Oxygen Normalized to the Catalyst's Specific Surface and to the Amount of Nickel Present in 1 g of the Catalyst, α ($g_{O^{2-}}/m^2 \cdot g_{Ni}$), on the Composition

at any reaction temperature and is in qualitative accordance with that of the dependence of the amount of chemisorbed oxygen on the composition (Table I). This suggests that the catalytic activity is determined by the amount of chemisorbed oxygen, which is also borne out by the linear interdependence of these two quantities (Fig. 3, straight line 1). The samples 1 and 2 are the only exception, which indicates that the catalytic activity of pure or virtually pure cadmium oxide is not determined by the amount of chemisorbed oxygen, which follows from the nature of this oxide. Since on cadmium oxide, which is substoichiometric with respect to oxygen¹², the chemisorption of oxygen cannot be assumed (and it also has not been observed – see Table I), it is conceivable that cadmium oxide in the system behaves from the point of view of the testing reaction as an indifferent admixture, not affecting directly the course of the reaction. From the viewpoint of the concept of bivalent catalytic centres⁶, the reaction rate is governed by the surface concentration of the minor acceptor catalytic centres constituted by the Ni^{3+} ions. The indirect influence of the cadmium oxide on the catalytic activity of the system examined lies in its affecting of the amount of oxygen chemisorbed on the surface of the mixed oxide (Table I) similarly as was the case with the system nickel oxide–magnesium oxide¹³. That one kind of catalytic centres is controlling the catalytic activity in the whole region of the catalyst composition is corroborated by the constant value of the apparent activation energy of the reaction, amounting to about $(7 \pm 1) \cdot 10^4 \text{ J/mol}$ for all samples.

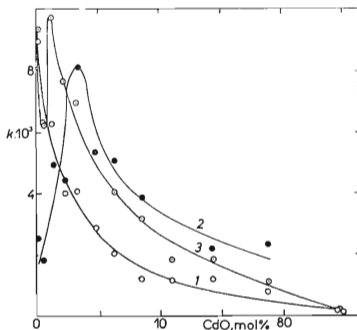


FIG. 2

Dependence of the Rate Constant k (l/g min) at 65°C on the Catalyst Composition
1 Unirradiated samples, 2 samples eight months old, 3 irradiated samples.

The above-mentioned shape of the dependence in question (Fig. 2, curve 1) differs essentially from that for the analogous system of the p-n semiconductors constituted by nickel and zinc oxides⁷, where the maximum catalytic activity was observed for samples with a low content of zinc oxide (6 mol % ZnO). One of the causes of this difference may be the different age of the systems examined (the NiO-CdO system was studied virtually immediately after the preparation, whereas the NiO-ZnO system was investigated after several months). This was confirmed by the study of the catalytic activity of samples of different composition which had been allowed to stand on air at room temperature for 8 months. The dependence of the catalytic activity of those samples on their composition is strongly nonmonotonic, exhibiting a maximum at approximately 13.5 mol % CdO (Fig. 2, curve 2). The shape of this dependence itself suggests that the mechanism of the reaction is here different from that on fresh catalysts. This is supported by the fact that the catalytic activity of older samples is no more determined by the amount of chemisorbed oxygen (Fig. 3, curve 2), the latter — as found — virtually not changing during the ageing. Analogously as in the case of the nickel oxide-zinc oxide system⁷ and some other two-component catalyst⁶, the aforesaid maximum can be explained by the surface concentration of the pairs of the acceptor and donor minor catalytic centres increasing with the increasing concentration of cadmium oxide in the sample, which results in a rise of the system's catalytic activity. The acceptor minor centres are probably constituted by the Ni³⁺ ions, as the donor minor centres can probably act the electrons stabilized

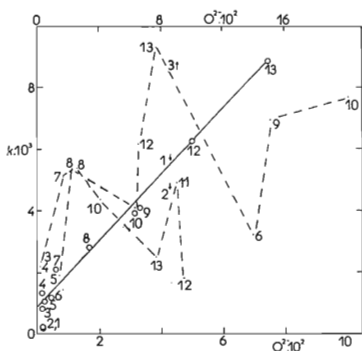


FIG. 3

Dependence of the Rate Constant k (1/g min) at 65°C on the Amount of Chemisorbed Oxygen O^{2-} (wt.%)

1 Unirradiated samples, 2 samples eightmonths old, 3 irradiated samples.

at the oxygen vacancies of cadmium oxide (it may be in principle also the Cd^+ ions, their presence in cadmium oxide is however questionable¹²). At the same time, as the content of cadmium oxide increases a charge interaction of the two oxides occurs (see the preceding part, Fig. 1) leading to a decrease of the concentration of the minor centres of both kinds, which based on the principle of bivalent catalytic centres results in a lowering of the catalytic activity. In addition, the decreasing dispersity of the particles particularly of cadmium oxide in this direction (Table I) also brings about a decrease of the catalytic activity of the system. A result of the simultaneous action of these mutually opposite factors is the observed maximum in the dependence discussed.

Based on these findings it can be concluded that while immediately after the sample preparation cadmium oxide affects the catalytic activity only indirectly, in the case of older samples the influence is direct. The kinetics of the testing reaction is in the latter case determined by the surface concentration of the minor catalytic centres of both nickel oxide (acceptor centres) and cadmium oxide (donor centres). The charge interaction of the two kind centres results in an equilibrium state, which obviously can establish only after a relatively long contact of the two oxides, as observed also with other two-component systems^{13,14}.

Significantly can the catalytic activity of the system studied be influenced by its prior gamma-irradiation (Fig. 2, curve 3): in the conditions applied the catalytic activity rises virtually in all cases. Exception is only the samples No 12 and 13, hence practically pure nickel oxide. This is in agreement with the finding¹⁵ that an absorbed dose of $4.75 \cdot 10^6$ J/kg does not alter the catalytic activity of nickel oxide prepared from the nitrate. This documents the general experience that a multicomponent catalytic system is usually more sensitive to ionizing radiation than a one-component catalyst.

Regarding the shape of the dependence of the catalytic activity of irradiated samples on their composition (Fig. 2, curve 3) being qualitatively the same as that of the analogous dependence for aged samples (except the samples No 12 and 13 mentioned) (Fig. 2, curve 2), the radiation applied speeds up those processes occurring during the sample ageing. Most probably, these are processes leading to the equilibrium of the charge defects in the sample rather than recrystallization processes whose radiation initiation is not very probable in the conditions applied. The radiation-induced free charge carriers obviously enable the equilibrium state to establish in the system rather quickly, similarly as observed for the nickel oxide-cupric oxide system¹⁴. This is proved also by the apparent activation energy of the reaction ($8 \cdot 10^4$ J/mol) being virtually (in the limits of measurement error) not changed on the irradiation, and also by the catalytic activity of the irradiated samples being no more determined by the amount of chemisorbed oxygen, analogously as in the case of aged samples (Fig. 3, curve 3).

The study of differently thermally treated samples (300–500°C) which had been allowed to stand at room temperature for 4 months showed that the catalytic activity (in this case normalized to the catalyst's specific surface) as well as the apparent activation energy of the testing reaction was in the limits of experimental error the same for all the treated samples. From this the conclusion can be drawn that the equilibrium state of the catalytic centres, which after that period has obviously been attained, cannot be affected by the above-mentioned heat treatment, which indicates a considerable stability of the system in question.

REFERENCES

1. Haissinski M. N.: *Jad. Energ.* 7, 73 (1961).
2. Gossner K., Körner D., Hite R.: *J. Catal.* 25, 245 (1972).
3. Voltz S. E., Weller S. W.: *J. Amer. Chem. Soc.* 76, 1586 (1954).
4. Nabe D. R.: *J. Indian Chem. Soc.* 37, 717 (1960).
5. Schwab G. M., Múčka V.: *Z. Phys. Chem. (Frankfurt am Main)* 93, 77 (1974).
6. Múčka V.: *This Journal* 42, 2074 (1977).
7. Múčka V., Cabicar J.: *This Journal* 40, 236 (1975).
8. Múčka V., Cabicar J., Motl A.: *This Journal* 40, 340 (1975).
9. Múčka V., Cabicar J.: *This Journal* 40, 947 (1975).
10. Mirkin L. I.: *Spravochnik po Rentgenostrukturnomu Analizu Polikristalov*. Gos. Izd. Fiz. Mat. Lit., Moscow 1961.
11. Múčka V., Cabicar J.: *This Journal* 40, 245 (1975).
12. Alekseenko L., Ermolaev A. V., Elchinskaya L. M.: *Zh. Fiz. Khim.* 6, 1640 (1964).
13. Múčka V.: *This Journal* 44, 1003 (1979).
14. Múčka V.: *This Journal* 42, 391 (1977).
15. Múčka V.: *This Journal* 41, 2159 (1976).

Translated by P. Adámek.