DECOMPOSITION OF HYDROGEN PEROXIDE ON A TWO-COMPONENT, PRE-IRRADIATED CATALYST OF THE TYPE NiO–ZnO

V.MÚČKA and J.CABICAR

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

The paper describes the catalytic activities of two-component catalysts NiO–ZnO differing in composition and influenced by pre-irradiation with γ rays and neutrons. The irradiation had a significant effect upon the catalytic properties. The degree of this effect was strongly dependent on the composition of a catalyst. The experimental evidence suggests that the effect was a resultant of two effects. One was markedly heat-stable; most likely it was the effect of radiation on the nickel in the catalyst. The other effect was rather labile, being positive or negative, depending on composition; qualitatively it can be ascribed to the influence of radiation on the adsorption-desorption equilibria of different forms of oxygen on the surface of the catalyst.

The effect of ionizing radiation on the catalytic activity of various catalysts for the decomposition of hydrogen peroxide has been treated in several papers[1]. The results of these studies are rather inconsistent. Some authors ascribe the effect of radiation to upsetting the crystalline lattice[2], possibly conditioned by the presence of the so-called activated oxygen[3]. According to other papers the decisive factor is the formation of free charge-carriers in an irradiated catalyst, or the presence of products of a nuclear transmutation[4]. A strong effect of adsorbed oxygen on the "sensitivity" of a catalyst to ionizing radiation is indicated by experiments with oxides of some transition metals[5−8]. The sensitivity of an oxide catalyst to ionizing radiation (expecially γ) seems to be given mainly by interaction of the formed free charge-carriers with pre-adsorbed oxygen on the surface of the catalyst[9,10].

The purpose of this work was to examine the effects of neutron–radiation and γ-radiation from a radium-beryllium source on the catalytic activities of NiO and ZnO in different ratios, prepared by calcination of carbonates of the two metals, in the decomposition of hydrogen peroxide. As has been shown[11], catalysts prepared in this way, in the concentration range $0-30$ mol % of ZnO, are composed of solid solutions of ZnO in NiO. This fact manifests itself markedly in the catalytic properties of a non-irradiated system by a non-monotone dependence of the specific catalytic activity of a sample on its composition[12]. This can be explained by interaction of the donor and the acceptor catalytic centres of the two oxides; the donor centres are considered to be the oxygen-deficient sites (in ZnO) and the acceptor centres the sites with overstoichiometric oxygen (in NiO). As ionizing radiation can well affect the adsorption–desorption equilibrium of oxygen on the catalyst surface, activities of these catalysts may be considerably changed after the irradiation.

EXPERIMENTAL

All the NiO–ZnO catalysts, within the whole concentration region of one component (0—100%), were prepared and analysed according to procedures described[13]. In this paper is also a method of the specific surface measurement described. The samples were irradiated in closed poly-ethylene cases by a radium–beryllium source of neutrons; the flux of heat neutrons was $2 \cdot 2 \cdot 10^{11}$ n/cm^2, that of epithermal neutrons was $8 \cdot 8 \cdot 10^9$ n/cm^2 and the total absorbed dose of γ-radiation was $2 \cdot 1 \cdot 10^{18}$ eV/g. The catalytic activities of the irradiated and the non-irradiated samples were determined by measuring the decomposition rates of a 2·5% solu-ion of hydrogen peroxide. The apparatus, procedure and the evaluation method were described earlier[12].

RESULTS

From analyses and measurements of specific surfaces of the irradiated samples (Table I) it becomes clear that like with the non-irradiated samples[12] the specific surface of a catalyst is strongly dependent on its composition. Comparison with the previous results[12] shows that under the given conditions ionizing radiation does not significantly affect the specific surface. Similarly it can be stated that an irradiated catalyst behaves like a non-irradiated one in other aspects. It exhibits the same colour change at the start of the reaction, which obeys the first-order kinetics.
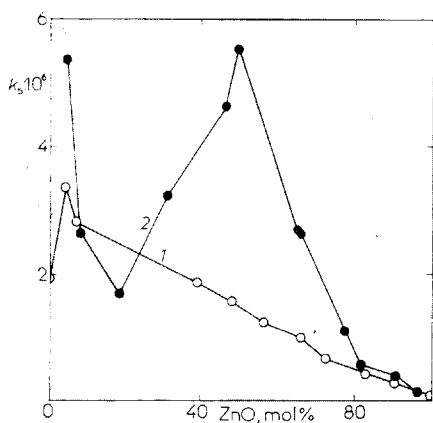

FIG. 1

Specific Catalytic Activity, k_s [mol/s m^2] in Relation to Composition of Non-Irradiated (1) and Irradiated (2) Catalysts at 35°C
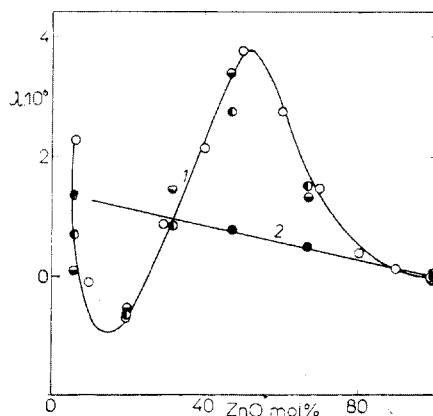
FIG. 2

Effect of Irradiation of Specific Catalytic Activity, λ [mol/s m^2], of Catalysts of Different Compositions and Thermal Annealing of this Effect

1 Total effect; 2 the residual effect after heating to 150°C (◐), 300°C (◑), 500°C (●), the symbol ○ refers to non-heated samples.

However, the effect of irradiation shows itself markedly in the dependence of the specific catalytic activity on composition of the irradiated samples (Fig. 1, curve 2); the same dependence for non-irradiated samples[12] (curve 1) is given for comparison. It is seen that the effect of irradiation on the catalytic activity can be positive or negative and is a function of the catalyst composition. It attained a maximum $(+250\%)$ with the sample having approximately equal contents of the two constituents.

The described effect of ionizing radiation was relatively heat-stable and was unchanged even 50 days (at room temperature) after the irradiation. Heating the irradiated samples for 1 h to $150-300°C$ in nitrogen did not affect their catalytic activities either; it was only at 500°C that they markedly changed (Fig. 2). For this comparison the irradiated and the non-irradiated samples were heated under the same conditions. It can be concluded that the irradiation effect survives even the temperature of 500°C and linearly decreases with the increasing content of zinc oxide (line 2).

The irradiation affected even the apparent activation energy of the process under study. The maximum negative effect, $\sim 40\%$, was observed at about 40 mol% of ZnO, which may have been due to the formation of a saturated solid solution of ZnO in NiO in this region[11]. This effect, however, was not so stable and a certain time after the irradiation the activation energy probably reached its original value (Fig. 3, the sample contained about 66 mol% of ZnO; with the non-irradiated sample the activation energy was 13·6 kcal/mol).

DISCUSSION

As the irradiated catalysts were identical in some fundamental properties with the non-irradiated ones (the same specific surface and the same crystalline structure
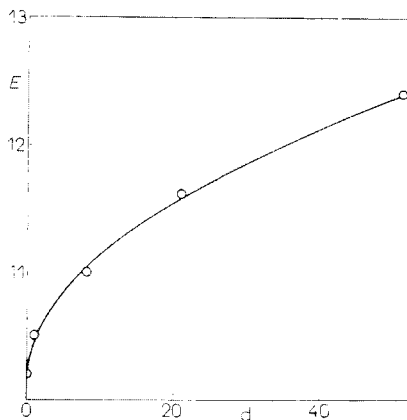

Fig. 3

Apparent Activation Energy of the Reaction, E [kcal/mol] as a Function of Time since the End of Irradiation d [days]

characteristic of the formation of solid solutions[11]) and since some fundamental parameters of the reaction were identical with those observed with the non-irradiated system[12] (first-order reaction in respect to the peroxide, colour change of samples with higher contents of NiO in the early stage of the reaction) it can be assumed that on the irradiated catalysts the decomposition of hydrogen peroxide proceeds by the same mechanism as on the non-irradiated catalysts, or by a similar one; in this mechanism the electrical charges of the two oxides are supposed to affect each other, thus influencing the reaction. To explain the observed effect of ionizing radiation we proceeded from the model used to interpret the properties of non-irradiated catalysts[12].

It can be stated that an ionizing radiation affects both the rate of the decomposition and the apparent activation energy of this reaction. Moreover it is possible to say that in general a change of the rate constant is not caused exclusively by a change in the apparent activation energy of the reaction. This suggests that the mechanism of the irradiation effect is a complex one. In accordance with other authors[14,15] we suppose that as a result of irradiation of the catalyst surface catalytic centres of one kind are partically deactivated, whereas the centres of the other kind are activated. This idea is supported by the observation that after an irradiation the recovering processes at room temperature change only the activation energy whereas the rate of the catalytic process, changed by the irradiation, remains constant.

Since heating the irradiated samples to 500°C did not obliterate the effect of the irradiation, but changed its character, depending on composition of the catalysts (Fig. 2, line 2), it seems that the irradiation produced both heat-labile changes and stable changes, affecting catalytic activity. The effect of the former on catalytic activity can be expressed by the difference between the total (original) effect (Fig. 2, curve 1) and the residual effect after the heating (Fig. 2, line 2).

It is evident that depending on composition of a catalyst the heat-labile irradiation effect can be positive or negative. This fact and the proved interaction of the two oxides are consistent with the electron theory of catalysis on semiconductor catalysts affected by ionizing radiation[16].

In a more detailed analysis of the possible interactions of an ionizing radiation with the mass of a catalyst the following mechanisms should be considered. The radiation can produce ionization through Compton's electrons or photo electrons. This increases the concentration of non-equilibrious, free charge-carriers, which may result in a change of the catalytic activity. In our case, however, the properties of the catalysts remained altered after the irradiation had stopped, and even after heating the samples, which rules out such an explanation. Nor can the irradiation effect be attributed to the so-called "burnishing" because the density of the neutron bombardment was relatively small. In view of the relative heat-stability of the two effects of radiation on the catalytic properties it is conceivable that the neutrons upset some points of the crystalline lattice. The experiments do not refute such an inter-

pretation, but the small density of the passed neutrons makes it unlikely that this mechanism might play a significant role.

In certain cases ionizing radiation can influence the catalytic activity by radiolysis of water adsorbed on the surface of the samples[9,17,18]. Either the water is removed as a catalytic poison from the surface, or there are formed inhibitors or promoters of the reaction by radiolysis. These processes can lead to one effect only (positive or negative). In this way it would be possible to explain the heat-stable positive effect of the radiation (Fig. 2, line 2). What makes this interpretation questionable are the facts that the effect weakens with the increasing content of ZnO, and can be detected even after heating to 500°C.

Irradiation of a catalyst by heat neutrons may also lead to irreversible nuclear processes, the products of which might affect the course of the catalytic reaction. In this way the heat-stable effect of the irradiation could be interpreted. The circumstance that this effect linearly decreases with decreasing content of nickel in the sample suggests that the effect is caused by the action of radiation on nickel. For this reason we paid attention to the nuclear conversion $^{62}_{28}Ni$ (n, γ) $^{63}_{28}Ni$ $\xrightarrow{\beta^-}$ $^{63}_{29}Cu$. A qualitative estimate revealed that the amount of the new component thus formed is in a region of trace concentrations (in the optimum case approx. $10^{-12}\%$ of nickel atoms could be converted). Other possible nuclear processes under the given conditions would produce yields lower still. Thus induced radioactivity is also negligible $(\sim nCi/g)$.

TABLE I

Composition and Specific Surface of the Irradiated Catalysts

%, w/w		%, w/w		mol%		Specific surface m²/g
Ni	Zn	NiO	ZnO	NiO	ZnO	
73·08	5·52	93·9	6·9	93·65	6·35	15·7
70·17	8·42	89·2	10·5	90·28	9·72	27·1
61·88	16·94	78·8	21·1	80·27	19·73	35·7
54·23	27·96	69·0	34·8	68·36	31·64	37·3
39·86	39·42	50·7	49·1	52·97	47·03	41·2
36·87	42·50	46·9	52·9	49·15	50·85	31·9
25·15	54·51	32·0	67·8	33·95	66·05	42·2
24·48	55·21	31·1	68·8	33·06	66·94	38·0
15·99	63·87	20·3	79·5	21·81	78·19	61·6
12·95	67·00	16·5	83·4	17·72	82·28	50·5
6·37	73·69	8·1	91·8	8·78	91·22	46·6
1·48	78·75	1·9	98·0	2·05	97·95	30·1
0·21	80·05	0·3	99·6	0·29	99·71	23·9

Despite these facts it is these processes that might be responsible for the heat-stable effect of irradiation (even a trace admixture can markedly influence the catalytic properties of some systems).

The less stable changes in a catalyst produced by the irradiation can be ascribed to the existence of a relation between the effect of radiation on catalytic activity and the overstoichiometric amount of oxygen chemisorbed on the surface of the sample. Since the mechanism of decomposition of hydrogen peroxide is probably affected even by the overstoichiometric oxygen of the catalyst[12] it is conceivable that even here the irradiation manifests itself through its effect on the adsorbed oxygen. The paragraph below interprets the radiation-produced heat-labile effect in terms of the proposed mechanism of the decomposition of hydrogen peroxide on non-irradiated catalysts[12] NiO—ZnO.

The surface of pure nickel oxide can be assumed to carry an equilibrium of different forms of oxygen (O°, O^-). In view of the p-semiconductive character of this oxide the equilibrium should be shifted in favour of the neutral form, O°, which indeed was found[9] to be the case. This means that after irradiation of the oxide and stabilization of the free charge-carriers on the adsorbed forms of oxygen the equilibrium of these forms shifts to the strongly bound form, O^-. For the electric neutrality to be preserved the concentration of Ni^{3+} ions increases, which, in turn, enhances the catalytic activity of this oxide (donor mechanism of the reaction). With increasing content of ZnO in the system ZnO—NiO the p-character of NiO decreases, and so does, consequentially, the positive effect of irradiation on the catalytic activity of the mixed oxide (Fig. 2, decreasing part of curve 1). The rising part of this curve can be interpreted from the behaviour of irradiated pure ZnO. As a result of the irradiation the adsorption equilibrium of oxygen gets shifted to the form O°, which promotes the catalytic activity of ZnO (acceptor mechanism of the reaction). This explains why an increase in the content of ZnO (up to 30 mol% of ZnO) practically compensates for the negative effect of the irradiation.

Consequently, in the sample containing about 30 mol% of ZnO (i.e. in the sample composed of a saturated solution of ZnO in NiO) the effect of the irradiation is practically zero. With a further increase in the content of ZnO in the system the solid solution no longer changes and the observed positive effect of the radiation on the catalytic activity is evidently due to the effect of radiation on the newly formed phase of zinc oxide.

As has been accounted for above on the basis of the electron mechanism, irradiation of this oxide should increase the catalytic acitivity. This might explain the observed increase in Fig. 2. However, with pure zinc oxide no effect of radiation on its catalytic properties was observed. This fact could be explained by the assumption that in pure zinc oxide the formed free charge-carriers are so unstable as to vanish before they can react with the adsorbed oxygen. This idea is supported by the observation that desorption of oxygen from the surface of ZnO following the irradia-

tion, which must accompany the process considered, was observed at rather low temperatures only[19]. By contrast, in two-phase systems (solution and pure oxide) the defective forms on the interphase can evidently stabilize the generated, free, charge--carriers to such an extent that after their diffusion to the surface they can react with the adsorbed oxygen. This also explains why the positive effect of radiation was maximum in the region beyond 50 mol% of ZnO, where the interphase area was probably greatest.

REFERENCES

1. Múčka V.: Chem. listy *62*, 709 (1968).
2. Uhara I., Kishimoto S., Hikino T., Kageyama Y., Hamada H., Numata Y.: J. Phys. Chem. *67*, 996 (1963).
3. Minačev Ch. M., Chodakov J. S.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk *1961*, 1227.
4. Venkateswarlu K. S., Virmani Y. P., Shankar J.: Indian J. Chem. *6*, 495 (1968).
5. Nachman M., Maxim I., Braun T.: J. Phys. Chem. Solids *20*, 307 (1961).
6. Yamashina T., Sano M.: Bull. Chem. Soc. Japan *38*, 180 (1965).
7. Yamashina T., Sano M.: J. Chem. Soc. Japan *87*, 553 (1966).
8. Yamashina T., Nagamatsuija A., Sano M.: Bull. Chem. Soc. Japan *41*, 2257 (1968).
9. Maxim I., Braun T.: J. Phys. Chem. Solids *24*, 537 (1963).
10. Gisquet E., Destriau M.: Bull. Soc. Chim. France *5*, 1455 (1969).
11. Múčka V., Cabicar J.: This Journal *40*, 245 (1975).
12. Múčka V., Cabicar J.: This Journal *40*, 236 (1975).
13. Pospíšil M., Cabicar J.: This Journal *38*, 2016 (1973).
14. Spilners A., Smoluchowski R.: *Reactivity of Solids*, p. 475. J. H. de Boer est.. Elsevier, Amsterdam 1961.
15. Smoluchowski R.: Radiation Res. Suppl. *1*, 26 (1959).
16. Volkenštejn F. F.: Kinetika i Kataliz *2*, 481 (1961).
17. Kohn H. W., Taylor E. H.: J. Phys. Chem. *63*, 500 (1959).
18. Boury M., Dalmal G., Imelik B., Prettre M.: J. Chim. Phys. *63*, 611 (1966).
19. Barry T. I.: *Proc. Int. Conf. Catalysis. Paris 1960*. Communication 70.