

## DECOMPOSITION OF HYDROGEN PEROXIDE ON NICKEL(II) OXIDE IRRADIATED BY $\gamma$ -RADIATION AND BY NEUTRONS

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Decomposition of hydrogen peroxide in aqueous solutions has been studied on nickel(II) oxide, prepared by different routes, irradiated prior to measurement by  $^{60}\text{Co}$   $\gamma$  radiation and by fast neutrons from an Am-Be source. Above a certain amount of absorbed dose, irradiation causes changes in the amount of oxygen chemisorbed on the surface, as well as changes in the catalytic activity of the catalyst. Both the character and the extent of these changes depend significantly on the way of oxide preparation.

The problem of the effect of ionizing radiation on a semiconductor type catalyst has been dealt with in a number of studies<sup>1</sup>. On the basis of previous findings it can be assumed that the modified catalytic activity of oxide catalysts caused by irradiation is in many cases due to charge perturbations in the irradiated samples which can become stabilized on the catalyst surface<sup>2,3</sup>. This can be interpreted in terms of the electron theory of catalysis even in studying the hydrogen peroxide decomposition<sup>4,5</sup>. As has been shown earlier<sup>6,7</sup>, irradiation of nickel(II) oxide by  $\gamma$  rays in the region of absorbed doses greater than  $10^6$  J/kg leads to an increase in its catalytic activity tested by the mentioned reaction, which is accompanied by proportional increase in the amount of chemisorbed oxygen. To the same conclusion came Maxim and Braun when studying the decomposition of hydrogen peroxide on nickel(II) oxide irradiated in a nuclear reactor<sup>8</sup>. As has been demonstrated by Schwab and Múčka<sup>9</sup>, the character of the change caused by irradiation in a reactor ( $\gamma + n$ ) depends substantially on the way of preparation of the used oxide, however, in the studies of the effect of  $\gamma$   $^{60}\text{Co}$  radiation no changes in the catalytic activity could be observed up to the absorbed dose  $10^6$  J/kg.

For this reason it seemed of interest to investigate the effect of  $\gamma$  radiation in the range of doses over  $10^6$  J/kg on the properties of nickel(II) oxide with respect to the way of its preparation and also to follow the effect of neutrons alone on nickel(II) oxide samples prepared by different routes.

### EXPERIMENTAL

The measurement of catalytic activity of nickel(II) oxide was performed using five samples of different origin: Nickel(II) oxide prepared from carbonate (sample C), from nitrate (N), from oxalate (O) as well as commercial samples, products of the firms Riedel de Haën (R) and Merck (M). All chemicals used were of the reagent grade purity. A detailed description of preparation, chemical analysis and microstructure determination is given in paper<sup>9</sup>. Irradiation

of samples by  $\gamma$  rays was carried out using a  $^{60}\text{Co}$  source (mean energy 0.8 MeV) at a dose rate 2.31 W/kg in glass ampoules at laboratory temperature and at atmospheric pressure. Total absorbed doses were  $4.75 \cdot 10^6$  J/kg, in some cases  $13.8 \cdot 10^6$  J/kg. Irradiation of samples by fast neutrons was carried out with an  $^{241}\text{Am-Be}$  source (mean energy 4–6 MeV) at laboratory temperature and at atmospheric pressure. Samples were placed in polyethylene wrapping and  $\gamma$  radiation was screened off by lead foil. Flow density of fast neutrons was  $1.58 \cdot 10^9$  neutrons/m<sup>2</sup>s and the density of passed neutrons was  $2.39 \cdot 10^{16}$  and  $4.45 \cdot 10^{16}$  neutrons/m<sup>2</sup>. The fraction of thermal neutrons did not exceed 5%. Catalytic activity of samples was measured immediately after irradiation, using the same method as with non-irradiated samples. The determination of catalytic activity was based on measuring the rate of oxygen evolution from the reaction system (1.2M solution of hydrogen peroxide) at constant temperature and pressure, at four different reaction temperatures, ranging from 15–50°C. The apparatus and measuring technique were described in an earlier publications<sup>4,9</sup>. With respect to the fact that the applied radiation led in no case to any change in the specific surface area of the samples (measured by low-temperature nitrogen adsorption<sup>10</sup>), their catalytic activity could be characterized by the rate constant of a 1-st order reaction, as related to unit weight of the catalyst. All samples (both irradiated and non-irradiated) were also analyzed as to the content of chemisorbed oxygen, by iodometric titration<sup>6</sup>.

## RESULTS AND DISCUSSION

From the found values of catalytic activity of both irradiated and non-irradiated samples ( $k$ ), of the apparent activation energy ( $E$ ) and of the amount of chemisorbed oxygen ( $A$ ), as seen in Table I, it is evident that the applied radiation is manifested by a change in the catalytic activity only in some of the samples. A marked decrease of this quantity can be observed particularly with samples C and O. Considering the fact that lower radiation doses did not result in any change of catalytic activity<sup>9</sup>, it can be assumed that a certain threshold value of the absorbed  $\gamma$  radiation must be reached to obtain a modification of the catalytic activity. This phenomenon was also observed by other authors<sup>6,7</sup> and is also characteristic for copper(II) oxide<sup>11</sup>. The cause obviously is that, to attain the modified state of surface, a certain minimum equilibrium concentration of induced defects is necessary in the crystals so that they might diffuse towards the surface and participate in the surface process, before they are removed by recombination or by any other mechanism.

A quite analogous conclusion can also be drawn on the behaviour of chemisorbed oxygen where we can assume (with regard to paper<sup>9</sup>) the existence of a threshold absorbed dose which can affect the amount of chemisorbed oxygen<sup>9</sup>. The fact that the amount of chemisorbed oxygen increases upon irradiation of all studied samples (C, N, O) can be explained according to previous studies<sup>2,8</sup> so that, as a result of irradiation of nickel(II) oxide by  $\gamma$  rays, the equilibrium of different forms of sorbed oxygen is probably shifted in favour of the chemisorbed form which can be detected by the described technique. However, this finding proves at the same time, that the changes in the catalytic activity of nickel(II) oxide caused by irradiation need not always be proportional to the changes in the amount of chemisorbed oxygen (a direct proportionality between both kinds of changes was reported by some authors<sup>6,7</sup>).

TABLE I

Rate Constant,  $k$  (1/g min) at 30°C, Apparent Activation Energy of the Reaction,  $E$  (J/mol) and Amount of Chemisorbed Oxygen,  $A$  (%  $O^{2-}$ ) for Samples Irradiated by  $\gamma$  Rays ( $D$ , J/kg)

$D \cdot 10^{-6}$	Sample				
	C	N	O	R	M
	$k \cdot 10^3$				
0.00	0.34	0.25	36.0	1.40	1.94
4.75	0.26	0.25	26.1	1.13	1.65
13.80	0.18	—	19.3	—	—
	$E \cdot 10^{-4}$				
0.00	7.1	7.5	—	7.6	7.8
4.75	7.4	7.6	—	8.5	7.5
	$A \cdot 10^2$				
0.00	7.8	6.4	0.5	—	—
4.75	12.7	14.8	1.6	—	—

Accordingly, even  $\gamma$  radiation alone seems to provoke a series of changes in the oxide, some of which can have an antagonistic effect on its catalytic activity (similarly as it was in the case of nickel(II) oxide irradiated in a nuclear reactor<sup>9</sup>). The qualitative character of catalytic centers remains probably unchanged, since the found value of the apparent activation energy of the reaction remains practically the same before and after irradiation (Table I).

Positive effect of irradiation explained by the increased concentration of  $Ni^{3+}$  ions as acceptor centers of the reaction (accompanied by the increased amount of chemisorbed oxygen)<sup>2,6,7,9</sup> can in this case be suppressed by recombination of the charge perturbations, induced by radiation, with the present catalytic centers of the reaction, which finally results in a negative effect of radiation on the catalytic activity of the sample. Obviously, the final observed effect depends on mutual balance of the antagonistic processes.

A qualitatively similar conclusion can be drawn from the results of measurements of samples irradiated by neutrons (Table II). The applied radiation practically does not affect the value of the apparent activation energy of the testing reaction in any sample, which is an evidence that no qualitative change in the character of catalytic centers occurs operative in the reaction. A change in catalytic activity can be observed only with sample O (decrease) where it is not accompanied by a change in the amount

TABLE II

Effect of Irradiation by Neutrons ( $D$ , neutrons/m<sup>2</sup>)  
Analogous quantities as in Table I.

$D \cdot 10^{-16}$	Sample				
	C	N	O	M	R
	$k \cdot 10^3$				
0.00	0.273	0.209	32.7	1.625	1.270
2.39	0.309	0.237	22.0	1.666	1.245
4.45	0.295	0.269	16.7	1.561	1.199
	$E \cdot 10^{-4}$				
0.00	7.7	6.9	6.0	7.5	9.1
2.39	7.4	8.2	5.5	6.9	7.7
4.45	6.5	8.2	6.7	8.3	7.0
	$A \cdot 10^2$				
0.00	7.8	6.4	0.5	35.0	23.7
2.39	6.5	7.7	1.5	—	—
4.45	6.0	9.1	0.0	9.3	10.3

of chemisorbed oxygen. On the other hand, samples M and R show a decrease in the amount of chemisorbed oxygen after irradiation, however, their catalytic activity remains unchanged. All this demonstrates that analogously to  $\gamma$  rays, the observed effect of irradiation depends on the way of preparation of the oxide catalyst. Since in our case the effect of nuclear transmutations in the irradiated oxide can most probably be excluded (owing to the relatively low fluency of neutrons, low effective cross-sections of nuclear reactions and the character of the found changes) it can be admitted that the decrease both in catalytic activity (sample O) and in the amount of chemisorbed oxygen (samples M, R) is the result of destruction of catalytic or adsorption centers by the applied radiation. In samples M and R it can be caused by their most rough surface and greatest specific area (as proved by electron microscope and by measurement of specific surface area). The fact that no change in catalytic activity was found in these samples indicates that new catalytic centers are formed by irradiation, different from the adsorption centers of oxygen (this kind of „compensation” effect was observed in a number of other works<sup>1</sup>).

The cause of the differing behaviour of sample O can be seen in that this oxide fundamentally differs in its catalytic properties from all remaining compared samples<sup>9</sup>. A more detailed explanation will require further investigation of this oxide from wider aspects.

On the basis of the results obtained so far it can be stated that even in the case of irradiation of oxide by neutrons the effect of the radiation on its catalytic properties is most probably of a complex character and the resulting observed effect is a function of several parameters, of which the way of preparation is undoubtedly an important one.

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