

## DECOMPOSITION OF HYDROGEN PEROXIDE ON A TWO-COMPONENT CATALYST NiO-ZnO WITH INCORPORATED RADIONUCLIDE $^{65}\text{Zn}$

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The paper deals with the effect of the radionuclide  $^{65}\text{Zn}$  incorporated into a two-component catalyst NiO-ZnO on its catalytic properties in the decomposition of hydrogen peroxide in an aqueous solution. The radioactivity of the catalyst has been found to modify essentially the catalytic activity of the system. This phenomenon is characteristically related to composition of the samples and cannot be suppressed even by heating the samples to 500°C. The effect of radioactivity can be elucidated qualitatively under the assumption that the emitted radiation affects the adsorption-desorption equilibrium of oxygen on the surface of a sample.

Some papers treating the problems of heterogeneous catalytic processes on catalysts influenced by an ionizing radiation have shown that in addition to the so-called "external" irradiation of a catalyst prior to a reaction, the "intrinsic" radioactivity of the catalyst can also affect the catalytic activity to a considerable degree<sup>1</sup>. It should be pointed out that the catalytically active constituent may not be identical with the radioactive agent. The mechanism of the effect is still rather obscure and seems to be rather complex since the radiation is operative in the course of the actual catalytic process.

The present paper describes the effect of a constant amount of the radionuclide  $^{65}\text{Zn}$  incorporated into the two-component catalytic system NiO-ZnO, the proportions of the components covering the whole composition range, on the catalytic activity in the decomposition of aqueous hydrogen peroxide. As was shown earlier<sup>2</sup>, in the region of 0 to 30 mol % of ZnO a solid solution of ZnO in NiO was formed in these catalysts, prepared under the given conditions. Pre-irradiation of these catalysts from a radium-beryllium source had a strong effect on their activities<sup>3</sup>. In view of this fact we considered it of interest to ascertain whether even the "intrinsic" irradiation of the system would affect its catalytic properties.

### EXPERIMENTAL

All the catalysts were prepared by co-precipitation of aqueous nickel and zinc nitrates, in different ratios, to carbonates, which were then calcinated under conditions described previously<sup>4</sup>. A constant quantity of the radionuclide  $^{65}\text{Zn}$  was added to the starting solutions in the form of nitrate, bringing the specific radioactivity of the catalysts to a value of 3 mCi/g. All chemicals were of A.G. purity. After analysis of the samples and measurement of their specific surfaces<sup>4</sup>

the samples were left standing in the air for months. In this time 1 g of a catalyst had emanated an energy of  $3.9 \cdot 10^{20}$  eV in the form of  $\gamma$ -radiation and its specific radioactivity decreased to a tenth of the original value. The catalytic activity was then measured on decomposition of 2.5% aqueous hydrogen peroxide under the same conditions as those used with the nonradioactive samples<sup>5</sup>. Comparison of the results with those obtained with the non-radioactive samples<sup>5</sup> gives some idea on the effect of radioactivity of a catalyst on its catalytic properties.

## RESULTS

The compositions of the catalysts and their specific surfaces are given in Table I. Comparison of these values with those found with the non-radioactive samples of the same compositions<sup>5</sup> shows again that the specific surface was a non-monotone function of the composition, with no appreciable effect of the presence of the radioactive component. Like with the non-radioactive samples<sup>5</sup>, or those bombarded by neutrons<sup>3</sup>, the reaction studied was of first order and in its early stage catalysts with higher contents of nickel oxide exhibited the previously described change of colour. Comparison of the specific catalytic activities of the radioactive and the non-radioactive<sup>5</sup> samples in relation to composition (Fig. 1) shows that the radionuclide

TABLE I

Composition and Specific Surface of the Catalysts

A Sample with a starting specific activity of 0.8 mCi/g; B sample with a starting specific activity of 22.5 mCi/g.

No	% (w/w)		% (w/w)		mol %		Specific surface m <sup>2</sup> /g
	Ni	Zn	NiO	ZnO	NiO	ZnO	
1	70.00	6.39	89.1	8.0	92.96	7.04	13.7
2	68.80	7.57	87.6	9.4	91.40	8.60	20.7
3	61.00	15.00	77.6	18.7	82.53	17.47	24.6
4	49.20	27.60	62.6	34.3	66.40	33.60	34.3
5	47.80	30.00	60.8	37.4	63.77	36.23	38.1
6	35.50	41.90	45.2	52.2	48.38	51.62	27.2
7	23.10	52.20	33.6	64.6	33.62	66.38	65.8
8	21.80	55.40	27.7	69.0	30.57	69.43	31.2
9	16.00	61.80	20.4	76.9	22.31	77.69	23.6
10	10.92	67.40	13.9	83.9	14.87	85.13	60.9
11	4.05	75.97	5.1	94.2	5.73	94.27	42.4
12	1.40	79.12	1.6	98.1	1.64	98.36	15.4
13	0.00	77.01	0.0	95.5	0.00	100.00	68.1
A	23.79	55.54	30.2	68.9	32.25	67.75	63.3
B	11.62	64.60	14.8	80.4	16.23	83.77	50.9

significantly altered the catalytic activity. In a wide range this quantity was independent of composition in the radioactive samples.

An absolute and a percentual expression of the effect of radioactivity on the catalytic activity in relation to composition of the system are shown in Fig. 2. The absolute

TABLE II

Effect of Specific Radioactivity on Catalytic Activity ( $k_s$  at 35°C) in Samples of Different Composition

A 67 mol% ZnO; B 84 mol% ZnO.

Sample	mCi/g	$k_s \cdot 10^7$ mol H <sub>2</sub> O <sub>2</sub> /s m <sup>2</sup>	<i>E</i> kcal/mol
A	0.0	6.6	11.9
	0.8	20.1	12.9
	3.0	6.4	12.7
B	0.0	3.0	9.6
	3.0	13.5	10.4
	22.5	12.7	12.8

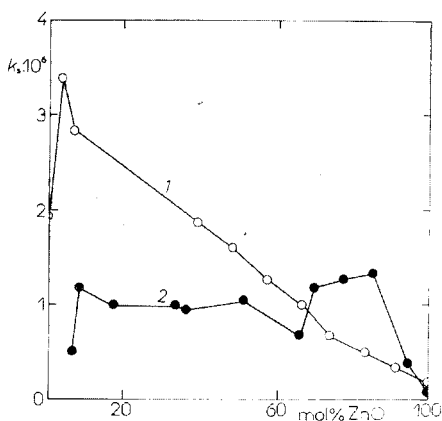


FIG. 1

Specific Catalytic Activities  $k_s$  (mol/s m<sup>2</sup>) of Non-Radioactive (1) and Radioactive (2) Catalysts as Functions of their Composition at 35°C

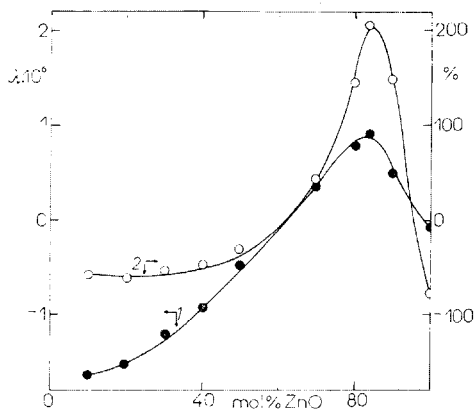


FIG. 2

Effect of Radioactivity of the Catalysts on their Catalytic Activity Expressed by Differences between the Specific Catalytic Activities,  $\lambda$  [mol/s m<sup>2</sup>] (1), and Relatively (2) The reaction temperature 35°C.

values of this effect are expressed by differences in specific catalytic activity between the radioactive and the non-radioactive samples of equal compositions; the effect of radioactivity was so strongly composition-dependent as to vary between the positive and the negative sides.

Table II suggests that the catalytic activity of a catalyst is also dependent on its specific radioactivity. It further follows from Table II that the apparent activation energy of the reaction is practically independent of the specific radioactivity of a catalyst.

By measuring the catalytic activities of radioactive samples that had been heated to different temperatures between 0 and 500°C under nitrogen for 1 h it was ascertained that virtually neither the catalytic activity nor the apparent activation energy was affected by the heating, in contrast to what had been observed with non-radioactive<sup>5</sup> and pre-irradiated<sup>3</sup> samples.

## DISCUSSION

Since some of the fundamental reaction parameters (order, apparent activation energy, colour change of the catalyst) were the same with the radioactive and the non-radioactive systems the reaction mechanisms on the two systems are probably identical. Comparison of the results in this paper with those obtained in studying neutron-bombarded catalysts of the same type<sup>3</sup> leads to the conclusion that the "intrinsic" irradiation of a catalyst and the "external" irradiation by  $\gamma$ -rays and neutrons have qualitatively different effects. This conclusion was also arrived at with other systems<sup>6</sup>.

To interpret the phenomena observed the following mechanisms of the effect of radioactivity on a catalyst can be considered as the most probable ones.

Radioactive disintegration of  $^{65}\text{Zn}$  gives rise to the stable isotope of copper, which may influence the catalytic properties of the system. A quantitative estimate revealed that in the time elapsed from preparation of the radionuclide to measuring the catalytic properties of the samples there could not have been formed more than  $7 \cdot 10^{-6}\%$  of copper. This value is too low and since, moreover, the effects of radioactivity in samples of different compositions were both positive and negative the formation of copper could hardly be responsible for the effect observed, at least not to a significant extent.

As in the system considered the radiation is operative even in the course of the reaction a radiolytic process also seems possible. If the radiolysis were homogeneous the effect observed would necessarily have the same value with samples of different compositions (in view of the fact that the samples had the same specific radioactivity). It must be borne in mind, however, that there might occur radiolysis in adsorbed state, possibly composition-dependent, but still the effect would have to be of the same sense (increase or decrease of catalytic activity), irrespective of the composition.

Structural defects, the so-called "burnishing" or cleaning effect of radiation<sup>7</sup> and the effect of a surface charge of the catalyst (due to emanation of charged particles<sup>8</sup>) are not probable in view of the small energy released from the radionuclide in the form of charged particles.

The catalytic activity of a radioactive sample may also be influenced by non-equilibrium charge carriers, playing a role in the reaction studied. Provided that the decomposition mechanism propounded for the non-radioactive system<sup>5</sup> is correct, the effect of radioactivity can qualitatively be interpreted like in the case of the pre-irradiated samples<sup>3</sup>. It seems justifiable to assume that the free charge carriers, generated in a sample by radioemanation, alter the adsorption-desorption equilibrium of oxygen on its surface, thereby affecting the catalytic activity. The state of the surface oxygen is given in this case by the actual concentration of non-equilibrium, free charge carriers in the sample (or on its surface), this concentration being essentially given by the specific radioactivity of the catalyst. As this was common for all the samples their specific catalytic activity was also independent of their composition (Fig. 1).

Since not even the heating of the catalysts to 500°C affected the catalytic activities of samples differing in composition we assume that the time from the end of the heating to the start of the measurements was sufficient, owing to the constantly emitted radiation, for the original state (of non-heated samples) to restore on the surface.

Nevertheless, other mechanisms are likely to be operative also. This idea can be inferred from, *e.g.*, the dependence of the specific catalytic activity on composition in the marginal regions and the dependence of the catalytic activity of the samples on their specific radioactivity.

#### REFERENCES

1. Múčka V.: Chem. listy 62, 709 (1968).
2. Múčka V., Cabicar J.: This Journal 40, 245 (1975).
3. Múčka V., Cabicar J.: This Journal, in press.
4. Pospíšil M., Cabicar J.: This Journal 38, 2016 (1973).
5. Múčka V., Cabicar J.: This Journal 40, 236 (1975).
6. Taylor E. H.: Advan. Catal. 18, 111 (1969).
7. Farnsworth H. E., Woodcock R. F.: *Proc. Int. Congr. on Catalysis*, p. 23. Philadelphia 1956.
8. Baru V. G., Volkenštejn F. F.: *Izv. Akad. Nauk, Otd. Chim. Nauk* 11, 1935 (1964).

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