

## DECOMPOSITION OF HYDROGEN PEROXIDE ON A CATALYST NiO—CuO PREPARED FROM CARBONATES AND EFFECT OF IRRADIATION ON THE CATALYST

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Catalytic activity of the catalyst of the NiO—CuO type, prepared from carbonates of both metals with different proportions of both oxides has been studied. Decomposition of hydrogen peroxide served as testing reaction. This system, containing in addition to the mentioned oxides also a certain amount of amorphous undecomposed carbonate, is characterized by non-monotonous dependences of both specific surface areas and specific catalytic activities on composition which indicates mutual interaction of both principal components of the catalyst. The presence of carbonate is most probably without any considerable effect on the catalytic activity of the sample. A similar, non-monotonous course, has also been found in the dependence of the amount of chemisorbed oxygen on composition. Both these dependences can be interpreted in terms of the electron theory of catalysis on semiconductive catalysts, assuming the validity of the principle of bivalent catalytic centers. The studied system is characterized by unstable catalytic activity, decreasing with time, which evidently is connected with recombination processes between the catalytic centers. Comparison of the results of the present study with those obtained in studying the same series of catalysts prepared from nitrates, allows to conclude that the way of preparation of the samples has a significant effect on their catalytic activities. Irradiation of the catalysts by  $\gamma$  radiation or by fast neutrons leads to an increase in the amount of chemisorbed oxygen, wherein the character of the dependence of the amount of oxygen on composition remains unchanged, which proves the heterogeneity of the catalyst surface also with respect to the weakly bound form of oxygen. Irradiation of samples by  $\gamma$  rays displays both positive and negative effect on the catalytic activity (in dependence on composition). The effect of fast neutrons is manifested in the first place by its so-called "polishing" effect which results in a decrease of the catalytic activity of samples.

The study of catalytic properties of some oxide catalysts in decomposition of hydrogen peroxide revealed a significant dependence of catalytic activity on the way of their preparation. This was the case with nickel(II) oxide<sup>1</sup>, copper(II) oxide<sup>2</sup> and zinc(II) oxide<sup>3</sup>. Catalytic properties of these catalysts could be explained on the basis of the principle of bivalent catalytic centers<sup>1-3</sup>. The same principle could also be applied to two-component catalysts of different composition<sup>4-6</sup> where it helped to elucidate some changes, observed after irradiation of the catalysts by ionizing radiation<sup>1-3,6-9</sup>. In the case of mixed catalyst nickel(II) oxide—zinc(II) oxide it was found, similarly

as in the case of one-component systems<sup>4,5</sup> that its catalytic properties are markedly affected by the way of preparation of the system and therefore it was necessary to verify this finding also for further types of mixed catalysts. For this purpose we have chosen the system nickel(II) oxide-copper(II) oxide, prepared by calcination of coprecipitated carbonates and we have compared the results with those obtained in studying the same system prepared by calcination of nitrates of the respective metals<sup>5</sup>.

In addition to this, the aim of the study of this system was also to verify the possibility of application of the reaction mechanism suggested for the system prepared from nitrates and also to investigate the effect of irradiation of the catalysts on their properties.

### EXPERIMENTAL

Mixed oxides of the series nickel(II) oxide-copper(II) oxide were prepared from solutions of copper(II) chloride and copper(II) nitrate (1 mol/l) of the reagent grade purity by gradual coprecipitation by a solution of potassium carbonate (1 mol/l) at laboratory temperature under vigorous stirring in such a way that the individual samples covered the whole composition range. The formed precipitate was left aside in the mother liquor with excess precipitating agent for 48 h at laboratory temperature. After filtration and thorough washing the samples were dried for 24 h at 110°C and subsequently calcinated for 4 h at 400°C. Then the samples were triturated and the fraction with average grain size 0.1 mm was selected for experiments.

The samples were analyzed electrolytically. Copper was separated from weakly acidic medium by 1.0–1.5 A current at 2.0–2.2 V at 70°C. Nickel was separated from the same solution, after alkalization, by 0.5–1.0 A at 2.8–3.2 V. Fine structure analysis of the samples was performed by X-ray diffraction, using the Debye-Scherrer method and the method of reversed beam with iron anode according to paper<sup>10</sup>. Specific surface areas of the samples were measured by means of the apparatus MSP by adsorption and desorption of nitrogen from the gaseous mixture hydrogen-nitrogen<sup>11</sup> (3 : 2). All studied samples were also analyzed as to the content of oxygen chemisorbed on their surface<sup>1</sup>.

TABLE I

Compositions and Specific Surface Areas,  $S$  ( $m^2/g$ ), of the Samples

Sam- ple	Weight %		$\Sigma$ weight %	$S$	Sam- ple	Weight %		$\Sigma$ weight %	$S$
	NiO	CuO				NiO	CuO		
1	88.2	0.4	88.6	39.80	7	36.0	42.3	78.3	1.96
2	63.9	0.8	64.7	7.22	8	46.0	48.7	94.7	2.65
3	75.9	4.6	80.5	11.32	9	15.9	50.1	66.0	1.59
4	89.6	17.4	107.0	53.10	10	0.2	62.8	63.0	2.45
5	66.3	31.1	97.4	54.60	11	9.8	85.8	95.6	8.02
6	55.4	40.3	95.7	32.80	12	0.0	105.0	105.0	17.40

Irradiation of the samples was carried out using the  $^{60}\text{Co}$  radiation, at the dose rate 2.31 W/kg so that the applied dose amounted  $5.4 \cdot 10^6$  J/kg and  $1.38 \cdot 10^7$  J/kg. Irradiation by fast neutrons was realized using a  $^{241}\text{Am}$ -Be source with a mean neutron energy 4–6 MeV. In this case the samples were screened from  $\gamma$  radiation (60 keV) by a lead sheet. Under these conditions the fraction of thermal neutrons was found to be less than 5%. The density of neutron flow was  $1.58 \cdot 10^9$  neutrons/m<sup>2</sup>.s and the density of passed particles was  $2.06 \cdot 10^{16}$  neutrons/m<sup>2</sup>. In both cases the irradiation was performed on air at laboratory temperature. Immediately after irradiation the catalytic activity of the samples was measured and compared with that of the non-irradiated samples.

Catalytic activity of the samples was tested using decomposition of an aqueous solution of hydrogen peroxide of the reagent grade purity, of the initial concentration 1.2 mol/l. The measurement was carried out at four different temperatures in the interval 20–35°C. Preliminary experiments showed that under the above given conditions the reaction proceeds in the kinetic region. Apparatus and the way of evaluation of catalytic activity were the same as described in paper<sup>4</sup>.

## RESULTS

Composition and specific surface areas of the studied samples are summarized in Table I. As can be seen, especially in samples 2, 9 and 10 the sum of weight per cent of oxides is lower than 100, whereas in samples 4 and 12 this value is higher than 100. This indicates a rather complicated character of the prepared system. Table I also markedly shows the non-monotonous character of the dependence of specific surface area of the samples on their composition.

By X-ray studies of the structure only two crystalline phases could be detected: cubic structure of nickel(II) oxide and monoclinic structure of copper(II) oxide; in both cases the size of lattice parameters agrees with the tabellated values. Only in the case of samples 4 (17.4 weight% CuO) and 12 (pure CuO) it was possible to detect on the Debyeograms also the most intense selective reflexions of metallic copper.

Study of irradiated samples proved that under the given conditions neither the composition nor the microstructure of the system are affected by the applied radiation.

The results of the study of the amount of chemisorbed oxygen (Fig. 1, curve 1) showed that the dependence of this quantity, normalized to unit surface area, on composition is non-monotonous, too. Two of the three maxima found lie in the marginal regions of composition and the third one lies in the region of approximately the same proportion of both oxides. The course of this dependence is qualitatively the same also in irradiated samples, whereas the total amount of chemisorbed oxygen increases upon irradiation of the catalyst (Fig. 1, curves 2 and 3).

Investigation of the decomposition of hydrogen peroxide to a high degree (40%) showed that the order of the reaction with respect to peroxide equals 1. Catalytic activity of all samples was defined as 1-st order rate constant ( $k$ ) or by this quantity

normalized to the specific surface of the samples ( $k_s$  specific catalytic activity) and the test reaction was followed to maximum 5% of the decomposition. As can be seen from Fig. 2 (curve 1) specific catalytic activity of the samples shows a distinctly non-monotonous dependence on their composition. The first maximum occurs in the region about 1 weight% CuO and the second, particularly marked, in the region with approximately the same proportion of both oxides. This character of the dependence remains unchanged even after irradiation of samples by  $\gamma$  radiation (curves 2 and 3) or by neutrons (curve 4), however, it is evident that irradiation has a non-negligible effect on their catalytic activity. Quantitative evaluation of this effect was carried out according to the relation

$$\Delta, \% = (k_s^+ / k_s) \cdot 100, \quad (1)$$

where  $k_s^+$  is the specific catalytic activity of the irradiated sample and  $k_s$  is the analogous value for a non-irradiated sample. The effect of  $\gamma$ -irradiation is both negative and positive in dependence on composition (Table II). Irradiation of samples by neutrons affects negatively their catalytic activity. In all cases the maximum negative effect on catalytic activity is found in the region with approximately the same proportion of both oxides.

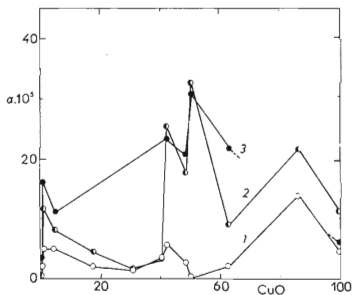


FIG. 1

Dependence of the Amount of Oxygen Chemisorbed on Unit Surface Area of Catalyst,  $\alpha$  ( $\text{g O}_2/\text{m}^2$ ), on Its Composition and on Irradiation

1 Without irradiation; 2 system irradiated by  $\gamma$  radiation ( $1.38 \cdot 10^7$  J/kg); 3 system irradiated by  $\gamma$  radiation ( $1.38 \cdot 10^7$  J/kg); 4 system irradiated by neutrons ( $2.06 \cdot 10^{16}$  neutrons/ $\text{m}^2$ ).

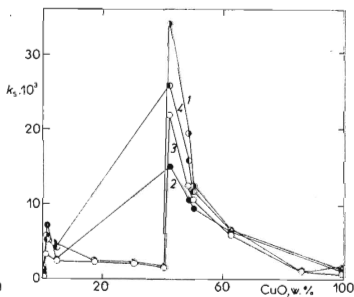


FIG. 2

Dependence of the Specific Catalytic Activity,  $k_s$  ( $\text{l}/\text{m}^2 \text{ min}$ ), at  $35^\circ\text{C}$  on the Composition of Samples and on Irradiation

1 Without irradiation; 2 system irradiated by  $\gamma$  radiation ( $5.4 \cdot 10^6$  J/kg); 3 system irradiated by  $\gamma$  radiation ( $1.38 \cdot 10^7$  J/kg); 4 system irradiated by neutrons ( $2.06 \cdot 10^{16}$  neutrons/ $\text{m}^2$ ).

Calculation of the values of apparent activation energy of the reaction showed that they vary for individual samples within the interval  $6.3 \cdot 10^4 \text{ J/mol} - 8.4 \cdot 10^4 \text{ J/mol}$  ( $\pm 1 \cdot 10^4 \text{ J/mol}$ ). Slightly lower values ( $4.2 \cdot 10^4 \text{ J/mol} - 5.4 \cdot 10^4 \text{ J/mol}$ ) were found only with samples having approximately the same proportion of both oxides (samples 7–9), whereas with irradiated sample this minimum was not observed.

From Fig. 3 (curves 1 and 2) it can be seen that the catalytic activity of a mixed catalyst decreases with time, while the value of the apparent activation energy increases. Thermal treating ( $90^\circ\text{C}$ , 2 h) of a sample, which had been set aside at laboratory temperature on air for 7 months, does not cause any change in either its catalytic activity or in the value of the apparent activation energy of the reaction. The

TABLE II

Effect of Irradiation ( $A$ , %) on the Catalytic Activity of Samples

*a* Samples irradiated by  $\gamma$  radiation ( $5.4 \cdot 10^6 \text{ J/kg}$ ); *b* irradiated by  $\gamma$  radiation ( $1.38 \cdot 10^7 \text{ J/kg}$ ); *c* irradiated by neutrons ( $2.06 \cdot 10^{16} \text{ neutrons/m}^2$ ).

Sample	CuO weight %	<i>a</i>	<i>b</i>	<i>c</i>	Sample	CuO weight %	<i>a</i>	<i>b</i>	<i>c</i>
1	0.4	52.3	—	—	7	42.3	40.0	72.6	76.4
2	0.8	128.5	62.0	96.5	8	48.7	42.0	49.7	70.3
3	4.6	56.7	55.0	102.5	9	50.1	48.7	89.0	96.6
4	17.4	—	126.5	—	10	62.8	116.4	74.7	78.7
5	31.1	—	94.8	—	11	85.8	—	100.0	—
6	40.3	—	80.0	—	12	105.0	90.0	67.8	89.2

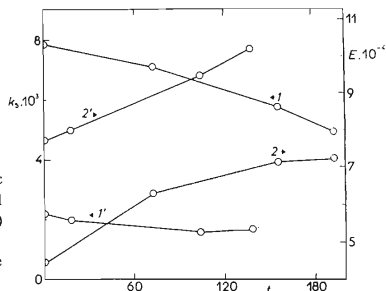


FIG. 3

Time Dependence  $t$ , (days) of the Catalytic Activity,  $k_s$  ( $\text{l/m}^2 \text{ min}$ ) at  $25^\circ\text{C}$  (1, 1') and of the Apparent Activation Energy,  $E$  ( $\text{J/mol}$ ) (2, 2') of Sample No 8

1' and 2' denote the same dependence after irradiation by  $\gamma$  rays ( $5.4 \cdot 10^6 \text{ J/kg}$ ).

above mentioned decrease in the catalytic activity with time in samples irradiated by  $\gamma$  rays of the dose  $5.4 \cdot 10^6$  J/kg is much slower than in non-irradiated samples (Fig. 3, curve 1'), however, even here the value of the apparent activation energy of the reaction increases (Fig. 3, curve 2').

Thermal treating ( $90^\circ\text{C}$ , 2 h) of sample 8, previously irradiated by  $\gamma$  rays (dose  $5.4 \cdot 10^6$  J/kg) and of sample 7 irradiated by dose  $1.38 \cdot 10^7$  J/kg (in both these samples irradiation led to a relatively great decrease in their catalytic activity (Table II)) causes, surprisingly enough, a further important decrease in their catalytic activity, while the value of their apparent activation energy does not change (Table III).

## DISCUSSION

The fact that in some samples the sum of weight % does not attain 100% (Table I) suggests the assumption that in this case the decomposition of carbonates is not complete under the given conditions of preparation. This assumption was directly verified by qualitative determination of carbonates in these samples (proof of carbon dioxide evolved from the samples upon addition of mineral acid as  $\text{BaCO}_3$ ). The given conditions of preparation enable the formation of amorphous<sup>12</sup> basic carbonates of different composition which could not be detected by X-ray diffraction. Their undefinability is also evidently the cause why the amount of remaining carbonate is different in individual samples. Just the formation of basic carbonate during the sample preparation might be responsible for the fact that in some samples (4 and 12) the decomposition during calcination proceeds in part up to free copper which is protected against further oxidation by the surface layer of oxide. We were led to this

TABLE III

Values of the Rate Constants  $k_s$  ( $1/\text{m}^2 \text{ min}$ ) at  $30^\circ\text{C}$  and of the Apparent Activation Energy of the Reaction  $E$  (J/mol) for Samples 7 and 8 Irradiated by  $\gamma$  Radiation ( $1.38 \cdot 10^7$  J/kg; sample 7 and  $5.4 \cdot 10^6$  J/kg; sample 8) before and after Thermal Treatment at  $90^\circ\text{C}$  for 2 h

*a* Samples before thermal treatment, *b* after thermal treatment.

Sample	$k_s \cdot 10^3$ $E \cdot 10^{-4}$	
	<i>a</i>	<i>b</i>
7	7.54	6.79
	8.3	9.0
8	3.47	2.95
	8.0	8.0

conclusion by the finding that in the analogous system prepared from nitrates the presence of free copper was not detected in the sample<sup>5</sup>.

The found non-monotonous dependence of the specific surface areas on the composition of the catalyst indicates a mutual interaction of both its components. Since the same was observed also in the case of other two-component catalysts (without a third component)<sup>4,5</sup>, this property cannot, even in this case, be attributed to the effect of the present carbonate. Comparison of the values of the specific surface areas of samples in the studied series with analogous samples of the same composition prepared from nitrates shows that the former ones are characterized by higher values of the mentioned quantity. This is in accordance with previous findings concerning other systems<sup>4,5</sup>, and even in this case it cannot be ascribed to the effect of the present carbonate, since just the samples containing lower amounts of carbonate (samples 4–6) have a great specific surface area.

Let us now try to elucidate the experimentally found dependence of the amount of chemisorbed oxygen on the composition of samples (Fig. 1, curve 1) in terms of the electron theory of chemisorption on semiconductors. Chemisorption of oxygen is known to proceed *via* an acceptor mechanism. Accordingly, the elevation of Fermi level on the semiconductor surface must lead to an increase in the amount of chemisorbed oxygen. This occurs, when copper(II) oxide is added to nickel(II) oxide (with respect to the experimentally found lower *p*-semiconductivity of the former oxide). In this way, we can explain the increase in the amount of chemisorbed oxygen in the region of excess of nickel(II) oxide. The subsequent decrease may be caused by the diminishing dispersity of copper(II) oxide. However, in the second marginal region of the system, increasing amount of nickel(II) oxide must cause the lowering of the Fermi level and according to this assumption the amount of chemisorbed oxygen should decrease which of course is in contradiction with the observed facts. Similarly, according to the mentioned assumption, samples containing free copper (samples 4 and 12) should contain greater amounts of chemisorbed oxygen than the other samples which, however, was not found either. With respect to this it must be admitted that chemisorption of oxygen on the studied system is probably not governed exclusively by electron mechanism. In addition to charge transfer, also the geometric factor can be operative in this case. According to the Balandine multiplet theory we can assume that two catalytic centers, in a suitable distance from each other, are necessary for dissociative adsorption of oxygen molecule. For nickel(II) oxide these can be pairs of  $\text{Ni}^{2+}$  ions. With increasing content of copper(II) oxide in the sample the pairs  $\text{Cu}^{2+}\text{—Cu}^{2+}$  or  $\text{Cu}^+\text{—Cu}^+$  and also the combined pairs  $\text{Ni}^{2+}\text{—Cu}^{2+}$  or  $\text{Ni}^{2+}\text{—Cu}^+$  can participate in this process. Therefore with increasing content of copper(II) oxide in the sample the surface concentration of the ion pairs able to chemisorb oxygen increases. Further increase of the concentration of copper(II) oxide evidently leads to its smaller dispersity, so that the

combined centers cannot take part in the chemisorption any more and consequently the amount of chemisorbed oxygen decreases. The maximum on the discussed dependence in the second marginal region of the system (excess of copper(II) oxide) can be explained quite analogously.

On the basis of this conception it is thus necessary, in order to be able to interpret the chemisorption of oxygen on this system, to admit a simultaneous effect of both electron and geometric factors. Most probably, beside the mentioned centers also other centers participate in this process, which are formed by different charge perturbations on the crystal surface. The presence of this kind of centers might serve to explain the maximum found in the region with approximately the same proportion of both oxides, for in this region the interface area of the multicomponent system attains its maximum value on which the maximum concentration of charge perturbations able to chemisorb oxygen can be stabilized. This explanation is also supported by a number of earlier observations<sup>4,5,8</sup>.

The above described mechanism of oxygen chemisorption remains probably unchanged also in samples which were irradiated by  $\gamma$  rays or by neutrons, because the character of the discussed dependence is also qualitatively the same (Fig. 1, curves 2 and 3). On the basis of earlier studies<sup>13</sup> of oxygen chemisorption on an irradiated *p*-semiconductor we can assume that the increased chemisorption after irradiation is due to the shift of the adsorption-desorption equilibrium of different forms of surface-bound oxygen towards the strongly bound (chemisorbed) form. These two results indicate that samples with marked ability to bind chemically oxygen on their surface are also characterized by an increased ability of physical sorption. Accordingly, it can be supposed that centers for physical sorption are found in the vicinity of centers for oxygen chemisorption and thus we can speak of the heterogeneity of the catalyst surface towards the weakly bound form of adsorbed particles.

Comparison of the dependence of specific catalytic activity of samples on their composition (Fig. 2, curve 1) with the same dependence for a system prepared from nitrates<sup>5</sup> shows that the course of this relationship is (except for the maximum in the region of excess of copper(II) oxide) qualitatively identical. Therefore we can assume in this case the same mechanism of elementary processes and the maximum in the region of excess of nickel(II) oxide can be explained by equilibrium between the donor ( $\text{Cu}^+$ ) and acceptor ( $\text{Ni}^{3+}$ ) reaction centers. The distinct maximum in the region of equal proportion of both oxides can be explained by the stabilization of perturbations — catalytic centers on the great surface of the interface. Also the lower value of apparent activation energy of the reaction in this region of compositions proves that we have to do with a qualitatively different kind of catalytic centers. Another direct proof is the dependence of catalytic activity of samples, normalized to unit amount of chemisorbed oxygen, on their composition (Fig. 4) from which it can be clearly seen that the maximum of catalytic activity in the middle region



of compositions is not determined by the amount of chemisorbed oxygen, whereas the maximum in the marginal region is determined just by this oxygen. This also supports the correctness of the suggested reaction mechanism.

The fact that in the studied series no maximum was found on the dependence of catalytic activity on composition in the region with excess of copper(II) oxide (contrary to the system prepared from nitrates) is an evidence that the starting substances from which the system has been prepared, have an important influence on its catalytic properties. It is possible that whereas in the "nitrate" system the first step during calcination is the formation of melt which is then transformed into finely dispersed oxides, in the preparation of the system from carbonates a system is obviously formed, characterized by low dispersity which hinders the mutual interaction of both oxides. This explanation is also supported by the finding that even the system nickel(II) oxide-zinc(II) oxide prepared from carbonates showed no maximum of catalytic activity in the region of excess of zinc(II) oxide<sup>4</sup>. Since in this case the system did not contain any undecomposed carbonate this fact cannot be ascribed to the presence of carbonate even in our case.

As the over-all character of the discussed dependence does not change after irradiation of the samples (Fig. 2), we can assume that the principal properties of the system are not affected by radiation. The decrease in the catalytic activity after irradiation by neutrons is probably caused by the so-called "polishing" effect of neutrons on the catalysts surface. This is also indicated by the fact that the maximum effect of radiation was observed in the region with equal proportion of both oxides, where the concentration of stabilized perturbations is the highest and further by the finding that irradiation of the samples did not cause any change in the apparent activation energy of the reaction.

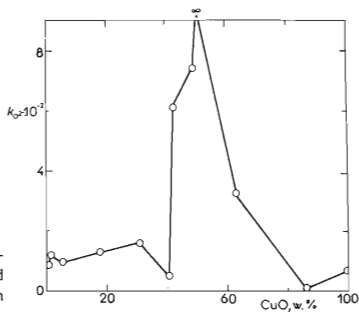


FIG. 4.

Dependence of the Catalytic Activity Normalized to the Amount of Chemisorbed Oxygen,  $k_{O_2} \cdot (l/g_{O_2} \cdot \text{min})$  on Composition

The finding that the effect of  $\gamma$  radiation is both positive and negative (in dependence on composition) can be explained so that the perturbations formed as the result of irradiation, which can serve as catalytic centers, can be either stabilized or can recombine with the already present centers of the reaction, thus leading to positive or negative effect, respectively. Which of these alternatives prevails, depends on the actual state of the given catalyst. This explanation is confirmed by the fact that both effects were observed with samples of different composition, if they were irradiated by various absorbed doses (Table II, columns *a*, *b*). At high concentration of catalytic centers the recombination process is probably favoured. Therefore the highest negative effect of irradiation is found in the region with equal proportion of both oxides. Here even the presence of carbonates might be manifested indirectly, since it contributes to the total concentration of perturbations in the system, as irradiation of a similar system nickel(II) oxide–zinc(II) oxide had a positive effect<sup>8</sup> in this region of compositions.

The observed decrease in the catalytic activity of the studied system with time (Fig. 3, curve 1) can also be estimated in terms of the above mentioned assumptions. Just the rather high perturbability of the system leads to diffusion and recombination processes. Therefore the greatest decrease was found with samples with the highest catalytic activity. In view of the fact that this process is accompanied by an increase of the apparent activation energy of the reaction (Fig. 3, curve 2), we can assume that the centers with higher catalytic activity are the first to take part in the recombination. After 7 months the system can be taken as equilibrated, since even thermal treating of such an aged sample does not change its catalytic properties. Irradiation of the sample causes also (as the result of the formation of new perturbations ready to recombine) that the system becomes equilibrated and the observed decrease of catalytic activity with time (Fig. 3, curve 1') is actually only fading out of this effect although the heterogeneity of the centers is even after irradiation still considerable (Fig. 3, curve 2'). Evidently, even here recombination starts in more effective centers and therefore also the apparent activation energy of the irradiated system is higher. Recombination processes, leading to lower catalytic activity, are accelerated by thermal treatment of the irradiated samples (Table III). In this stage, however, the centers with approximately the same catalytic effectivity are obviously already recombined (no change in the apparent activation energy). This means that recovering processes compensate, to some extent, the difference in energetic levels of various kinds of catalyst surface.

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