DECOMPOSITION OF HYDROGEN PEROXIDE
ON A MIXED NiO–MgO CATALYST AND THE EFFECT
OF IONIZING RADIATION ON THE CATALYST

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The decomposition of hydrogen peroxide in aqueous solution was studied on the NiO–MgO two-component catalyst, which occurs as solid solution in the whole composition region (0—100% component fractions). The results indicate that the mutual influencing of the two oxides shows up predominantly in the different amount of oxygen chemisorbed on the surface, which may be due to the different particle size of the various catalysts. The catalytic activity of the samples, being proportional to the amount of chemisorbed oxygen, is thus in a nonlinear relation to the catalyst composition. From the view point of the concept of bivalent catalytic centres, the catalytic activity can be thus assumed to be controlled by the concentration of the minor donor reaction centres constituted by the Ni^{3+} ions. In addition, catalytic centres of another kind, probably charge one, take part in the catalytic activity of the system in question. The two kinds of catalytic centres can be affected by the temperature of calcination during the preparation of the oxides, their heat treatment, and also by gamma-irradiation of the system. The equilibrium state of the two kinds of catalytic centres is attained rather slowly at room temperature.

During the study of the decomposition of hydrogen peroxide on two-component oxide catalysts, the catalytic activity has been frequently observed to be a nonmonotonic nonadditive function of the catalyst composition[1-6]. This can be generally explained by mutual interaction of the two oxides, which even can result in the formation of a new compound[6]. The works[1-6] seem to indicate that this interaction is not conditioned by the formation of a solid solution in the catalyst, decisive for its occurrence being rather the physicochemical properties of the two oxides, particularly their dispersity. In our previous works[1-5] we were concerned with the decomposition of hydrogen peroxide on two-component catalysts constituted by oxides possessing the p- or n-semiconductive characteristics. It appeared therefore interesting to examine the catalytic properties of a two-component system whose one component is a semiconductor and the other an insulator. For this we chose the nickel oxide–magnesium oxide system, varying the composition in the whole region of fractions 0—100%.

The aim of the present work was to find out if in the system chosen the two oxides affect each other and if the observed catalytic properties can be explained in terms of the concept of bivalent catalytic centres introduced previously[7]. Furthermore, this work deals with the effect of ionizing radiation on the catalytic properties of the system in question.

EXPERIMENTAL

Mixed nickel and magnesium oxides were prepared by coprecipitation of solutions of the metal nitrates with a potassium carbonate solution (all in concentration 1 mol/l). The precipitate was filtered out, decanted, and washed until negative reaction for nitrate ions, then it was dried at 120°C for 3 h and finally calcinated in an electric furnace at 600°C on air for 6 h (for two samples the temperatures 400 and 800°C, respectively, were used). From the ground oxides the fraction of the average grain size 0·1 mm was picked out. The mixed oxides were chemically analyzed by chelatometric titrations both in the absence and in the presence of sodium cyanide[8]. The amount of chemisorbed oxygen was determined iodometrically in weakly acidic medium. The structure of the catalyst was studied by X-ray diffraction, by the Debye–Scherrer method and by the back reflection method for an accurate determination of the diffraction line positions. The size of the coherent regions of the samples was calculated from the diffraction line half widths. The specific surface of the samples was measured by means of nitrogen desorption from a nitrogen–hydrogen mixture (after prior low-temperature adsorption). The catalytic activity of the catalysts was tested by the decomposition of hydrogen peroxide in an aqueous solution (1·2 mol/l). The kinetics of the decomposition was measured by monitoring the rate of the oxygen liberation from the system at constant temperature and pressure[1]. The tentative experiments showed that in the reaction conditions applied the reaction proceeds in the kinetic region. The measurements were performed at four different temperatures in the range from 20 to 35°C. The catalytic reaction was usually monitored up to 5% decomposition of the peroxide, and the acatlytic cativity was characterized by the 1st order rate constant. The effect of the sample heat treatment cn the catalytic activity was examined in some instances; such samples were heat treated prior to use at 80 to 500°C for 1 h. The effect of ionizing radiation on the catalytic activity was investigated with oxides prior irradiated from ^{60}Co so that the absorbed dose of gamma radiation was $1·09 . 10^6$ J/kg. The catalytic activity of the irradiated oxides was tested in the same conditions as that of the unirradiated samples.

RESULTS

Physical properties. As can be seen from Table I, the sum of the wt.% of the oxides in most cases does not attain 100%, and the specific surface of the samples
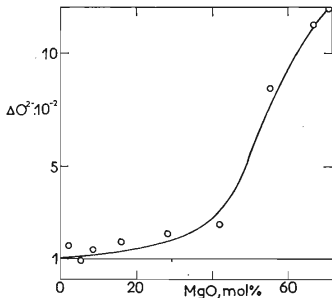
Fig. 1

Effect of the Radiation on the Amount of Chemisorbed Oxygen Δ_{O^2-} (%) for Samples of Different Compositions

depends markedly and nonmonotonically on the catalyst composition. Neither the composition nor the specific surface of the samples is changed on the irradiation. The amount of the chemisorbed oxygen is also a nonmonotonic function of the catalyst composition, with a pronounced decreasing tendency with the increasing content of magnesium oxide, both for the unirradiated and irradiated systems. The irradiation of the catalyst results in an enhancement of the oxygen chemisorption. This effect, expressed through the quantity $\Delta_{O^{2-}}$ (%) = $(O^{2-\prime}/O^{2-})$. 100, where $O^{2-\prime}$ and O^{2-} are the amounts of the oxygen chemisorbed (wt.%) on the irradiated and unirradiated samples, respectively, increases with the increasing content of magnesium oxide (Fig. 1) (for the samples with high contents of magnesium oxide, No 11–13, where the chemisorbed oxygen cannot be detected by the technique applied, the effect of the radiation could not be evaluated). From a comparison of the samples calcinated at different temperatures (Table I, samples No 4a, 4, 4b, and 10a, 10, 10b)

TABLE I

The Measured Physicochemical Parameters of the System Studied

S Specific area, O^{2-}, $O^{2-\prime}$ amounts of oxygen chemisorbed on the unirradiated and irradiated samples, respectively, A, B the O^{2-} quantity related to the catalyst surface and to the nickel content, respectively, L size of the coherent regions; 4a, 10a calcinated at 400°C; 4b, 10b calcinated at 800°C.

No	NiO	MgO	NiO	MgO	S	O^{2-}	$O^{2-\prime}$	A	B	L
	wt.%		mol%		m^2/g	10^4	wt.%	10^7 g/m^2	10^2 mg/g	nm
1	96.9	0.0	100.0	0.0	11.1	400	360	360	53	51.1
2	94.8	1.9	98.0	2.0	9.8	150	189	153	20	92.2
3	92.8	2.7	97.1	2.9	15.3	470	328	307	64	44.3
4	84.8	8.4	91.0	9.0	16.7	220	265	132	33	—
4a	86.2	8.3	91.2	8.8	29.0	2 267	—	781	334	21.8
4b	88.4	8.9	90.8	9.2	1.9	298	—	1 570	43	—
5	78.7	15.1	84.0	16.0	17.5	110	160	63	18	37.3
6	67.9	25.5	71.8	28.2	23.2	160	288	69	29	24.7
7	55.1	40.0	57.9	42.1	37.3	37	82	10	9	25.4
8	40.6	60.0	43.4	56.6	59.5	19	154	3	6	15.4
9	29.3	60.7	32.6	67.4	60.6	6	65	1	3	18.2
10	25.4	64.9	28.2	71.8	109.3	4	46	0.4	2	16.5
10a	22.0	63.0	25.8	75.2	110.5	570	—	52	333	14.4
10b	26.2	71.9	26.7	73.3	16.3	212	—	130	103	—
11	9.3	82.2	10.2	89.2	59.7	—	—	—	—	17.7
12	1.3	90.6	1.4	98.6	61.6	—	—	—	—	16.7
13	0.0	93.5	0.0	100.0	28.6	—	—	—	—	30.7

it follows that samples calcinated at a lower temperature (400°C) display a higher amount of chemisorbed oxygen, and that a higher calcination temperature brings about a lower specific surface of the catalyst. The X-ray diffraction study of the mixed oxides revealed that the system was composed only of the cubic structure of the two oxides, which in the whole composition region $(0-100\%$ of a component$)$ formed solid solution, described recently[9]. It has been also found that the irradiation of the system in the conditions applied has no measurable effect on the magnitude of the lattice parameter of the cubic structure. From the measurements of the widths of the selective reflections it follows that the size of the coherent regions of the cubic structure $(L,$ Table I$)$ changes appreciably particularly in the regions of high content of one component and has an overall decreasing tendency with the increasing content of magnesium oxide (particularly in the range of excess nickel oxide). The calcination temperature has no essential effect upon this value.

The heat treatment of the catalysts at a higher temperature (400°C, 500°C) leads to a decrease of their specific surface (Table II), both for unirradiated and irradiated samples; the influence of the heat treatment is, however, considerably lower than that of the temperature of calcination. The heat treatment also results in an enhanced chemisorption of oxygen practically in all cases (Table II), the microstructure of the samples remaining intact.

TABLE II

Effect of Heat Treatment on the Specific Surface of Unirradiated (S) and Irradiated (S') Samples and on the Amount of Chemisorbed Oxygen (O^{2-})

Sample No	t °C	S	S'	O^{2-}
		m^2/g		10^4 wt.%
1	—	—	—	400
	300	—	—	425
2	—	—	—	150
	300	—	—	340
3	—	15·3	15·1	470
	300	—	—	335
	400	15·0	14·5	—
	500	14·5	13·9	—
5	—	—	—	110
	300	—	—	288
9	—	60·6	60·5	6
	400	—	65·2	—
	500	54·7	40·8	194

The amount of chemisorbed oxygen increases with the ageing of the samples, as found by measuring it with samples which had been allowed to stand on air at room temperature for different periods (Table III). The ageing affects considerably neither the specific surface value nor the microstructure of the samples.

Catalytic activity. The study of the catalytic activity has revealed that the reaction proceeds as a 1st order process with respect to hydrogen peroxide up to a high degree of decomposition (40%). The rate constant related to 1 g of the catalyst is a non-monotonic function of its composition (Table IV); with the increasing content of magnesium oxide the rate constant first drops rapidly (down to 40% of its initial value at 2·0 mol % MgO), then it increases (123% of the initial value at 2·9 mol % MgO) and decreases again monotonically down to the value pertinent to pure magnesium oxide, which is several times lower than that pertinent to pure nickel oxide. This character of the variations is the same at all reaction temperatures and for both the unirradiated and irradiated samples. The effect of the applied radiation on the catalytic activity of the system is expressed through the quantity $\Delta_k (\%) = (k'/k) \cdot 100$, where k and k' are the reaction rate constants at 35°C on the unirradiated and irradiated samples, respectively; it can be both greater or less than 100%, but not very markedly in either case (Table IV). The apparent activation energie for the unirradiated and irradiated samples, E and E', respectively, virtually do not depend upon the composition and lie near the value $6·4 \cdot 10^4$ J/mol (Table IV). Regarding the

TABLE III

Effect of the Sample Ageing (τ) on the Amount of Chemisorbed Oxygen (O^{2-}), the Catalytic Activity (k) at 35°C, and on the Apparent Activation Energy of the Reaction (E)

Sample No	τ days	O^{2-} 10^4 wt.%	k 10^4 l/g min	E 10^{-4} J/mol
1	0	—	183	7·1
	49	—	163	8·7
2	0	150	73	6·9
	106	256	364	8·5
3	0	—	225	5·4
	59	—	477	8·0
5	0	—	84	6·5
	120	—	193	8·4
9	0	6	18	5·2
	120	194	25	5·9
13	0	—	6	8·5
	60	—	3	9·8

fact that this value has been obtained with the error $\pm 1 . 10^4$ J/mol, the value for unirradiated samples with a high content of magnesium oxide (No $11-13$) seem to be higher, approaching $9 . 10^4$ J/mol. Such an increase has not been observed for irradiated samples, which is reflected in the low Δ_E values characterizing the effect of irradiation (defined analogously as the Δ_k values) (Table IV). The effect of the calcination temperature appears in a pronounced decrease of the catalytic activity of the samples, marked particularly in the case of the sample No 4, where the increasing calcination temperature brings about a decrease of the apparent activation energy as well (Table IV).

The heat treatment of the samples brings about an increase of their catalytic activity if the temperature exceeds 100°C (Table V). This effect lowers with the increasing content of magnesium oxide. The value of the apparent activation energy decreases on the heat treatment too, which again is appreciable particularly in the case of samples with a high content of nickel oxide (Table V).

TABLE IV

Catalytic Activity (k) at 35°C and the Apparent Activation Energy (E) for Unirradiated and Irradiated (k', E') Samples and the Effect of Irradiation on These Quantities (Δ_k, Δ_E)

The meaning of the symbols a, b as in Table I.

Sample No	MgO mol.%	k	k'	Δ_k %	E	E'	Δ_E %
		10^4 l/g min			10^{-4} J/mol		
1	0·0	183	183	100	7·1	9·0	129
2	2·0	73	88	119	6·9	5·9	86
3	2·9	225	225	100	5·4	5·8	107
4	9·0	100	110	110	5·6	5·8	104
4a	8·8	188	—	—	8·1	—	—
4b	9·2	3	—	—	5·5	—	—
5	16·0	84	96	115	6·5	7·4	114
6	28·2	98	82	84	6·9	6·2	90
7	42·1	31	—	—	7·2	7·8	108
8	56·6	33	30	93	6·2	6·3	102
9	67·4	18	23	129	5·2	7·0	135
10	71·8	18	19	106	6·4	6·8	106
10a	75·2	21	—	—	5·2	—	—
10b	73·3	10	—	—	6·9	—	—
11	89·8	11	10	94	10·3	5·1	50
12	98·6	5	6	109	8·2	6·0	73
13	100·0	6	5	86	8·5	6·7	79

The study of the effect of ageing on the catalytic properties of the system showed (Table III) that the ageing of the samples was accompanied by an increase of their catalytic activity (except for the pure components) and at the same time the value of the apparent activation energy of the reaction rose mildly too. Both effects were more marked with samples containing more nickel oxide.

DISCUSSION

Physicochemical parameters. The fact that the sum of the weight percentages of the two oxides does not for most samples attain 100% (Table I) indicates that the system under study is not composed only of nickel and magnesium oxides. It can be thus assumed that in the calcination conditions applied the starting carbonates were not decomposed quantitatively, similarly as in the case of the two-component nickel oxide—cupric oxide catalyst[4], where amorphous carbonates were detected. Their presence, however, did not affect the catalytic properties of the system. Carbonates in the system nickel oxide–magnesium oxide were really found by means of infrared spectroscopy; they are here probably amorphous, too, as proved by the results of the X-ray diffraction examination.

TABLE V
Effect of Heat Treatment on the Catalytic Activity (k) at 35°C and on the Apparent Activation Energy (E) for Different Samples

Sample No	t °C	k 10^4 l/g min	E 10^{-4} J/mol
1	—	163	8·7
	300	590	5·2
2	—	364	8·5
	300	740	5·2
3	—	477	8·0
	80	417	7·8
	100	437	7·6
	200	642	6·4
	300	720	4·3
	400	759	4·8
	500	982	—
5	—	193	8·4
	300	262	8·2
9	—	25	5·9
	300	36	7·4
	400	—	6·7

The nonmonotonic dependence of the specific surface on the sample composition indicates, similarly as with most two-component catalysts, mutual influencing of the two oxides, which shows up also in the nonlinear dependence of the size of the coherent regions on the sample composition. The latter dependence can be assumed to be at least partly the cause of the aforesaid dependence of the specific surface on the composition, because the specific surface of the samples markedly depends upon the size of their crystallites (Fig. 2, curve a). The fact that the radiation applied did not alter the specific surface nor the structural parameters of the samples can be explained by the relatively low total dose, with which such changes are not very likely.

The mutual influencing of the two oxides is borne out also by the dependence of the amount of chemisorbed oxygen on the sample composition. This dependence is not due to the different specific surface values of the various samples, since the amount of the chemisorbed oxygen per a sample surface unit $(A$, Table I) decreases with increasing content of magnesium oxide. This could be explained in terms of the oxygen chemisorption on nickel oxide solely, which would comply with the electronic theory of chemisorption on semiconductors, regarding the fact that nickel oxide is a typical p-semiconductor, whereas magnesium oxide displays no type of semiconductivity (confirmed experimentally). However, the amount of chemisorbed oxygen per a unit amount of nickel in the sample (assuming a uniform distribution of the two oxides therein) decreases with the increasing content of magnesium oxide too $(B$, Table I), which is in disagreement with the results of the work[9]. From this it follows that either the nickel oxide is more concentrated in the nucleus of the catalyst grain, or the presence of magnesium oxide has a negative bearing on the ability of nickel oxide to chemisorb oxygen. The amount of chemisorbed oxygen may be also affected by the different particle size of the catalyst. In this case the
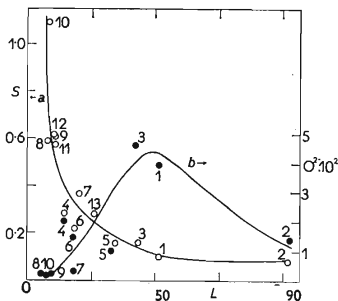

FIG. 2

Dependence of the Specific Surface S (m^2/g) (a) and of the Amount of Chemisorbed Oxygen O^{2-} (b) on the Particle Size L (nm) For the sample numbering see Table I.

existence of an optimum particle size, for which the oxygen chemisorption is highest, is to be assumed (Fig. 2, curve b).

The enhanced chemisorption of oxygen observed on the gamma irradiation of the sample (Fig. 1) in the region of excess nickel oxide can be explained in terms of a change of the sorption equilibrium of the weakly and strongly adsorbed oxygen in favour of the chemisorbed form, as has been observed for pure nickel oxide[10,11] or mixed nickel and zinc oxide[12]. However, since the effect of the radiation applied increases with increasing content of magnesium oxide in the sample (measured up to 80 mol % MgO), an interaction with magnesium oxide seems to play the primary part. Regarding the dielectric properties and stoichiometric composition of this oxide, the radiation can be supposed to give rise to nonequilibrium charge carriers in it, and these can serve as the donor adsorption centres for the chemisorption of oxygen.

The observed effect of the calcination and heat treatment temperatures on the specific surface of the samples (Tables I, II) is obviously accounted for by sintering processes, to which the sample is subjected at higher temperatures and that are more substantial during the process of the oxide structure formation than during the heat treatment of the already crystallized structure. The different amounts of oxygen chemisorbed on differently calcinated or differently thermally treated samples (Tables I, II) also cannot be explained by the observed change of their specific surface. The effect of these parameters on the above quantity can be associated with the different adsorption–desorption equilibrium of oxygen on the nickel oxide surface (the chemisorption on magnesium oxide at temperatures below 500°C is negligible[9]). The relatively slow establishing of this equilibrium, which has been assumed also for other oxide systems[13], is probably also the cause of the observed increase of the amount of chemisorbed oxygen with the sample ageing (Table III).

Catalytic activity. The catalytic activity of pure nickel oxide being about 30 times higher than that of magnesium oxide (Table IV) is in agreement with the results obtained by other authors[14]. The observed nonmonotonic dependence of the catalytic activity on the system composition (Table IV) can be due to the different specific surface of the individual samples (Table I). The dependence of the rate constant k on the specific surface (Fig. 3, curve a) gives evidence, however, that the specific surface of the samples measured by adsorption is not the only quantity determining the catalytic activity of a mixed system (similarly has been stated for the two-component cobalt monoxide–iron trioxide system[15]).

Regarding the fact that magnesium oxide is a dielectric and the catalytic activity of nickel oxide is determined by the amount of chemisorbed oxygen[10,11], it is feasible that the amount of the chemisorbed oxygen is decisive also for the catalytic activity of the system in question. The dependence of the rate constant k on the amount of chemisorbed oxygen (Fig. 3, straight line b) fully bears out this assumption. It can be thus assumed that decisive for the catalytic activity of the system in question

is the surface concentration of the minor donor catalytic centres constituted by the Ni^{3+} ions (the oxygen in the NiO–MgO system is chemisorbed on Ni^{2+} ions, which on the chemisorption are „converted" to Ni^{3+}; for details see[9]). These donor centres are in equilibrium with the major Ni^{2+} acceptor centres, and the system can be characterized in terms of the concept of bivalent catalytic centres[7] by the constants $D = A = Ni$, $d = a = 1$, $\delta = \alpha = 2$, which are equal to those characterizing pure nickel oxide. The fact that the straight line b of Fig. 3 does not pass through the origin of the coordinate system evidences that the catalytic activity of the samples with a high content of magnesium oxide (samples No 11–13) is not determined by the amount of the chemisorbed oxygen, a different reaction mechanism occurring on the catalysts; this is also corroborated by the found higher value of the apparent activation energy of the testing reaction for these samples (Table IV). With regard to the dielectric properties of magnesium oxide it is feasible that the catalytic centres of the reaction in these samples are the charge defects stabilized at the lattice defects of the crystal, which on the irradiation recombine with the newly formed nonequi librium charge carriers. This recombination can account for the lowering of the apparent activation energy of the reaction, taking place on the irradiation. Since the total catalytic activity does not change on the irradiation, it is reasonable to as sume a compensating catalytic effect, which is obviously due to the formation of new more active catalytic centres on the irradiation. In the case of the other samples (No 1–10), the irradiation changes neither their catalytic activity nor the apparent reaction activation energy, although the amount of the chemisorbed oxygen increases (Fig. 1); this is in contrast to the above conclusion that decisive for the catalytic
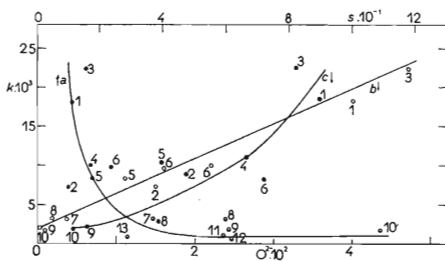

Fig. 3

Dependence of the Rate Constant k (l/g min) at 35°C on the Specific Surface S (m^2/g) (a) and on the Amount of Chemisorbed Oxygen O^{2-} (wt.%) for the Unirradiated (b) and Irradiated (c) Systems

For the sample numbering see Table I.

activity of these samples is the surface concentration of the Ni^{3+} ions. This apparent discrepancy can be explained so that the radiation-induced oxygen chemisorption does not lead to the formation of Ni^{3+}, ions as mentioned above. For this reason also the catalytic activity of the irradiated samples is not directly proportional to the amount of chemisorbed oxygen (Fig. 3, curve c).

With some two-component oxide catalysts, a significant effect of ionizing radiation has been observed[4,5,12] particularly in the region of approximately equal contents of the two oxides, where the largest area of the highly defective interface can be supposed. Since the system analysed forms solid solutions in the whole concentration region, the concentration of the defects, at which the radiation-induced free charge carriers could stabilize, is rather low, and thus the effect of radiation is insignificant in this region too.

The decrease of the catalytic activity of the samples with the increasing temperature of their calcination (Table IV) could be explained by the change of the concentration of the chemisorbed oxygen (Table I). The quantitative evaluation shows, however, that the reaction rate constant normalized to unit amount of chemisorbed oxygen is not the same for differently calcinated samples. The dependence of the rate constant k on the specific surface of differently calcinated samples is linear (the slope of the straight line determining the specific catalytic activity is $6 \cdot 35 \cdot 10^{-4}$ l/m^2 min for the sample No 4 and $1 \cdot 82 \cdot 10^{-5}$ l/m^2 min for the sample No 10). From this it follows that the calcination temperature has an effect upon the surface concentration of the catalytic centres that are not associated with the amount of the chemisorbed oxygen and whose surface concentration is proportional to the specific surface of the sample. This hypothesis is corroborated by the decrease of the apparent activation energy of the reaction with the increasing temperature of calcination, observed particularly for the sample No 4 (Table IV). This also indicates that the increasing calcination temperature brings about a decrease of the surface concentration of the less active centres and at the same time the formation of new, more active catalytic centres (the compensation effect). The different slopes of the linear relations discussed imply different surface concentrations of these calcination-affected centres. It can be thus deduced that lattice defects occur formed on the surface of the crystals of the mixed oxide during the calcination.

The effect of the heat treatment on the catalytic activity of the system can be explained essentially in the same manner. Here, similarly as in the case of the different calcination, the catalytic activity of differently thermally treated oxides is not determined by the amount of chemisorbed oxygen. Unlike the former case, however, the catalytic activity of thermally treated samples is not determined by their specific surface either. Its rise with the increasing heat treatment temperature is, however, obviously also associated with the thermal activation of the catalytic centres, as evidenced by the marked decrease of the apparent activation energy of the testing reaction.

The dependence of the catalytic activity on the sample age (Table III), too, can be explained neither by the change of the specific surface nor by the change of the amount of chemisorbed oxygen (the rate constant for the sample No 2 increases five times after 106 days, while the amount of chemisorbed oxygen rises only 1·7 times; for the sample No 9, the corresponding values are 1·4 and 32·3, respectively). The cause of these changes can be sought in the processes of stabilization and recombination of the lattice defects, which can serve as the catalytic centres for the testing reaction. The increase of the apparent activation energy with the sample ageing indicates that in these processes leading to thermodynamically equilibrium system dominate the stabilization of the less active and recombination of the more active catalytic centres of the testing reaction.

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