DECOMPOSITION OF HYDROGEN PEROXIDE ON NICKEL OXIDE–MANGANESE SESQUIOXIDE TWO-COMPONENT CATALYSTS AND EFFECT OF IONIZING RADIATION ON THEM

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Received June 25th, 1979

The catalytic and some physico-chemical properties were studied of nickel oxide–manganese sequioxide two-component catalysts with various proportions of the constituents. Decomposition of hydrogen peroxide in aqueous solution with the initial concentration 1·2 mol l^{-1} served as testing reaction. The catalyst components affect each other; the effect, being highest in the region of 20—30 mol.% manganese sequioxide, brings about an enhanced dispersity of the system, with the result of increased surface area, increased amount of overstoichiometric oxygen, and deficit in chemical analysis. Furthermore, the mutual component influencing appears in the specific catalytic activity of the system and in the amoutn of overstoichiometric oxygen per unit surface area, which is highest at 85 mol.% Mn_2O_3. A model of the mechanism is suggested for the reaction under study, based on the concept of bivalent catalytic centres, assuming that during the reaction, the high valency manganese species are gradually reduced as far as divalent manganese; this accounts for the occurrence of the observed two or three stages of hydrogen peroxide decomposition. Neither the mechanism of interaction of the two oxides nor the mechanism of the hydrogen peroxide decomposition changes on prior gamma irradiation of the catalyst. However, the irradiation affects markedly the catalytic activity of the system, the effect for catalyst of different composition being qualitatively different. Within the suggested concept of the reaction mechanism, the observed changes can be interpreted in terms of formation of non-equilibrium charge carriers (electrons) resulting from the ionization both in the surface layer and in the catalyst bulk; after stabilization on the surface, the carriers may serve as adsorption centres for chemisorption of oxygen or may recombine with the catalytic centres of the reaction under study.

The catalytic activity of oxide of manganese in decomposition of hydrogen peroxide has been extensively studied, particularly in view of the fact that manganese in the oxide may occur in different oxidation states. The results of most studies[1–3] indicate that the catalytically active manganese species are the Mn^{2+} and Mn^{3+} states. Moreover, however, the valency state in the oxide appears not to be the only factor determining the catalytic activity of the latter in decomposition of hydrogen peroxide: the arrangement of the manganese ions in the oxide lattice is of importance as well[4]. It has been also found[2–4] that the oxidation state of manganese in the oxide varies during the hydrogen peroxide decomposition, which appears in changing kinetics of the reaction. This has been observed also with a carrier catalyst where the oxide of manganese was applied to magnesium oxide[5] or to the gamma modification of aluminium oxide[6] (in the latter case, where the decomposition was conducted on the applied manganese dioxide, the authors suggest that the carriers of the catalytic activity were Mn^{3+} and Mn^{4+} ions). Changes in the oxidation state of manganese have been observed also in zinc oxid–manganese sesquioxide and nickel oxide–manganese sesquioxide two-component catalysts engaged in gas phase decomposition of hydrogen peroxide[7].

Although the catalytic activity of oxide of manganese in decomposition of hydrogen peroxide may be affected by a number of factors, the oxidation state of manganese on the catalyst surface seems to be among the most important parameters. In connection with the results of our previous works[8,9] dealing with the activity of various systems in decomposition of hydrogen peroxide, which underline the significance of the oxidation state of the catalytically active catalyst component based on the concept of bivalent catalytic centres[8], the nickel oxide–maganese sesquioxide system has been studied from this point of view in the present work. It also appeared interesting to investigate to what extent the catalytic activity of the system can be affected by its prior irradiation by ionizing radiation.

EXPERIMENTAL

The nickel oxide–manganese sesquioxide catalysts were prepared by mixing solutions of nitrates of the metals (reagent grade purity), concentration 1 mol l^{-1}, in different proportions so as to obtain a series of samples covering the whole concentration region from 0% to 100% one component. After evaporation of the mixed solutions to dryness on water bath, the crystalline nitrates were annealed on air in an electric resistance furnace. Within the first 30 min the furnace temperature rose from room temperature to 540°C with the rate of 18°C/min; at 540°C the samples were then calcinated for 4 h. In such conditions, nickel nitrate transformed into nickel oxide and nitrate of manganese into manganese sequioxide[10]. The oxides were ground and screened and the fraction of grain size 0·05—0·125 mm was taken for subsequent work. The samples were analyzed chelatometrically, the amount of surface oxygen iodometrically. The microstructure of the catalysts was investigated by X-ray diffraction (Cu anode); the average size of the coherent regions of nickel oxide and manganese sesquioxide was determined from the broadening of the selective reflections. The specific surface area of the samples was measured by means of low-temperature adsorption and subsequent desorption of nitrogen from nitrogen–hydrogen mixture. The catalytic activity of the samples was tested in decomposition of hydrogen peroxide in aqueous solution with the initial concentration 1·2 mol l^{-1} at four different temperatures, *viz.* 20, 25, 30, and 35°C. The kinetics of decomposition was determined by measuring the rate of evolution of oxygen at constant temperature and pressure. In each experiment, 0·01 g of the catalyst was used except for the samples from the regions of low concentrations of either component, where 0·1 g of sample was taken. Preliminary experiments evidenced that in such conditions, with constant stirring of the system during the reaction, the hydrogen peroxide decomposition proceeds in the kinetic region and is not limited by transport phenomena. The catalytic activity of the catalysts studied was characterized by the 1st order reaction rate constant. The measurements were carried up to a high degree of hydrogen peroxide decomposition (occasionally even to complete decomposition) to enable changes in the reaction kinetics, if occurring, to be pursued. Chemical analysis of the hydrogen peroxide solution proved that in the conditions applied, the catalysts did not dissolve significantly during the reaction. Prior to the testing, parts of the catalysts were irradiated by ^{60}Co gamma radiation so that the total dose was $8 \cdot 10^5$ Gy. Immediately after the irradiation, their catalytic activity was examined in the same manner as that of the non-irradiated samples.

RESULTS

As the chemical analysis of the prepared catalysts confirmed (Table I), the samples covered fairly uniformly the entire composition region (0–100% one component) and the catalytic systems under study really were constituted by nickel oxide and manganese sesquioxide (the sum of the weight per cent of the oxides amounted to 100% within the error of analysis). The highest deficit in chemical analysis (ap-

TABLE I

Composition, amount of overstoichiometric surface oxygen on non-irradiated (O^{2-}) and irradiated ($O^{2-\prime}$) samples and specific surface area (S) of the catalysts

Sample No	NiO wt.%	Mn_2O_3 wt.%	Total wt.%	NiO mol.%	Mn_2O_3 mol.%	O^{2-} wt.%	$O^{2-\prime}$ wt.%	S $m^2 g^{-1}$
1	97·0	0·0	97·9	100·0	0·0	0·045	0·081	97·9
2	95·1	3·2	98·3	98·9	1·1	0·056	0·356	20·7
3	85·3	13·3	98·6	93·1	6·9	0·096	0·710	24·7
4	73·3	23·7	97·0	86·8	13·2	0·069	0·589	25·3
5	59·4	33·5	92·9	78·9	21·1	0·111	0·521	38·5
6	50·3	43·4	93·7	71·0	29·0	0·102	0·635	32·3
7	40·0	53·3	93·3	61·4	38·6	0·094	0·761	22·6
8	33·5	63·1	96·6	52·9	47·1	0·106	0·579	13·9
9	24·2	73·0	97·2	41·2	58·8	0·085	0·443	10·7
10	12·8	82·9	95·7	24·6	75·4	0·088	0·556	9·8
11	7·3	90·8	98·1	14·4	85·6	0·094	0·500	5·0
12	2·3	96·7	99·0	4·9	95·1	0·069	0·630	1·6
13	0·0	97·7	97·7	0·0	100·0	0·065	0·799	0·7

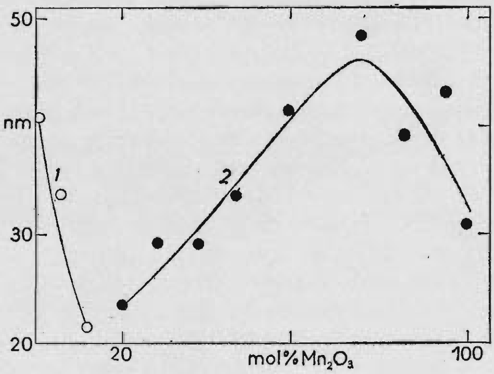

FIG. 1.

Dependence of the size of coherent regions on the sample composition. *1* Nickel oxide, *2* manganese sequioxide proximately 7%) appeared in samples with 20–30 mol.% Mn_2O_3. In roughly the same region, the maximum amount of overstoichiometric surface oxygen and the maximum specific surface area were found. The X-ray diffraction study revealed that the system was constituted by nickel oxide and manganese sesquioxide with a small content of manganese dioxide, the amount of the last decreasing with increasing proportion of nickel oxide. No changes in the structure could be traced by X-ray diffraction after the interaction of the catalyst with the hydrogen peroxide solution. As follows from measurements of the size of the coherent regions for the two crystalline phases of the system (Fig. 1), the size of nickel oxide crystallites decreases with increasing proportion of manganese sesquioxide (curve *1*), whereas the size of the manganese sesquioxide crystallites increases in this direction, attains a maximum of about 46 nm in the region of 70–80 mol.% Mn_2O_3, and decreases again with further increasing proportion of manganese sesquioxide (curve *2*). Irradiation affects significantly the amount of overstoichiometric oxygen on the catalyst surface (Table I), this amount being several times higher than on the corresponding non-irradiated samples in all cases. Samples containing oxide of manganese invariantly possess a higher amount of overstoichiometric oxygen than pure nickel oxide.

The kinetics of decomposition of hydrogen peroxide on the system examined was conducted to a high degree of decomposition (38%, 54%, 95%) to find that with pure nickel oxide (sample No 1) and with sample containing 1·1 mol.% Mn_2O_3 (sample No 2) the reaction proceeds as one of 1st order with a conspicuous deviation from this integral order in the sense of an autocatalytic process, apparent particularly in the initial stage of the reaction. In contrast to this, in the case of samples with higher proportions of oxide of manganese the reaction slows down at the end of the initial stage and subsequently proceeds as one of 1st order virtually until the complete decomposition of hydrogen peroxide (second stage) with a rate lower than that in the first (initial) stage. In the case of samples in which there is no or only a very small proportion of nickel oxide (samples No 13 and 12, respectively), the second stage is succeeded by a third one, remarkable by a high activity of the catalyst. The dependences are depicted in Fig. 2 as plots of natural logarithms of the actual hydrogen peroxide concentrations *vs* the period of decomposition at 30°C for samples No 1 (pure NiO), No 3 (6·9 mol.% Mn_2O_3), and No 13 (pure Mn_2O_3) Irradiation of the catalyst does not alter the character of the kinetic curves, the latter being preserved for a long time (followed for 2 years). Only reduction of the sample with hydrogen in mild conditions (300°C, 15 min) results in the third stage of the decomposition reaction not appearing at all and the rate of the second stage decreasing substantially.

In view of the above-mentioned complex nature of the kinetic curves for hydrogen peroxide decomposition, the rate constant of the reaction (by which the catalytic activity of the samples is characterized) was evaluated for all of the decomposition stages. The rate constant is a nonmonotonic function of the catalyst composition in all reaction stages (Fig. 3): it increases with the proportion of oxide of manganese up to the content of 20 mol.% Mn_2O_3, then, for the first reaction stage, does not vary substantially, and only in the region of high contents of oxide of manganese it drops down to the value corresponding to that for pure oxide of manganese (curve *1*). The rate constant of the second stage of decomposition also grows with increasing content of oxide of manganese, attains its maximum at about 30 mol.% Mn_2O_3, and subsequently decreases monotonically (curve *2*). The rate constant of the third stage also depends considerably on the catalyst composition: for pure manganese sesquioxide it is appreciably lower than for the sample with 95·1 mol.% Mn_2O_3 (curve *3*), the dependence could not be pursued in more detail, as the third stage of decomposition could only be traced in the two above cases. The reaction rate normalized to the specific surface area of the catalyst gave the specific catalytic activity of the samples (k_s), rising slowly with the increasing proportion of manganese sesquioxide up to the content of 85 mol.% Mn_2O_3 in both the first and the second stages, and then rising quickly with further increase of the manganese sesquioxide content (in the third phase, however, pure manganese sesquioxide exhibits a significantly lower specific catalytic activity than sample with 5 mol.% nickel oxide) (Fig. 4). The shape of the dependences shown in Figs 3 and 4 for the temperature 30°C is typical also of the other temperatures applied. From the dependences, the apparent activation energy of the reaction was calculated; its value decreases with increasing proportion of manganese sesquioxide in the catalyst (Table II). The first and second

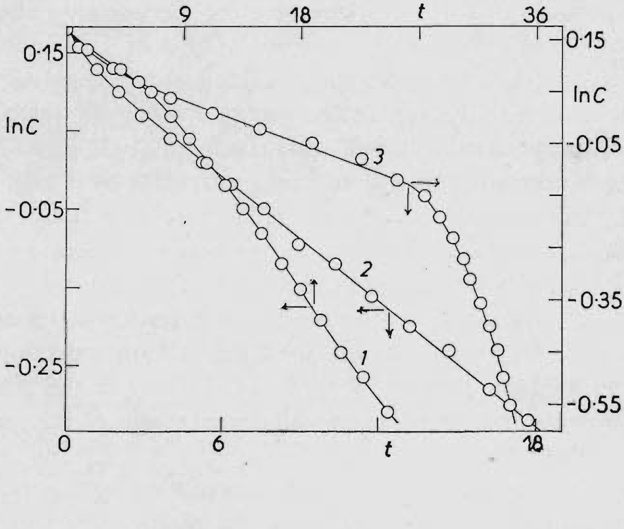

FIG. 2

Course of decomposition of hydrogen peroxide on nickel oxide *1*, NiO–Mn_2O_3 mixed oxide *2*, and manganese sesquioxide *3* at 30°C, *t* [min] stages do not differ essentially as far as this energy is concerned, but the third stage proceeds with an apparent activation energy several times higher.

The shape of the dependence of catalytic activity (normalized with respect to the catalyst weight or surface area) on the composition for prior irradiated systems is qualitatively roughly the same as in the case of non-irradiated samples. The previous catalyst irradiation affects most the absolute value of its catalytic activity. This can be expressed by means of the impact of irradiation $\Delta = (k'_s/k_s) \cdot 100$ (where k'_s and k_s are the specific catalytic activities of the irradiated and the non-irradiated samples, respectively) and its dependence on the system composition (Fig. 5). Apparently,

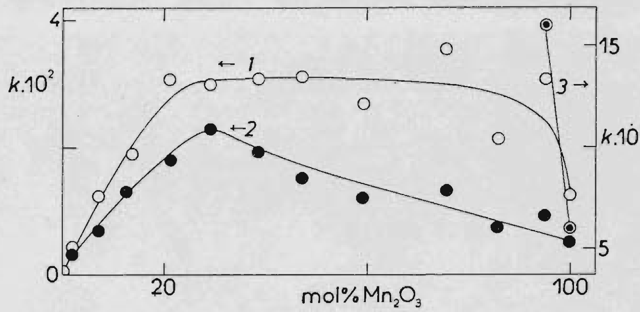

FIG. 3

Dependence of the rate constant k (l g^{-1} . min^{-1}) at 30°C on the catalyst composition in the first *1*, second *2* and third *3* reaction stages

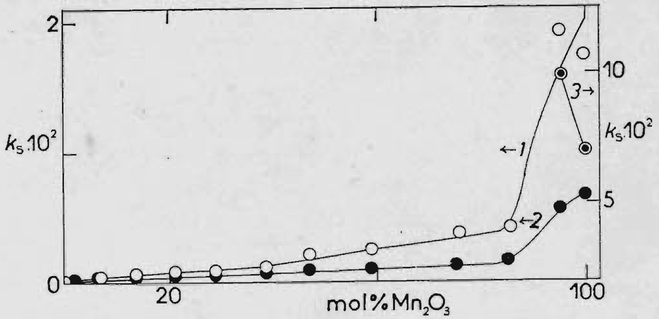

FIG. 4

Dependence of the specific catalytic activity k_s (l m^{-2} min^{-1}) at 30°C on the catalyst composition in the first *1*, second *2* and third *3* reaction stages

TABLE II

Values of the apparent activation energy in the various reaction stages for non-irradiated (E) and irradiated (E') catalysts

Sample No	E, kJ mol^{-1} 1st stage	E, kJ mol^{-1} 2nd stage	E, kJ mol^{-1} 3rd stage	E', kJ mol^{-1} 1st stage	E', kJ mol^{-1} 2nd stage	E', kJ mol^{-1} 3rd stage
1	86	—	—	74	—	—
2	59	63	—	57	—	—
3	52	50	—	50	—	—
4	59	55	—	41	42	—
5	53	41	—	57	29	—
6	58	44	—	53	29	—
7	39	38	—	40	22	—
8	42	46	—	32	19	—
9	36	40	—	51	43	—
10	46	48	—	41	46	—
11	37	37	—	50	—	—
12	30	29	74	25	44	14
13	8	19	44	2	14	77

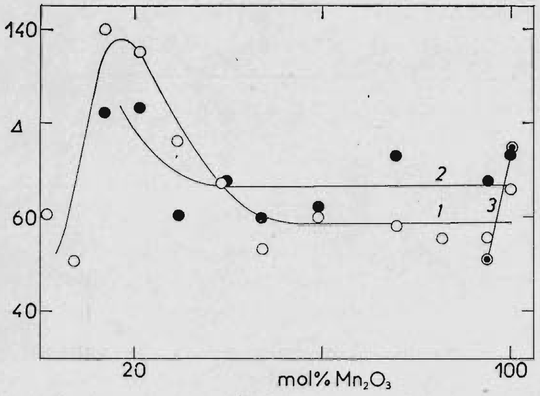

FIG. 5

Dependence of the impact of irradiation Δ (%) on the catalyst composition in the first *1*, second *2* and third *3* reaction stages the effect of irradiation is most pronounced in the first stage of the reaction (curve *1*). In the case of samples with low proportions of manganese sesquioxide (1·1 and 6·9 mol.%) the catalytic activity is only 50% of that exhibited by the non-irradiated samples, whereas in the region of about 20 mol.% Mn_2O_3 the catalytic activity of the irradiated systems exceeds that of the non-irradiated ones (approximately 140%); with further increase in the manganese sesquioxide content up to 50 mol.% the positive effect of irradiation decreases monotonically (down to roughly 50% of the original catalytic activity), and then it does not vary any more. In the second stage of decomposition, only a negative effect of irradiation is observed (approximately 73% of the original catalytic activity), and moreover, this is limited to samples containing more than 20 mol.% manganese sesquioxide (curve *2*). In the third stage of hydrogen peroxide decomposition, the catalytic activity of pure manganese sesquioxide remains nearly unaffected by irradiation (90% of the original activity), but if the sample contains 5 mol.% NiO, its activity drops down to 40% on irradiation (curve *3*).

The apparent activation energy of the reaction in the first and second stages is not affected significantly by ionizing radiation within the limits of measurement (± 10 kJ mol^{-1}) (Table II); an exception is sample No 8, where in the second stage the energy decreased on irradiation to 42% of the original value. Significantly, however, is the energy affected by irradiation in the third stage of decomposition; in the case of sample No 12 it dropped down to 19% of the original value.

DISCUSSION

The nonmonotonic dependences of the specific surface area of the samples and of the amount of overstoichiometric surface oxygen on the composition evidence that the two oxides in the catalyst affect each other; the effect appears to be most pronounced in the range of 20 – 30 mol.% Mn_2O_3, where the highest deficit in chemical analysis was also found. This deficit may be due to the fact that both nickel oxide and oxide of manganese can contain excess oxygen, which can form solid solution with the latter oxide[11]. This is also borne out by the content of manganese dioxide in the sample decreasing with increasing proportion of nickel oxide, as found by X-ray diffraction study. The fact that this occurs in this very range may be associated with the size of crystallites being here smallest for the two oxides (Fig. 1). The maximum specific surface area for samples of this composition, probably accounted for by the high dispersity of the system, is obviously also the cause of the high content of overstoichiometric surface oxygen in these samples, as the amount normalized with respect to the specific surface area is a monotonic function of the composition (Fig. 6) both for non-irradiated (curve ○) and irradiated (curve ●) systems. The ascending nature of the dependence indicates a higher affinity of manganese sesquioxide to oxygen as compared with nickel oxide, and the nonlinearity of the dependence again documents the mutual influencing of the two oxides, highest in the region of 80 – 90 mol.% Mn_2O_3. This characteristics does not alter on irradiation of the systems, only the total quantity of chemisorbed oxygen increases.

The course of decomposition of hydrogen peroxide on pure nickel oxide and on sample with low content of manganese sesquioxide (1·1 mol.%) with autocatalytic features is consistent with the previous findings[12] and can be interpreted, in terms of the concept of bivalent catalytic centres, by increasing concentration of the minor acceptor catalytic centres during the reaction. Starting from the sample containing about 7 mol.% Mn_2O_3, manganese sesquioxide obviously begins to contribute to the catalytic activity, as the initial reaction rate decreases in the course of the reaction to a constant value (Fig. 2, curve 2). This implies that as the reaction proceeds, the surface concentration of the minor catalytic centres, determining the catalytic activity, decreases. Since in view of the above-mentioned well-known course of the reaction on pure nickel oxide this hardly is reduction of Ni^{3+} ions, it is the oxidation state of manganese that probably changes. This assumption has been confirmed by various authors[2–7], who established changes in the manganese oxidation state during hydrogen peroxide decomposition. Since hydrogen peroxide reduces any higher oxide of manganese as far as manganese oxide (as proved by ESR method[5]), the observed change in catalytic activity may be due to reduction of manganese in the catalyst surface layer. The fact that on samples with high content of manganese sesquioxide (95·1 mol.%) and on pure oxide of manganese another change in the kinetics of the reaction – its acceleration – occurs (Fig. 2, curve 3) can be related to the findings[1,4]

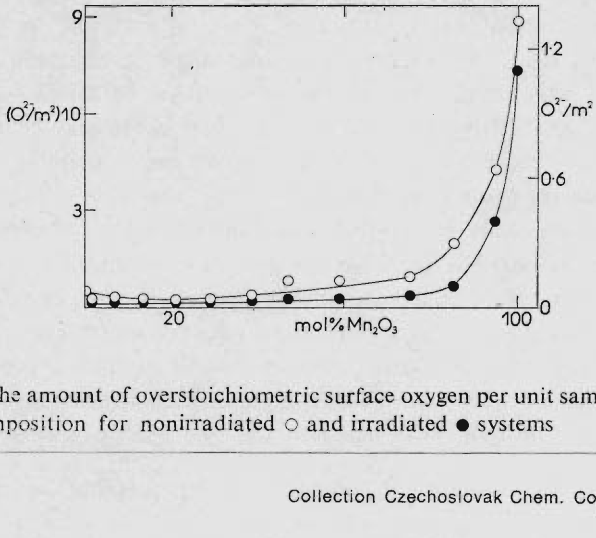

FIG. 6

Dependence of the amount of overstoichiometric surface oxygen per unit sample surface O^{2-}/m^2 (%) on the composition for nonirradiated ○ and irradiated ● systems that on the surface of the oxide which is in contact with hydrogen peroxide, a highly active stationary layer constituted by Mn^{3+} and Mn^{2+} ions is formed. It can be thus inferred that only on the two above samples (No 12 and 13) the stationary layer is formed, hence manganese is reduced as far as the divalent state, on action of hydrogen peroxide; this then accounts for the high catalytic activity of the oxide, obviously conditioned by a high concentration of the minor donor catalytic centres constituted by Mn^{2+} ions. In all the remaining samples with lower proportions of manganese sequioxide (except for samples No 1 and 2), the higher valency forms of manganese are responsible for their stationary catalytic activity; the nickel oxide present can be assumed to prevent the reduction of manganese to the divalent state. The presumed changes in the oxidation state of manganese during the reaction could be proved neither by X-ray diffraction examination of the catalyst after its interaction with hydrogen peroxide, nor by a comparison of the catalyst activity indicated by the oxygen evolved from the reacting system with that measured by titrating the non-decomposed hydrogen peroxide (based on the fact that reduction of a higher oxide of manganese to a lower oxide is accompanied by formation of one mol of oxygen from one mol of hydrogen peroxide, whereas during catalytic decomposition, one mol of hydrogen peroxide affords only 1/2 mol of oxygen). This indicates that the oxidation-reduction processes concerned only occur on the sample surface and cannot be detected by the above methods.

In view of the above considerations, the hydrogen peroxide decomposition on the samples containing manganese sesquioxide (except for the sample No 2 with a low content of the oxide) can be assumed to proceed in accordance with the following model based on the concept of bivalent catalytic centres. On the surface of a prepared catalyst, manganese ions occur in a high oxidation state (Mn^{5+}–(Mn^{7+})), and as the minor acceptor centres, which are in equilibrium with the major Mn^{4+} or Mn^{3+} centres, they ensure the initial, comparatively high catalytic activity (the reaction proceeds through the donor mechanism). The equilibrium between the donor and the acceptor centres is disturbed by the rather fast reduction of the high-valency manganese ions by hydrogen peroxide, whereby the concentration of the minor catalytic centres, and thus also the catalytic activity of the catalyst, decreases (the first stage of decomposition is therefore relatively short). The reduction results then in a state where on the catalyst surface there are Mn^{4+} ions serving as the minor acceptor centres, in equilibrium with the major Mn^{3+} donor centres and ensuring the stationary catalytic activity of all of the catalysts containing nickel oxide (except for sample No 12 with a low content of the latter); nickel oxide, as mentioned above, prevents manganese from being reduced to a lower oxidation state. In the case of pure manganese sesquioxide and of sample with a low content of nickel oxide (No 12), this second stage of decomposition is a quasi-steady state; this is conditioned by the further proceeding reduction of tetravalent or trivalent manganese, bringing about additional decrease in the surface concentration of the minor Mn^{4+} acceptor centres, which should result in a decrease in the catalytic activity of the sample. This decrease, however, is made up for by the increase in the catalytic activity due to newly formed minor donor catalytic centres represented by Mn^{2+} ions, which are in equilibrium with the major Mn^{3+} acceptor centres. As the reduction proceeds, the role of these catalytic centres becomes more significant, and as a result, the reaction is accelerated up to a steady state (third stage of the decomposition), which, in agreement with the works[1,3,4], is characteristic by a very high catalytic efficiency. In this stage the reaction proceeds through the acceptor mechanism until the complete decomposition of hydrogen peroxide.

Within the model suggested it is thus supposed that in the first stage of decomposition the catalytic centres are Mn^{5+} (Mn^{7+}) ions in equilibrium with Mn^{4+} or Mn^{3+} ions, in the second stage this role is taken over by the Mn^{4+}–Mn^{3+} centre pair, and in the third stage the activity is ensured by the Mn^{2+}–Mn^{3+} centres. Interaction of other pairs of manganese ions of different valency is, of course, not ruled out. The fact that on a short reduction of sample with low proportion of nickel oxide (No12) the third stage of decomposition does not appear, can be explained within the concept suggested so that if the reduction goes as far as divalent manganese, the size of the crystallites of the reduced manganese dioxide (or of species carryinge, Mn^{2+} ions created during the reaction) is so large that charge interaction of manganese forms of different valency is prevented similarly as observed with nickel oxide[12]. This is supported by the fact[13] that manganese dioxide on its own does not exhibit a high catalytic activity in the reaction in question. The observed decrease in catalytic activity in the second stage of the reaction after reduction of the sample with hydrogen can be explained likewise.

From the standpoint of the above concept it is not surprising that in some papers[6] the catalytic activity of oxide of manganese is attributed to Mn^{3+}–Mn^{4+} ions, in other papers[1,4], to Mn^{2+}–Mn^{3+} ions. The suggested model of the reaction mechanism based on the concept of bivalent catalytic centres can account for a number of other, often contradictory findings concerning the catalytic activity of oxide of manganese in hydrogen peroxide decomposition[3], such as the observation that with increasing concentration of Mn^{3+} ions on the manganese dioxide surface its catalytic activity rises. The fact that with increasing oxidation state of manganese sesquioxide its activity increases can be similarly explained too. In both cases the responsible phenomenon is the increase in the concentration of the minor acceptor centres of the reaction (Mn^{3+} ions in the former case, Mn^{4+} ions in the latter case). Conversely, these findings indirectly bear out the correctness of the mechanism suggested.

From the point of view of the kinetics discussed it is interesting that for each sample, the transition from the first reaction stage to the second occurs at a definite degree of hydrogen peroxide decomposition, independent of the reaction temperature (Fig. 7). It can be deduced that the reduction of the higher-valency manganese forms, leading to the second stage, proceeds rather readily, with a low apparent activation energy. The nonmonotonic shape of the dependence indicates a mutual influencing of the two oxides, appearing also in this connection. The attained degree of decomposition for the transition from the second reaction stage to the third also depends on the sample composition, being higher for sample containing some nickel oxide (No 12) than for pure oxide of manganese (No 13) (Table III). This again is probably associated with the fact that nickel oxide is in way of reduction of manganese to the lowest oxidation state. In contrast to the first transition between the reaction

TABLE III

Dependence of the attained degree of decomposition of hydrogen peroxide (S) on transition from the second to the third reaction stage on the reaction temperature

Sample No	S (%) for the temperature, °C			
	20	25	30	35
12	76·1	69·3	67·1	62·9
13	35·1	31·8	28·2	24·6

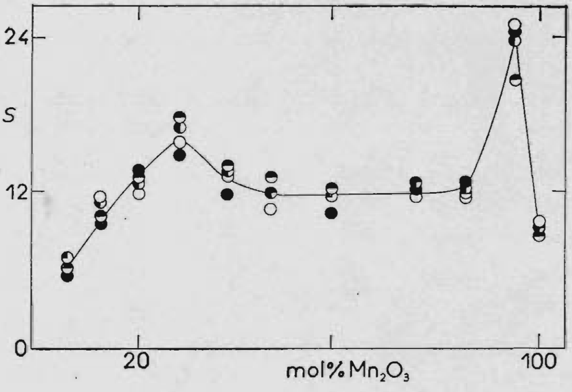

FIG. 7

Dependence of the degree of decomposition of hydrogen peroxide S (%) attained on transition from the first to the second reaction stage on the catalyst composition. ○ 20°C, ● 25°C, ◐ 30°C, ⊖ 35°C stages, however, the attained degree of decomposition decreases here linearly with increasing reaction temperature; apparently, the assumed reduction process leading to the third reaction stage is accelerated by increasing temperature, the reduction being probably somewhat more difficult from the energy point of view than the reduction of the higher-valency manganese forms. Also, the apparent activation energy in the third stage is higher than that in the first two stages, as observed also during the study of catalytic properties of pure oxide of manganese[4].

In all the samples studied (except for the pure constituents) both components contribute to the catalytic activity, influencing one another; this applies to all of the three reaction stages. This is proved not only by the dependence shown in Fig. 7, but primarily by the dependence of the catalytic activity on the system composition (Fig. 3). Comparing this dependence with the analogous dependence of the specific catalytic activity (Fig. 4), we can relate the observed enhanced catalytic activity of samples with 20–30 mol.% Mn_2O_3 to their large specific surface area stemming from their high dispersity. The nonlinear nature of the dependence of specific catalytic activity on the composition, however, points to a mutual influencing of the two oxides. The qualitatively identical shapes of this dependence and the analogous dependence of the amount of overstoichiometric oxygen normalized with respect

TABLE IV

Order of the catalysts according to the increasing amount of overstoichiometric surface oxygen (O^{2-}) and the corresponding values of the rate constant (k) in the first two stages of the reaction proceeding at 35°C

Sample No	O^{2-} wt.%	k, ml g^{-1} min^{-1} 1st stage	k, ml g^{-1} min^{-1} 2nd stage
1	0·045	0·4	—
2	0·056	7·1	7·2
13	0·065	12·5	5·9
4	0·069	27·3	11·7
12	0·069	35·6	19·3
9	0·085	36·4	17·0
10	0·088	49·1	16·9
11	0·094	30·0	11·7
7	0·094	42·3	25·3
6	0·102	42·9	30·5
8	0·106	43·3	20·5
5	0·111	45·1	24·9

to the catalyst surface area (Fig. 6) indicate that the specific catalytic activity in the first two stages of decomposition has a connection with the amount of overstoichiometric surface oxygen. This is supported by the reaction rate constant rising approximately linearly with the amount of the oxygen (Table IV). As the higher content of overstoichiometric oxygen on the sample surface is probably associated with the higher valency of manganese in the oxide, and as in the first two reaction stages higher-valency manganese ions act – according to the model suggested – as the minor centres (and the catalytic activity of nickel oxide is also proportional to the amount of chemisorbed oxygen[12]), the catalytic activity of the sample must increase with increasing content of overstoichiometric oxygen. In this sense the catalytic activity in the third reaction stage is no more associated with the amount of overstoichiometric oxygen (compare Fig. 4, curve *3*, and Fig. 6, curve *1*), because here it is divalent manganese ions that act as the minor centres of the reaction. It can be thus claimed that the cause of the nonlinear dependence of the specific catalytic activity on the sample composition (Fig. 4, curve *1* and *2*) is the fact that nickel oxide interacts with oxide of manganese so that it to an extent prevents formation of higher-valency manganese forms in the oxide (Mn^{n+} for $n > 3$), which are detected by iodometric titration (this is indicated also by the X-ray diffraction study). In this manner nickel oxide operates in the concentration region of 100 – 15 mol.% NiO; at lower concentrations this effect is substantially lower and ultimately vanishes. In view of the conclusion that nickel oxide affects negatively reduction of manganese to the divalent state, it can be stated more generally that nickel oxide in the system in question stabilizes manganese in the trivalent state.

Furthermore, it can be concluded that manganese sesquioxide contributes more to the catalytic activity of the $NiO–Mn_2O_3$ mixed oxide. This is supported also by the shape of the kinetic curves of hydrogen peroxide decomposition (Fig. 2), convex – as typical of manganese sesquioxide – even for samples with manganese sesquioxide contents as low as 7 mol%. This is obviously due to the multiply higher specific catalytic activity of manganese sesquioxide as compared with that of nickel oxide (Fig. 4), as observed also in gas phase decomposition of hydrogen peroxide[14].

The fact that no changes occur in the shape of the kinetic curves, shape of the dependence of the catalytic activity on the sample composition, or shape of the dependence of the normalized amount of overstoichiometric surface oxygen on the catalyst composition, on prior irradiation of the system, warrants the assumption that the nature of the interaction of the two oxides as well as the mechanism of the reaction is the same on the irradiated systems as on the non-irradiated ones. As the apparent activation energies of the first and the second stages do not vary within the error of measurement (Table II), the irradiation seems not to induce qualitative changes in the catalytic centres; the observed changes in the catalytic activity (Fig. 5) are thus obviously due to changes in the surface concentration of the catalytic centres. A direct effect of radiation on nickel oxide at the doses applied is probably negligible[12,15], so that the changes observed obviously originate from interaction of the ionizing radiation with oxide of manganese.

If the suggested model of the reaction mechanism is correct, the observed increase in the amount of overstoichiometric oxygen on irradiation of the sample (and, hence, increase in the higher-valency manganese forms) should in the first and second stages of the decomposition bring about an enhanced catalytic activity of the samples (increase in the concentration of the minor catalytic centres). In fact, however, no dependence was found in the irradiated systems between the amount of overstoichiometric oxygen and the catalytic activity, which indicates that the radiation-induced chemisorption of oxygen takes place on centres not identical with the catalytic centres of the reaction. The effect of radiation on the catalytic activity (Fig. 5) can be then interpreted as follows. The radiation induces ionization of the ions present (probably of manganese) and formation of free charge carriers (electrons), both in the catalyst bulk and on its surface. By ionization of manganese(III) ions on the surface, higher-valency manganese ions are created, serving as the minor centres for the reaction; as a result, the catalytic activity of the sample increases. The released electrons may be stabilized by chemisorption of oxygen on the catalyst surface. This process is thus responsible for the rising catalytic activity as well as for the corresponding increase in the amount of the overstoichiometric oxygen. In addition, however, ionization occurs also in the catalyst bulk. The electrons released can diffuse to the surface and either stabilize on various crystal defects, serving then as adsorption centres for chemisorption of oxygen, or recombine with the higher-valency form of manganese ions. The former process results in an enhanced oxygen chemisorption, not associated with the catalytic activity, the latter process gives rise to a reduction in the surface concentration of the minor catalytic centres of the reaction and thereby to a drop of the catalytic activity of the sample. The resulting effect of irradiation is then given by a superposition of these phenomena. In most of the samples studied, recombination of electrons with the catalytic centres and chemisorption of oxygen on the centres created by stabilization of the electrons formed in the sample bulk probably predominate, which results in a decrease in the catalytic activity with simultaneous increase in the amount of overstoichiometric surface oxygen. Only in the sample with approximately 20 mol.% Mn_2O_3, where a positive effect of irradiation was observed, the former mechanism indicated – ionization of manganese(III) ions on the sample surface and thus increase in the surface concentration of the minor catalytic centres of the reaction – probably prevails. This is obviously associated with the fact that this catalyst exhibits the highest dispersity (Fig. 1) and, consequently, the highest specific surface area (Table I). This concept of competitive processes can account for the observed effect of radiation on the catalytic activity of the system in the first and second reaction stages (Fig. 5, curves *1*, *2*). However, in the case of the sample with 20 mol.% Mn_2O_3 the positive effect of irradiation in the second stage is not so pronounced as in the first stage, because in the second stage the catalyst surface has been modified by the reaction itself. The observed decrease in the catalytic activity in the third stage for irradiated samples (Fig. 5, curve *3*) may be due to the above-mentioned radiation-induced oxidation of manganese to a higher valency, with the consequent decrease in the concentration of the minor catalytic centres of the reaction. However, the simultaneous lowering of the apparent activation energy of the reaction on the irradiated sample No 12 (Table II) points to additional essential changes, occurring in the sample on irradiation. These are probably secondary changes, which only manifest themselves in a higher stage of the catalytic reaction, similarly as has been observed in the study of Fischer–Tropsch reaction on irradiated iron catalyst[16]. Nickel oxide plays here probably also a significant role, since in the case of pure oxide of manganese the discussed effect of irradiation on its catalytic activity has not been observed.

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Translated by P. Adámek.