# DECOMPOSITION OF HYDROGEN PEROXIDE ON NICKEL OXIDE-MOLYBDENUM TRIOXIDE TWO-COMPONENT CATALYSTS AND EFFECT OF GAMMA RADIATION AND NEUTRONS ON THEM

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Decomposition of hydrogen peroxide in aqueous solution was studied on nickel oxide–molybdenum trioxide two-component catalysts with various proportions of the constituents covering the entire region of 0—100% of one component. The systems were found to comprise the two oxides and, in the region of 18—92 mol.% $MoO_3$, a small quantity of nickel molybdate, which, however, does not affect appreciably their catalytic activity. A change in the kinetics of the reaction was found in its initial stage, which is probably associated with surface reduction of $Mo^{6+}$ ions (major catalytic centres) to ions in lower oxidation state (minor centres) whose surface concentration determines the catalytic activity. The nickel oxide present probably accelerates this process, obviously occuring also during the ageing of the catalysts. In the regions of very low contents of one component the catalytic activity is determined by that of the major constituent, but is appreciably affected by the admixture oxide. In the range of 15 mol.% $MoO_3$ both oxides contribute significantly to the catalytic activity; the activity is rather high, which is explained in terms of the concept of bivalent catalytic centres. In addition to the minor centres constituted by $Ni^{3+}$ and probably also $Mo^{5+}$ ions, determining the catalytic activity of the system, catalytic centres of another kind also take part in the reaction; these may be associated with structure defects on the catalyst surface. The greatest part play these centres in catalysts with roughly equal proportions of the two constituents. Neither the mutual influencing of the two components of the system nor the mechanism of the testing reaction alters on prior irradiation of the system by gamma radiation or by neutrons. The irradiation, however, has a negative effect on the catalytic activity of the sample with 2·7 mol.% $MoO_3$, both kinds of catalytic centres (of charge and structure nature, respectively) being probably affected. In the case of catalyst with 76·2 mol.% $MoO_3$, radiation of both kinds induces increase in the catalytic activity; this is probably due to the establishment of a new equilibrium of the charge defects acting as catalytic centres in the reaction in question.

Decomposition of hydrogen peroxide in aqueous solution can serve as a convenient testing reaction for investigation of properties of various catalytic systems. The results obtained with a number of oxide-type catalysts[1-4] indicate that among the decisive factors governing the catalytic activity is the oxidation state of the catalytically active component. From this point of view, those systems are of particular interest in which the active component can occur in different oxidation states. Among them is also oxide of molybdenum, in which the latter can be present in various oxidation states, from $Mo^{3+}$ up to $Mo^{6+}$ (refs[5-8]).

In the present work, the catalytic properties have been investigated of two-component catalytic systems constituted by molybdenum trioxide and nickel oxide in various proportions from 0 to 100% of one component. The catalytic activity was examined in hydrogen peroxide decomposition; some physical and physico-chemical parameters of the systems and their "sensitivity" to prior irradiation by gamma rays or by fast neutrons were also determined.

## EXPERIMENTAL

The catalysts composed of oxides of nickel and molybdenum in different proportions were prepared from aqueous solution of nickel nitrate and ammoniacal solution of molybdenum trioxide. The chemicals were c.p. grade. The solutions were mixed in various proportions and evaporated to dryness on paraffin bath. The residue then was dried at 105°C for 12 h, and, by subsequent calcination on air at 430°C for 2 h, transformed into nickel oxide–molybdenum trioxide mixture. Chemical analysis of the samples was performed so that after dissolving nickel oxide in hydrochloric acid and molybdenum trioxide in ammonium hydroxide, nickel was determined gravimetrically as nickel dimethylglyoximate and molybdenum polarographically. The overstoichiometric surface oxygen was determined by iodometric titration in weakly acidic solution. The microstructure of the samples was examined by X-ray diffraction by using modified Debye–Scherrer method employing X-ray tube with copper anode. The specific surface area of the catalysts was measured *via* desorption of nitrogen after previous low-temperature adsorption of nitrogen from nitrogen hydrogen mixture. The catalytic activity of the samples was tested in decomposition of aqueous solution of hydrogen peroxide (*p.a.*) with the initial concentration 1·2 mol $l^{-1}$; the kinetics of the reaction was examined by determining the rate of evolution of oxygen from the reacting system (at constant temperature and pressure). The measurements were carried out at four differentt emperatures, *viz.* 30, 35, 40, and 45°C. In each measurement, 25 ml of hydrogen peroxide solution and 0·05 to 1·00 g of the catalyst (according to the catalytic activity) were used. The mixtures were stirred vigorously during the measurements; as proved by preliminary experiments, in such circumstances the reaction proceeds in the kinetic region. The reaction kinetics conducted up to a 2·6% degree of decomposition was treated as a 1st order process, and the catalytic efficiency of the catalyst was characterized by the 1st order reaction rate constant normalized with respect to either the catalyst weight (catalytic activity) or to its specific surface area (specific catalytic activity). The catalytic activity of prior irradiated samples was evaluated likewise. The gamma irradiation was performed by means of a $^{60}$Co source, the total dose applied was 8·6 . $10^5$ Gy; for the irradiation by fast neutrons, a $^{252}$Cf source was used with the fluency of 6·86 . $10^{15}$ $m^{-2}$ $s^{-1}$, which corresponded to the dose of 28·1 Gy.

## RESULTS

As the results of chemical analysis evidence (Table I), the samples prepared are constituted by nickel oxide and molybdenum trioxide. The highest deficit in chemical analysis (about 1·6 wt.%) was found for samples in the composition region of 18 – 92 mol.% $MoO_3$, the lowest deficit occurs in the case of the pure components, particularly molybdenum trioxide. The specific surface area of the catalysts varies non-monotonically with their composition (Table I), its maximum value was found for samples with approximately 18 mol.% $MoO_3$; the surface area values do not alter on irradiation. Measurable amounts of overstoichiometric surface oxygen were only detected on samples with excess nickel oxide (molybdenum trioxide content below 18 mol.%), both for non-irradiated and irradiated systems (Table II). This amount, irrespective of the radiation treatment of the catalyst, also depends non-monotonically on the system composition, with a marked minimum at 0·1 mol.%

TABLE I

Composition and specific surface area ($S$) of the catalysts

| Sample No | $MoO_3$ wt.% | NiO wt.% | Total wt.% | $MoO_3$ mol.% | $S$ $m^2 g^{-1}$ |
|---|---|---|---|---|---|
| 1 | 0·0 | 98·7 | 98·7 | 0·0 | 8·8 |
| 2 | 0·9 | 97·6 | 98·5 | 0·5 | 5·4 |
| 3 | 1·8 | 96·7 | 98·5 | 0·9 | 3·6 |
| 4 | 5·0 | 94·0 | 99·0 | 2·7 | 35·7 |
| 5 | 14·0 | 84·8 | 98·8 | 7·9 | 41·1 |
| 6 | 29·3 | 68·9 | 98·2 | 18·1 | 46·2 |
| 7 | 50·3 | 48·4 | 98·7 | 36·1 | 17·5 |
| 8 | 71·0 | 27·3 | 98·3 | 57·5 | 19·8 |
| 9 | 84·9 | 13·8 | 98·7 | 76·2 | 7·5 |
| 10 | 94·3 | 4·2 | 98·5 | 92·2 | 4·2 |
| 11 | 97·9 | 1·3 | 99·2 | 97·6 | 2·5 |
| 12 | 99·1 | 0·6 | 99·7 | 98·9 | 2·3 |
| 13 | 99·7 | 0·0 | 99·7 | 100·0 | 2·2 |

TABLE II

Amount of overstoichiometric surface oxygen ($O^{2-}$) on non-irradiated systems (*A*), gamma irradiated systems (*B*), and neutron irradiated systems (*C*)

| Variant | $O^{2-}$ (wt.%) for sample No | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| *A* | 0·08 | 0·04 | 0·04 | 0·11 | 0·05 | 0·05 | 0·00 |
| *B* | 0·26 | 0·05 | 0·04 | 0·19 | 0·06 | 0·06 | 0·01 |
| *C* | 0·11 | 0·04 | 0·03 | 0·14 | 0·04 | 0·04 | 0·00 |

$MoO_3$ and maximum at 2·7 mol.% $MoO_3$. Irradiation of the system brings about an enhanced amount of overstoichiometric surface oxygen practically only in the case of pure nickel oxide; notably effective is here gamma irradiation. The microstructure study, in accordance with the results of chemical analysis, confirmed that the systems are constituted by nickel oxide and molybdenum trioxide; in the region of 18–92 mol.% $MoO_3$, however, small quantities of nickel molybdate were found in addition, too. Irradiation of the catalysts does not induce, within the limits of error, changes in their microstructure.

The catalytic curves (dependence of natural logarithm of the actual concentration of hydrogen peroxide on time) for pure nickel oxide revealed that the decomposition up to the applied degree of conversion proceeds as a 1st order reaction, both for the non-irradiated and the irradiated oxide (Fig. 1, curves *1*, *2*, *3*). In contrast to this, on pure molybdenum trioxide the decomposition departs in the initial stage from 1st order kinetics in that the reaction rate gradually increases, both for the non-irradiated and the irradiated samples (Fig. 1, curves $\bar{1}$, $\bar{2}$, $\bar{3}$). In higher stages of the decomposition, the 1st order patterns are obeyed. The catalytic activity measurements were therefore carried out in this stationary stage of the reaction. In the case of samples containing both components, the departure from the 1st order kinetics grows appreciably with increasing content of molybdenum trioxide; it does not change on prior irradiation of the catalysts (Fig. 2).

The catalytic activity of the systems studied is a distinct nonmonotonic function of their composition (Fig. 3): it drops with increasing content of molybdenum trioxide to a minimum at 3 mol.% $MoO_3$, then increases to a maximum at approximately 15 mol.% $MoO_3$, decreases continuously, and in the range of high excess of molybdenum trioxide rises up to the value corresponding to pure molybdenum trioxide, a value several times lower than that corresponding to pure nickel oxide. The character of this dependence is the same for non-irradiated and irradiated samples. The apparent activation energy of the testing reaction is a nonmonotonic function of the system composition too (Fig. 4) and again, analogous for the non-irradiated and the irradiated samples. In the region of excess one component, the apparent activation energy decreases somewhat with increasing content of the minor component (the changes are, however, almost within the limits of error). An expressive maximum of this dependence was found for samples with 15–20 mol.% $MoO_3$, a minimum, for sample with approximately equal molar proportions of the two constituents.

Irradiation of the systems by gamma radiation or by fast neutrons in the conditions applied shows up appreciably in the catalytic properties only in the case of the catalysts with 2·7 and 76·2 mol.% $MoO_3$ (Fig. 5), the catalytic activity decreasing in the former case (by 22·7% for gamma radiation and 36·4% for neutrons) and increasing in the latter case (by 40% for gamma radiation and 20% for neutrons) (Fig. 5, curves *1*, *2*). Moreover, the decrease and increase in the catalytic activity seem to be associated with a lowering and a mild rise, respectively, in the apparent activation

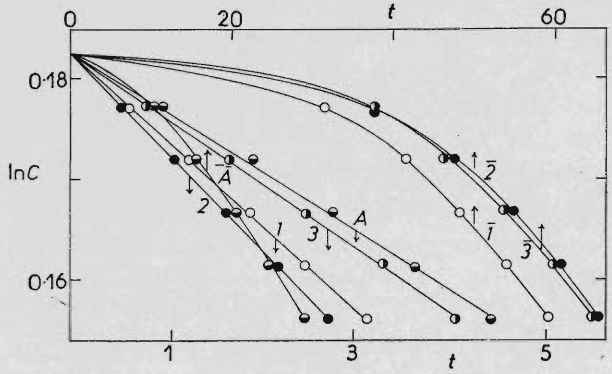

FIG. 1

Dependence of natural logarithm of the actual concentration of hydrogen peroxide *c* on time *t* (min) for reaction on nickel oxide *1*—*3* and molybdenum trioxide $\bar{1}$—$\bar{3}$ at 30°C. *1*, $\bar{1}$ Non-irradiated oxide, *2*, $\bar{2}$ gamma-irradiated oxide, *3*, $\bar{3}$ oxide irradiated by neutrons; *A*, $\bar{A}$ the same dependence without irradiation of nickel oxide and molybdenum trioxide, respectively, measured one year after the catalyst preparation

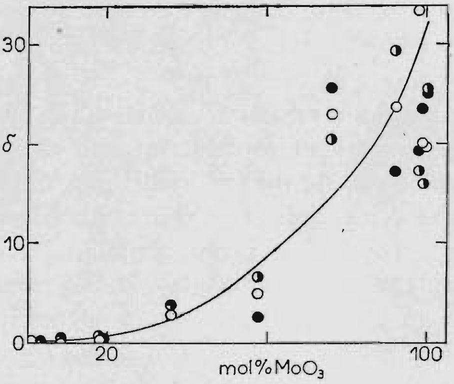

FIG. 2

Maximum deviation δ (min $g^{-1}$) from 1st order kinetics obtained from the kinetic curves of decomposition. ○ Non-irradiated samples, ● gamma-irradiated samples, ◑ samples irradiated by neutrons

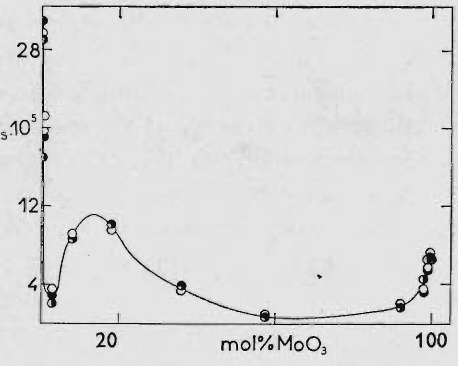

FIG. 3

Dependence of specific catalytic activity $k_s$ (l $m^{-2}$ $min^{-1}$) on the catalyst composition. Temperature 45°C; ○ non-irradiated catalysts, ● gamma-irradiated catalysts, ◑ catalyst irradiated by neutrons energy of the reaction (Fig. 5, curves $\bar{1}, \bar{2}$); the observed variations in the apparent activation energy, however, are nearly within the limits of error of measurements ($\pm 8\%$). The changes in the catalytic activity induced by irradiation are here expressed *via* the irradiation impact value $\Delta = 100(k_s^+ - k_s)/k_s$, where $k_s^+$ and $k_s$ are the specific catalytic activities of the irradiated and the non-irradiated catalysts, respectively. The changes in the apparent activation energy are expressed likewise.

## DISCUSSION

Among the causes of the observed deficit in chemical analysis of the catalysts prepared (Table I) may be the different amount of water adsorbed on their surface. The overstoichiometric oxygen present in the system may contribute to the deficit too, particularly in the region of excess nickel oxide (where its occurrence on the catalyst surface was proved experimentally). This is consistent with the fact that the deficit for nickel oxide exceeds that for molybdenum trioxide. However, as the deficit is highest in the region where an amount of nickel molybdate was detected by X-ray diffraction (18—92 mol.% $MoO_3$), it is conceivable that the molybdate may also contribute to the systematically lower results of chemical analysis.

The mutual influence of the two oxides in the samples manifests itself in the nonmonotonic dependence of their specific surface area on the composition, which in turn is probably the cause of the nonmonotonic dependence of the amount of over-

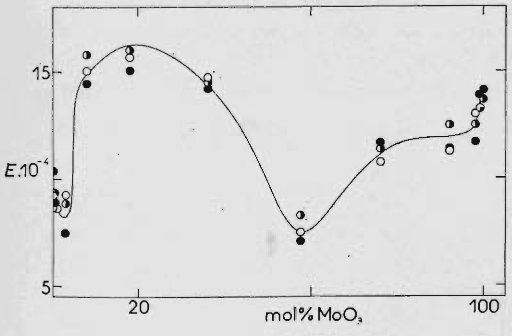

FIG. 4

Dependence of apparent activation energy $E$ (J $mol^{-1}$) on the catalyst composition. ○ Non-irradiated catalysts, ● gamma-irradiated catalysts, ◑ catalysts irradiated by neutrons

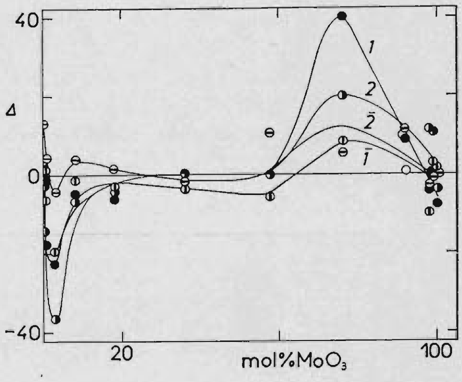

FIG. 5

Relative changes $\Delta$ (%) in the specific catalytic activity of the catalysts *1*, 2 and in the apparent activation energy of the reaction $\bar{1}, \bar{2}$ for the catalysts studied. $1, \bar{1}$ Irradiation by gamma radiation, $2, \bar{2}$ irradiation by neutrons stoichiometric surface oxygen (Table II); in fact, this amount normalized with respect to the catalyst surface decreases monotonically with increasing proportion of molybdenum trioxide, both for non-irradiated and irradiated samples (Fig. 6). This decrease is noticeable particularly in the region of low contents of molybdenum trioxide, which points to a significantly higher affinity of nickel oxide to oxygen as compared with molybdenum trioxide.

The observed departure from 1st order kinetics in the initial stage of the reaction in the sense of an autocatalytic process (Fig. 1) is obviously due to the presence of molybdenum trioxide, because it increases with the content of the latter (Fig. 2). Analogously as with other oxide-type systems, it can be assumed in terms of the concept of bivalent catalytic centres[1] that the increase in the catalytic activity in the initial reaction stage is a result of a change in the oxidation state of molybdenum on the catalyst surface during the initial stage of hydrogen peroxide decomposition up to a stationary state, determining then the steady catalytic activity of the samples (this effect has been observed with other systems, such as NiO–$Mn_2O_3$, ref.[9]). Because molybdenum in the trioxide occurs in the highest oxidation state[5] ($Mo^{6+}$), it is probably partly reduced on the surface to a lower state ($Mo^{5+}$ or even $Mo^{4+}$) in the initial stage of the catalytic reaction. This implies that from the standpoint of the concept of bivalent catalytic centres, the minor catalytic centres of the reaction are here $Mo^{5+}$ or $Mo^{4+}$ ions, the increasing concentration of which in the initial reaction stage brings about rising catalytic activity of the catalyst. These ions are then in equilibrium with the major catalytic centres constituted by $Mo^{6+}$ ions. The decomposition of hydrogen peroxide proceeds on these centres according to the general scheme[1], the acceptor elementary catalytic process on the minor donor catalytic centres being essential to the catalytic activity of the sample. This concept is indirectly supported by the fact that in molybdenum trioxide, $Mo^{5+}$ ions have been detected[8], and these serve as the catalytic centres in dehydrogenation of ethane[10]. Similarly[11], in hydrogenation of ethylene the catalytic activity of molybdenum trioxide has been found to increase with proceeding reduction of $Mo^{6+}$ to $Mo^{4+}$ ions, and these two ion species may then interact to give rise to $Mo^{5+}$ ions[10]. Assuming this concept to be true, equilibrium concentrations of the donor and acceptor centres ($Mo^{5+}$, $Mo^{6+}$) should also establish during the ageing of the catalyst. This is borne out by the fact that with molybdenum trioxide that was allowed to stand on air at room temperature for approximately a year, the above departure from the 1st order kinetics is smaller than with a fresh sample (Fig. 1,

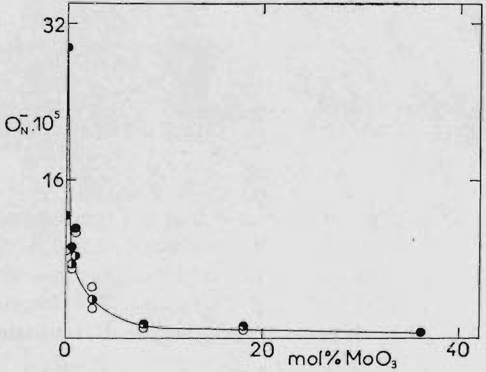

FIG. 6

Amount of the overstoichiometric surface oxygen normalized with respect to the sample surface area ($g_{O^{2-}}$ $m^{-2}$) on the catalysts studied. ○ Non-irradiated samples, ● gamma-irradiated samples, ◑ samples irradiated by neutrons curve A). The reaction rate in the steady state is virtually the same for the two samples. In the case of nickel oxide, where no departure from 1st order was observed in the conditions applied, the kinetics of the processes involved practically does not change on ageing (Fig. 1, curve A). The effect of age on the catalytic properties of oxide-type catalysts has been observed with other systems too (*e.g.*, nickel oxide–copper oxide[12]).

Within the scope of the reaction model suggested it can be deduced from the nonlinear monotonic shape of the dependence of the discussed departure $\delta$ on the system composition (Fig. 2) that nickel oxide has an effect on the way in which the equilibrium between the donor and the acceptor centres of molybdenum trioxide ($Mo^{5+}$, $Mo^{6+}$) establishes in the initial stage of hydrogen peroxide decomposition. The fact that in the region of excess molybdenum trioxide the $\delta$ value decreases with increasing content of nickel oxide more than linearly indicates that nickel oxide either raises the rate of surface reduction of hexavalent molybdenum to a lower oxidation state during the reaction, or lowers the degree of the surface reduction of molybdenum corresponding to the steady-state catalytic activity. In view of the significantly higher affinity of nickel oxide to oxygen in comparison with molybdenum trioxide (Fig. 6), the former hypothesis seems to be more likely. This is also borne out by the observed dependence of the specific catalytic activity on the catalyst composition (Fig. 3), which in the case that the latter alternative is correct (provided that the reaction proceeds exclusively or predominantly *via* the mechanism suggested) would have to be monotonically decreasing in the direction of increasing proportion of nickel oxide. The two alternatives may, possibly, only play a role in the region of low concentrations of nickel oxide (up to 20 mol.%), where the specific catalytic activity was found to decrease with increasing content of nickel oxide.

The observed dependence of specific catalytic activity of the systems on their composition (Fig. 3) can be interpreted — based on the model mechanism suggested — as follows. In accordance with the general theory of semiconductors, adition of a small quantity of molybdenum trioxide to nickel oxide should bring about a decrease in the concentration of $Ni^{3+}$ in the latter oxide; this is borne out by the rapid drop of the amount of chemisorbed oxygen in this range (Fig. 6). As the rate of hydrogen peroxide decomposition on nickel oxide is governed by the surface concentration of $Ni^{3+}$ ions, serving as the minor acceptor catalytic centres[1,13], the catalytic activity of samples with low contents of molybdenum trioxide must be appreciably lower than in the case of pure nickel oxide. This is the reason why in this edge region of catalyst composition the specific catalytic activity was found to drop rapidly with increasing quantities of small additions of molybdenum trioxide. As the proportion of molybdenum trioxide increases (above 5 mol.%), it starts to contribute directly to the catalytic activity. Since in this region the catalytic activity grows nonlinearly with increasing content of the trioxide and attains its maximum at the concentration of approximately 15 mol.% $MoO_3$, it appears that in addition to the $Ni^{3+}$–$Ni^{2+}$ and $Mo^{5+}$–$Mo^{6+}$ pairs of catalytic centres, the mixed pairs of the acceptor-donor type, *viz.* $Ni^{3+}$–$Mo^{5+}$ and $Mo^{6+}$–$Ni^{2+}$, play here a part too. After surpassing the molybdenum trioxide content of 15 mol.%, the extent of charge interaction of the two oxides, which is prerequisite for the establishment of the mixed pairs, obviously diminishes (probably because of the lowering dispersity of molybdenum trioxide), with the result of the specific catalytic activity decreasing with increasing proportion of molybdenum trioxide. In the other edge region, with excess molybdenum trioxide, the situation is analogous to that with the region of excess nickel oxide: the catalytic activity is governed by molybdenum trioxide, hence by the concentration of the $Mo^{5+}$ and $Mo^{4+}$ ions; and since on addition of small quantities of nickel oxide to molybdenum trioxide the concentration of molybdenum ions of lower oxidation state decreases, so must the catalytic activity of the catalyst, which is consistent with the experiment. The fact that the drop is not so marked as in the case of nickel oxide with addition of molybdenum trioxide may be due to a new equilibrium of the catalytic centres, shifted in favour of the $Mo^{5+}$ or $Mo^{4+}$ ions, establishing on the catalyst surface in the initial stage of the hydrogen peroxide decomposition (Fig. 1, curves $\bar{1}$, $\bar{2}$, $\bar{3}$). The fact that in the two side regions the apparent activation energy decreases slightly with increasing content of the minor component (Fig. 4) warrants the assumption that in addition to the decrease in the concentration of the minor catalytic centres, determining the reaction rate ($Ni^{3+}$ and $Mo^{5+}$ ions), some qualitatively different and apparently more efficient catalytic centres play here a part. Their creation may be associated with structure defects appearing as the other component is added to the pure oxide. These catalytic centres manifest themselves most in the range of approximately equal proportions of the two catalyst constituents, where the reaction proceeds with the lowest apparent activation energy, similarly as observed with other two-component catalysts in hydrogen peroxide decomposition[2,12,14–16], or with molybdenum trioxide–titanium dioxide system in oxidation of 1-butene or butadiene, where the catalytic centres have been found[17] to form on the oxide interface; and as the interface area is obviously largest in the region of equal proportions of the two components, the above catalytic centres operate here to the greatest extent too. Since in the region of 10–20 mol.% $MoO_3$, where according to the model suggested the mixed catalytic centres can be assumed to participate, the apparent activation energy of the testing reaction is highest (Fig. 4), it can be deduced that hydrogen peroxide decomposition on these centres is somewhat more energetically demanding.

The above conclusions concerning the dependences of the specific catalytic activity and of the apparent activation energy on the catalyst composition apply both to the non-irradiated and the irradiated systems, because qualitatively the dependences are the same (Figs 3 and 4). This implies that neither the mutual influencing of the catalyst components nor the mechanism of the testing reaction alters on application of ionizing radiation. The negative changes in the catalytic activity and in the apparent activation energy of the reaction observed on irradiation of catalysts with low contents of molybdenum trioxide (Fig. 5) can be explained in terms of recombination of the created non-equilibrium electrons with the acceptor catalytic centres of nickel oxide ($Ni^{3+}$) determining its catalytic activity (in view of the model suggested, the catalytic activity of a catalyst is in this composition region given by that of nickel oxide). However, the facts that the specific catalytic activity decreases also on irradiation by neutrons, and that the apparent activation energy decreases too, indicate that in addition to the mechanism described, there occurs also some other interaction of the radiation with the catalytic centres on the catalyst surface. This may involve, *e.g.*, an effect on the centres associated with structure defects. In the case of neutrons, this may be the so-called polishing effect bringing about a decrease in the catalytic activity, whereas in the case of gamma radiation, this may be a stabilization of the electrons created by ionization on the existing centres of structural origin (decrease in the catalytic activity) and also on additional structure defects giving rise to new catalytic centres of the reaction (decrease in the apparent activation energy). Qualitatively similar processes can lead to the opposite effect – increase in the catalytic activity accompanied by a slight increase in the apparent activation energy – at another composition of the catalyst, as observed in the range of 75 mol.% $MoO_3$. The fact that the maximum positive change in the catalytic activity was not found for the catalyst with approximately equal proportions of the two components suggests that the radiation applied affects not only the catalytic centres associated with structure defects in the crystal, but also those associated with charge defects on the catalyst surface. Since for the catalyst of that composition the change in the apparent activation energy is not very marked, the latter mechanism seems to predominate in this case.

## REFERENCES

1. Múčka V.: This Journal *42*, 2074 (1977).
2. Múčka V., Klumpar J.: This Journal *43*, 557 (1978).
3. Múčka V.: This Journal *44*, 1003 (1979).
4. Múčka V.: This Journal *44*, 1015 (1979).
5. Remy H.: *Anorganická chemie*, Vol. 2, p. 186. Published by SNTL, Prague 1962.
6. Sardi A.: Acta Chim. (Budapest) *39*, 146 (1963).
7. Hegedüs A. J., Sasvari K., Neugebauer J.: Z. Anorg. Allg. Chem. *293*, 56 (1957).
8. Vorobev L. N., Talipov G. Sh.: Zh. Fiz. Khim. *52*, 361 (1978).
9. Múčka V.: This Journal *46*, 1860 (1981).
10. Ward M. B., Lin M. J., Lunsford J. H.: J. Catal. *50*, 306 (1977).
11. Lombardo E. A., Houalla M., Hall W. K.: J. Catal. *51*, 256 (1978).
12. Múčka V.: This Journal *42*, 391 (1977).
13. Schwab G. M., Múčka V.: Z. Phys. Chem. (Wiesbaden) *93*, 77 (1974).
14. Múčka V., Cabicar J.: This Journal *40*, 947 (1975).
15. Múčka V., Cabicar J., Motl A.: This Journal *40*, 340 (1975).
16. Múčka V., Malý P.: This Journal *41*, 3679 (1976).
17. Vankove D., Op S. R., Fernandez A.: J. Catal. *57*, 253 (1979).

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