DECOMPOSITION OF HYDROGEN PEROXIDE ON NICKEL OXIDE–VANADIUM PENTOXIDE CATALYSTS AND THE EFFECT OF IONIZING RADIATION ON THEM

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Some physico-chemical and catalytic properties of nickel oxide–vanadium pentoxide two-component catalysts were studied over the entire concentration region of the components, using the decomposition of hydrogen peroxide in aqueous solution as the test reaction. The two oxides were found to affect each other, which appeared in the dependences of the specific surface area, the V^{4+} ion concentration, and the catalyst activity on the system composition. At low vanadium pentoxide concentrations (up to 15 mol%) the reaction takes place on nickel oxide modified with vanadium pentoxide, whereas in the region of higher vanadium pentoxide concentrations the decomposition of the peroxide is catalyzed primarily in the homogeneous phase by vanadium(V) peroxide ions; in sample with 30 mol% V_2O_5, trivalent vanadium also plays a part. With catalysts obtained by a mere mechanical mixing of the two oxides, a modified activity was observed in the region of high excess of nickel oxide. The activity of catalyst, particularly pure nickel oxide, is increased by its partial reduction and decreased by its exposition to gamma radiation if the dose is higher than 10^5 Gy. The effects observed are interpreted in terms of the concept of bivalent catalytic centres.

The activity of vanadium pentoxide as a heterogeneous catalyst has been found to be affected significantly by the presence of tetravalent vanadium in the oxide; this applies, for example, to oxidations of some organic substances[1,2] as well as to the decomposition of dinitrogen oxide[3]. The tetravalent state of vanadium in the pentoxide can be induced by a higher valency oxide[4,5] such as MoO_3 or by exposing the catalyst to ionizing radiation[6,7]; a higher catalyst activity thus emerges, *e.g.*, in the oxidation of benzene[4] or benzopyrene[8] or in the conversion of 2-propanol[7]. The significance of V^{4+} and V^{5+} ions has been confirmed also for a supported vanadium catalyst, *e.g.*, in the isotopic exchange reaction between protium and deuterium[6].

Combined with the fact that — as follows from the concept of bivalent catalytic centres — the presence of ions in two different valency states is important for the decomposition of hydrogen peroxide[9] and also can account for the sensitivity of catalyst to ionizing radiation[10–13], the above facts suggest that interesting information might be gained from a study of two-component catalysts of vanadium pentoxide with nickel oxide using the reaction mentioned as the test process.

In view of this, some physico-chemical and catalytic properties of nickel oxide–vanadium pentoxide catalysts are investigated in the present work, using a series of samples covering the entire region of composition and testing them in the decom-

position of hydrogen peroxide in aqueous solution, with the aim to seek whether the two oxides affect each other and whether the concept of bivalent catalytic centres applies to this catalyst system. A study of the sensitivity of the system to ionizing radiation is also included.

EXPERIMENTAL

The catalysts were prepared by mixing solutions of nickel nitrate *p.a.* (2 mol l^{-1}) and ammonium vanadate *p.a.* (0·25 mol l^{-1}, dissolved in hot water) in the requisite proportions, evaporating, and calcinating the solid in air in an electric furnace at 400°C for 4 h. Samples of the catalysts were taken for chemical analysis: after grinding them in an agate mortar, the samples with excess nickel oxide (samples No 13—19, Table I) were dissolved in concentrated hydrochloric acid and nickel was determined in them gravimetrically as diacetyldioximate while vanadium was determined chelometrically in the filtrate after reduction with sodium sulphite ($V^{5+} \rightarrow V^{4+}$), whereas samples No 1—12 were dissolved in concentrated hydrochloric acid with a small amount of hydrogen peroxide, nickel was extracted into chloroform, re-extracted into water, and de-

TABLE I

Chemical composition, specific surface areas S and size of the coherent regions of nickel oxide L_{NiO} and vanadium pentoxide $L_{V_2O_5}$

Sample No	Content, % (m/m)			Content of V_2O_5 mol%	S $m^2\ g^{-1}$	L_{NiO} nm	$L_{V_2O_5}$ nm
	V_2O_5	NiO	total				
1	97·6	0·0	97·6	100·0	3·8	—	54
2	94·4	1·1	95·5	97·2	4·4	—	94
3	91·6	2·6	94·2	93·6	5·3	—	223
4	91·2	3·4	94·6	92·6	5·1	—	87
5	89·3	6·0	95·3	87·0	4·3	—	64
6	88·8	6·7	95·5	84·5	5·7	—	87
7	83·3	12·5	95·8	73·2	10·1	—	73
8	72·6	23·5	96·1	55·9	12·6	—	75
9	67·8	30·0	97·8	48·2	15·4	—	87
10	57·5	41·2	98·7	36·5	17·1	—	95
11	54·2	45·6	99·8	27·7	16·8	—	106
12	43·1	52·8	95·9	25·0	18·7	42	56
13	26·1	71·6	97·7	13·1	19·2	64	200
14	12·6	83·5	96·1	8·1	23·7	52	—
15	10·2	85·2	95·4	4·7	28·1	49	—
16	7·6	88·2	95·8	3·4	27·3	49	—
17	4·9	92·0	96·9	2·1	25·1	59	—
18	2·9	95·2	98·1	1·2	21·6	57	—
19	0·0	96·3	96·3	0·0	13·2	61	—

termined chelometrically, as was vanadium in the initial phase. The specific surface area of the catalysts was measured by low-temperature ($(N_2)_l$) adsorption of nitrogen from a nitrogen–hydrogen mixture (1 : 3) and its subsequent desorption at room temperature. Their crystal structure was examined by X-ray diffraction using a modification of theDebye–Scherrer method. The size of the coherent regions of the two oxides was determined based on the broadening of the selective reflections. All the samples were investigated by the EPR method on an ERS-200 spectrometer (Carl Zeiss, Jena). The amount of the overstoichiometric chemisorbed oxygen was determined by iodometric titration; only samples No 19—14 were treated in this manner, those with higher contents of vanadium pentoxide apparently undergoing dissolution during the procedure. Prior to their testing, some of the samples were subjected to reduction with hydrogen on a thermobalance at 350°C. The extent to which the vanadium pentoxide dissolved in the hydrogen peroxide solution was evaluated so that the suspension was filtered in preselected intervals over a Sinpor 6 membrane filter and vanadium in the filtrate was determined chelometrically. The pH changes in the hydrogen peroxide solution were monitored on a PHM-64 pH-meter (Radiometer, Copenhagen). Portions of all of the catalysts were exposed, prior to the testing, to gamma radiation of a ^{60}Co source so that the total dose was 10^5 and 10^6 Gy; the tests were performed immediately after the irradiation, applying the same conditions as for the non-irradiated samples. The kinetics of the test reaction (decomposition of hydrogen peroxide solution, initial concentration 1·2 mol l^{-1}) was measured in terms of the rate of evolution of oxygen at four different temperatures, *viz* 25, 30, 35, and 40°C, and a constant pressure. The volume of the oxygen evolved was measured by means of a gas burette. The overall error of mesurement did not exceed ±2%.

RESULTS

Physico-Chemical Properties

The composition of the mixed catalysts prepared, their specific surface area and size of coherent regions of the two oxides involved are given in Table I. The two oxides made up in average 96% of the sample mass.

The specific surface area of the samples is a nonmonotonic function of their composition, exhibiting a marked maximum at 4·7 mol % V_2O_5. As the crystal structure examination revealed, the systems consist of two phases, of nickel oxide and of vanadium pentoxide, samples No 8 – 12 exhibited also the most intense reflections of vanadium sesquioxide, in the remaining vanadium-containing samples these reflections could only be traced after their reduction with hydrogen at a temperature in excess of 350°C. In the partly reduced samples with higher nickel contents, selective reflections of nickel metal could also be detected. While for nickel oxide the size of the coherent regions is independent of the sample composition within the limits of measurement error, for vanadium pentoxide this parameter is affected by the catalyst composition markedly, attained its maxima in samples with 13·1 and 93·6 mol% V_2O_5.

The EPR spectra of all of the samples exhibited a signal belonging to the V^{4+} ion, which allowed the relative abudance of these ions in the samples to be evaluated (Fig. 1). As the content of vanadium pentoxide is increased, the concentration

of V^{4+} ions rises, the concentration increase is rapid in the side regions and rather slow in the wide central region.

The amount of chemisorbed oxygen normalized with respect to the catalyst mass increasing content of vanadium in sample, while this quantity normalized with respect to the sample surface area decreases (Table II); both rise if the samples have been aged or exposed to gamma radiation.

Vanadium pentoxide is found to dissolve in the hydrogen peroxide solution. After a rapid start the dissolution slows down (Fig. 2, curve *1*). The relative amount of dis-

TABLE II

Amount of chemisorbed oxygen normalized per unit catalyst mass, A (10^{-2}% (m/m)) and per unit surface area, B (10^{-5} g_0^{2-} m^{-2})

Sample No	Initial sample		Sample aged for 3 months		Sample exposed to 10^5 Gy radiation dose	
	A	*B*	*A*	*B*	*A*	*B*
17	5·0	2·0	7·6	3·0	7·8	3·1
18	4·9	2·2	6·6	3·0	7·4	3·4
19	3·3	2·5	4·3	3·3	5·8	4·4

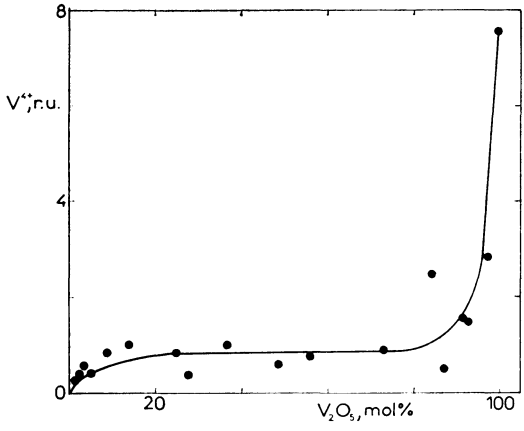

FIG. 1

EPR signal response to V^{4+} ions in dependence on the catalyst composition

solved vanadium pentoxide decreases linearly with increasing content of nickel oxide in sample (Fig. 2, curve 2). The process is accompanied by a rapid drop of pH of the solution in the first stage of the reaction (Fig. 2, curve 3).

Catalyst Activity

For the kinetic study the decomposition of hydrogen peroxide was monitored for a longer period. In the conditions applied the process was found to be one of the first order, only in the initial stage a departure from this course was observed in the sense of retardation, this departure being greater the higher content of vanadium pentoxide in catalyst. For samples with small contents of vanadium (up to 3·4 mol%) this initial stage was not observed at all. The kinetics of the reaction was independent of the stirring speed and obeyed the Arrhenius relation within the temperature region followed.

The catalyst activity was expressed by the 1st order rate constant normalized per unit catalyst mass (k_m), this quantity is a nonmonotinic function of the contact composition, exhibiting a minimum, though not very marked, at approximately 30 mol% V_2O_5 (Fig. 3, curve *1*). The catalyst activity also drops in the presence of a small amount (1·2 mol%) of vanadium pentoxide. Exposition to radiation does not affect the shape of the dependence appreciably, only for samples with low contents of vanadium pentoxide the activity is lowered. Qualitatively identical is also the shape of the analogous dependence of the specific catalyst activity, *i.e.* the rate

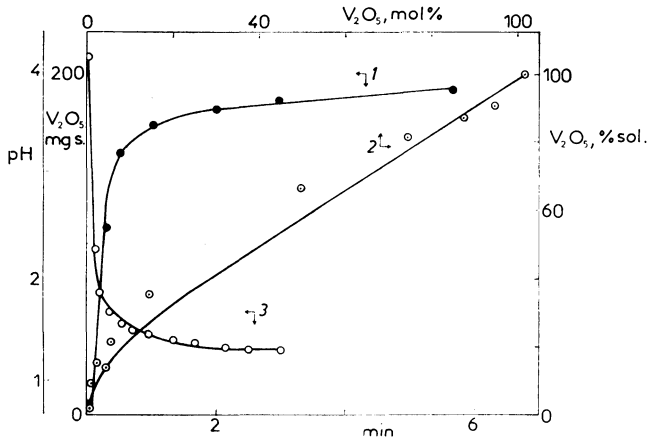

FIG. 2

Kinetics of vanadium pentoxide dissolution *1*, relative amount of dissolved vanadium pentoxide in dependence on the catalyst composition 2, and the drop in the pH during the process *3*

constant normalized with respect to the catalyst surface area. The shape of the dependence of the rate constant k_m on the initial composition of the homogeneous system was also similar, only the minimum at 30 mol% V_2O_5 and the sharp change at low concentrations of vanadium pentoxide were absent. The homogeneous system was prepared so that after the complete decomposition of hydrogen peroxide the catalyst was filtered out on a Sinpor 6 membrane filter, concentrated hydrogen peroxide was added to filtrate in an amount such that its concentration became again 1·2 mol l^{-1}, and its homogeneous phase decomposition was monitored – Fig. 3, curve *3*. For samples prepared by mechanical mixing of the components, on the other hand, the dependence was entirely different, it was virtually linear over the whole composition region, but similarly as with the mixed oxide, in the range of low contents of vanadium pentoxide (up to 1·2 mol%) the catalyst activity dropped rapidly with increasing concentration of this oxide (Fig. 3, curve *2*).

The minimum in the dependence of the catalyst activity on the composition (Fig. 3, curve *1*), observed for sample with 30 mol% V_2O_5, has a more expressive counterpart in the corresponding dependence of the apparent activation energy of the reaction, both for the nonirradiated and the irradiated samples (Fig. 4, curve *1*). For samples prepared by a mere mixing of the components no such a minimum is observed (Fig. 4, curve *2*).

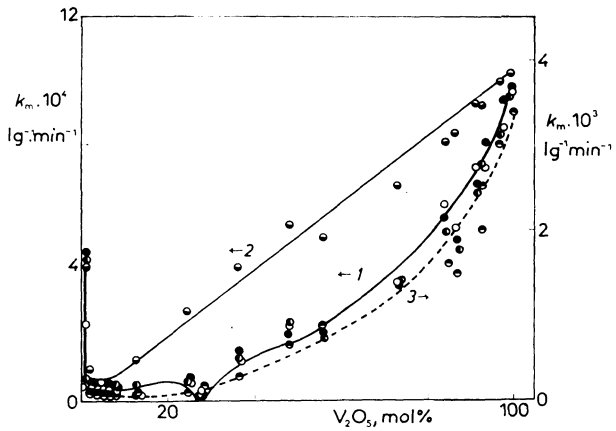

FIG. 3

Dependence of the rate constant k_m at 30°C on the composition of the catalysts; ● nonirradiated samples, ◐ samples exposed to a gamma dose of 10^5 Gy, ○ samples exposed to a gamma dose of 10^6 Gy (curve *1*); 2, ◒ samples prepared by mechanical mixing of the pure components; *3*, ◓ homogeneous samples after the separation of the catalyst (measured at 40°C)

The activity of pure nickel oxide is appreciably affected by its partial reduction with hydrogen (Fig. 5), in dependence on the reduction period, it exhibits first a slight decrease and then a marked increase up to a maximum value. This quantity decreases to the constant value if the reduction period is further prolonged. With the mixed catalysts this effect was not observed.

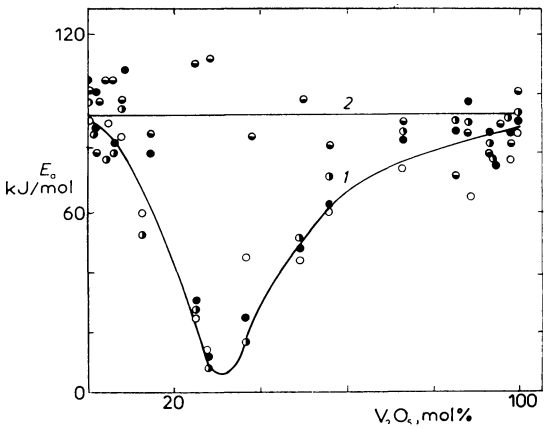

FIG. 4

Dependence of the apparent activation energy E_a on the composition of the catalysts; ● non-irradiated samples, ◑ samples exposed to a gamma dose of 10^5 Gy, ○ samples exposed to a gamma dose of 10^6 Gy (curve *1*), ◒ samples prepared by mixing the two components (curve 2)

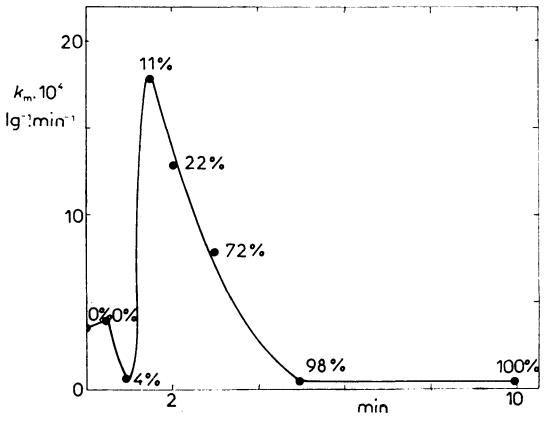

FIG. 5

Dependence of the rate constant k_m on the time of reduction of nickel oxide (sample No 19); degree of reduction in % (m/m)

DISCUSSION

Although vanadium pentoxide has a pronounced tendency to form solid solutions with other oxides[14], no formation of solid solution was observed in our case. Nonetheless, the two oxides concerned affect each other, as revealed by the nonmonotonic character of the dependences of the specific surface area and of the size of the vanadium pentoxide coherent regions on composition. This affecting apparently consists in charge interactions, leading even to the formation of a new phase of vanadium sesquioxide in the range of 30 mol% V_2O_5, as evidenced by the X-ray diffraction patterns. Another evidence of this mutual affecting is also in the appreciably nonlinear dependence of the content of V^{4+} ions on the sample composition (Fig. 1). The fact that even low quantities of nickel oxide (2·8 mol%) induce a rapid drop in the V^{4+} ion concentration in vanadium pentoxide is consistent with the general theory of semiconductors: the impurity of ions (Ni^{2+}) whose valency is lower than that of the major oxide (V^{5+}) brings about a lowering in the concentration of lower valency ions (V^{4+}) in the latter oxide. This also agrees with the conclusions derived for the molybdenum trioxide–vanadium pentoxide system, where the formation of V^{4+} ions has been found[5] to occur by virtue of the presence of the former oxide. A similar charge interaction of the two oxides can be assumed to occur in the side region with excess nickel oxide, where the concentration of Ni^{3+} ions in nickel oxide should drop with increasing concentration of vanadium pentoxide. The fact that the amount of chemisorbed oxygen per unit mass of catalyst, which is indicative of the concentration of Ni^{3+} ions in nickel oxide, increases in this direction (Table II) is due to the increasing concentration of dissolving vanadium pentoxide, which interferes with the iodometric titration of Ni^{3+} ions as has been proved experimentally. The increase in this quantity observed on aged catalysts or on catalysts previously exposed to radiation is ascribed to the establishing of the equilibrium state, promoted by the irradiation.

The dissolution of vanadium pentoxide in hydrogen peroxide solution results in the creation of diperoxoorthovanadate(V) ions which in acid medium are in turn transformed to peroxovanadate(V) ions[15]:

$$V_2O_5 + H_2O = V_2O_5.H_2O \qquad (1)$$

$$V_2O_5.H_2O + 4\,H_2O_2 = 2[VO_2(O_2)_2]^{3-} + 6\,H^+ + 2\,H_2O \qquad (2)$$

$$[VO_2(O_2)_2]^{3-} + 6\,H^+ = [V(O_2)]^{3+} + H_2O_2 + 2\,H_2O \qquad (3)$$

Diperoxoorthovanadate(V) imparts to the solution a yellow colour and in agreement with Eq. (*2*) leads to a decrease in its pH (Fig. 2, curve *3*). This decrease is counteracted by the consecutive reaction (*3*) giving rise to the peroxovanadate(V)ions,

the pH becomes steady and the solution acquires a red-brown colour. Since the dissolution of vanadium pentoxide is hindered by the nickel oxide present (Fig. 2, curve 2), the pH of solution for samples with excess nickel oxide decreases only slightly and reaction (*3*) does not take place at all, the vanadium dissolved remains in the form of diperoxoorthovanadate and the solution has a steady yellow colour. The partial dissolution of vanadium pentoxide during the test reaction is probably responsible also for the departure of the reaction from the 1st order course in its first stage. This departure diminishes as the content of nickel oxide is increased, the relative amount of dissolved vanadium pentoxide decreasing too.

The catalyst activity depends on the composition in a complex nonmonotonic manner. The minimum at 30 mol% V_2O_5 may be associated with the presence of vanadium sesquioxide; the catalyst exhibits also a low apparent activation energy, hence, the reaction occurs on some highly active catalytic centres which are present in a rather small amount. Provided that the bivalent catalytic centres concept[9] holds for this system, it can be assumed that these centres can be V^{3+} ions in equilibrium with V^{5+} ions, this equilibrium making possible the transfer of two electrons within a reaction event. Clearly, the presence of vanadium sesquioxide is conditioned by interaction of vanadium pentoxide with nickel oxide, the minima discussed being absent from the dependences obtained for the simple mechanical mixtures of the two components.

Of practical interest is the appreciable lowering in the catalyst activity of nickel oxide in the presence of low quantities of vanadium pentoxide. Thie effect can be accounted for by the concept of bivalent catalytic centres, according to which the activity of nickel oxide is governed by the Ni^{3+} ions present[10]; really, the concentration of these ions decreases as the content of vanadium pentoxide is increased. It can be thus concluded that in the range of excess nickel oxide the reaction takes place on this oxide affected by vanadium pentoxide, the minor catalytic centres being the Ni^{3+} ions which are in equilibrium with the major Ni^{2+} centres. From the fact that for this system no maximum on the dependence discussed is observed in the region of excess nickel oxide such as has been found for some other two-component catalysts (zinc oxide–cadmium oxide for instance[13]), it can be inferred that in this system no Ni^{2+}–V^{5+} or V^{4+}–Ni^{3+} mixed catalytic centres play a part. This may be a consequence of the dissolution of vanadium pentoxide in the hydrogen peroxide solution.

A similar charge interaction is indicated by the EPR signals also in the range of excess vanadium pentoxide, where the concentration of V^{4+} ions diminishes as nickel oxide is introduced. In terms of the bivalent catalytic centres principle, a sharp decrease in the catalytic activity should follow; however, this could not be observed because in this composition region vanadium pentoxide dissolved rapidly in the solution.

The markedly nonlinear decrease in the catalyst activity with increasing content of nickel oxide over a wide composition region might be related to the decreasing fraction of vanadium pentoxide dissolving into the solution; this explanation, however, cannot be accepted because the latter decrease is linear. Also, the nonlinear course of the dependence is explanaible neither in terms of some influencing of the liquid phase homogeneous catalytic reaction by the undissolved solid because the course is qualitatively identical if the reaction occurs in the homogeneous phase only (in the presence of diperoxoorthovanadate(V) or peroxovanadate(V) solely, Fig. 3, curve *3*), nor in terms of changes in the solution acidity or hydrogen peroxide concentration induced by reactions (*1*)–(*3*), because for the catalysts constituted by mechanical mixtures of the two oxides, where these changes should be basically the same, the dependence of the catalyst activity on its composition is linear. For a better understanding of this effect a detailed study of the catalytic decomposition of hydrogen peroxide in liquid phase in the presence of diperoxoorthovanadate and/or peroxovanadate would have to be undertaken.

Decreasing linearly with increasing nickel oxide content up to 98·8 mol% NiO, the activity of catalysts prepared by mixing portions of the pure components is apparently determined by the relative abundance and activity of the constituents. However, extrapolated to zero content of vanadium pentoxide the straight line does not give the activity of pure nickel oxide; instead, it gives a lower value corresponding to nickel oxide affected by vanadium pentoxide. This indicates that even in the oxide mixtures the nickel oxide experiences a charge interaction from the vanadium pentoxide present in a low concentration (1·2 mol%) in the same manner as in the mixed catalyst. This in turn suggests that in the mechanical mixture with a concentration of vanadium pentoxide not exceeding 1·2 mol% the decomposition of hydrogen peroxide takes place on nickel oxide affected by the other component, whereas at higher concentrations of vanadium pentoxide the catalyst activity is determined by the sum of the activities of the two components in the mixture – the vanadium(V) peroxo ions formed on the dissolution of vanadium pentoxide, and the modified nickel oxide. The possible affecting of the surface properties of nickel oxide by vanadium pentoxide in their mechanical mixture may be associated with the solubility of the latter in the hydrogen peroxide solution, and is realized probably *via* the adsorbed peroxo compounds of vanadium(V) on the nickel oxide surface. The decrease in the activity of nickel oxide brought about by the presence of a small quantity of vanadium pentoxide might also be interpreted in terms of the adsorbed soluble vanadium compounds blocking the catalytic centres of nickel oxide; however, this explanation is not quite acceptable because the activity of these compounds themselves is more than twice that of pure nickel oxide (Fig. 3, curve *1*). More likely, the peroxo compounds of vanadium(V) affect the nickel oxide (its surface layer) in the same manner as the vanadium pentoxide in the mixed catalyst, *i.e.*, by lowering the concentration of Ni^{3+} ions.

The concept of bivalent catalytic centres can also account for the changes in the catalytic properties of nickel oxide occurring on its partials reduction. The initial decrease observed after a 4% reduction is probably associated with the reduction of trivalent nickel, hence, with a decrease in the concentration of the minor catalytic centres of the reaction. The reduction of the oxide to a higher degree, 4–11%, leads to the formation of nickel metal, as observed by X-ray diffraction measurement. As a result, new minor donor centres constituted by nickel metal (or Ni^+ ions) are created. and the decomposition proceeds *via* the acceptor mechanism similarly as observed with nickel oxide prepared by decomposition of nickel oxalate[10]. The concentration of these centres increases with increasing degree of reduction up to 11%, and so does the catalyst activity. At higher degree of reduction the reduced nickel particles apparently tend to form agglomerates, as evidenced by the size of the nickel coherent regions, which by X-ray diffraction measurements was found to be 52, 58, and 114 nm for the degrees of reduction of 11, 22, and 98%, respectively. These agglomerates cannot enter the charge interaction with nickel oxide, similarly as we observed for nickel oxide prepared from nickel metal[10], and so in this region of degrees of reduction (11–98%) the catalyst activity decreases. Additional increasing of the degree of reduction, up to a complete reduction of nickel, has no effect on the catalyst activity, the reaction taking place practically on nickel metal by the donor mechanism on the minor Ni^{2+} centres which are in equilibrium with the major centres of nickel metal.

For the mixed catalysts No 6 and No 14, no effect of the degree of reduction on the catalyst activity was observed, apparently because – as has been demonstrated

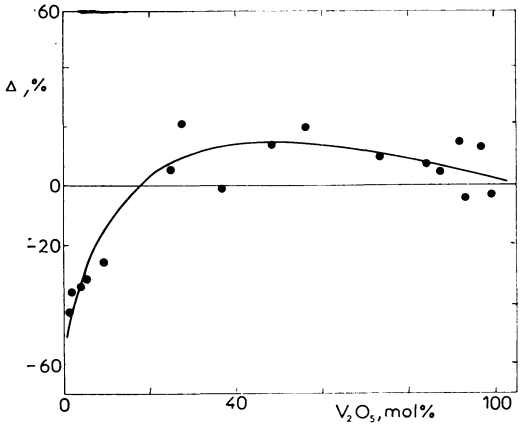

FIG. 6

Effect of irradiation by a dose of 10^6 Gy Δ on the catalyst composition

– with these samples the decomposition of hydrogen peroxide occurs predominantly in the homogeneous phase under the catalytic effect of peroxovanadate(V) ions.

The gamma irradiation, by either of the doses applied, does not alter qualitatively the shape of the dependence of the activity on the catalyst composition. This implies that the mechanism of the interaction of the two components and the mechanism of the test reaction remain unchanged by the irradiation. Quantitatively is the effect of the ionizing radiation on the catalyst activity expressed by the parameter $\Delta = 100(k_m^* - k_m)/k_m$, where k_m^* and k_m are the rate constants on the irradiated and the nonirradiated catalysts, respectively (Fig. 6). While a gamma dose of 10^5 Gy does not change the catalyst activity within the limits of experimental error, exposition to a dose of 10^6 Gy brings about a decrease in the activity of catalysts with low contents of vanadium pentoxide (below 15 mol%). This agrees with the fact that a gamma dose lower than 10^6 Gy leaves the activity of nickel oxide catalyst intact[10,16]. For nickel oxide the negative effect is rather pronounced, $\Delta = -66\%$. It si consistent with the data of ref.[17], where the effect of irradiation has been also shown to depend substantially on the origin of the oxide. Since in contrast to the present work, no effect of irradiation is reported in ref.[17] for the oxide prepared by calcination of nickel nitrate, it can be concluded that the effect of irradiation is a complex phenomenon calling for additional investigation. It can only be stated that generally the correlation between the amount of chemisorbed oxygen and the catalyst activity[16] will not hold for nickel oxide previously exposed to gamma radiation. This stems probably from the fact that in the irradiated oxide at least two processes operate affecting the catalyst activity in opposite sense[10,17]. The fact that the negative effect of irradiation diminishes with increasing content of vanadium pentoxide to nearly vanish for samples with more than 15 mol% V_2O_5 may be associated with the dissolution of this oxide in the hydrogen peroxide solution. This dissolution may be responsible also for the absence of a positive effect of irradiation on the activity of pure vanadium pentoxide which might have been expected in view of the radiative formation of tetravalent vanadium in the pentoxide[6,7].

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