DECOMPOSITION OF HYDROGEN PEROXIDE ON CERIUM DIOXIDE–NICKEL OXIDE TWO-COMPONENT CATALYSTS AND THE EFFECT OF IONIZING RADIATION ON THEM

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Some physical and catalytic properties of cerium dioxide–nickel oxide two-component catalysts have been studied over the entire composition region, employing the decomposition of hydrogen peroxide in aqueous solution as a model catalytic process. The two oxides have been found to affect each other, particularly for NiO contents of 9·1 and 96·7 mol%; the mutual influencing, the nature of which in the conditions applied remains unaffected by heat treatment of the sample or by its exposition to ionizing radiation, is manifested by the nonmonotonic dependences of the oxidation power and of the specific activity of the catalysts on their composition. This can be interpreted in terms of the concept of bivalent catalytic centres, assuming that for nickel oxide the centres consist of Ni^{2+}–Ni^{3+} ion pairs, for cerium dioxide they consist of Ce^{3+}–Ce^{4+} ion pairs, and that in the region of the mutual influencing, Ni^{2+}–Ce^{4+} ion pairs play a major role. Within the scope of this concept, the increase in the oxidation power of all the catalysts in question and a simultaneously decrease in the specific activity of the pure nickeloxide exposed to ionizing radiation can be explained in terms of the ionization effect.

Cerium dioxide has not been as yet studied extensively as a catalyst, although this oxide catalyzes various reactions such as the decomposition of hydrogen peroxide[1] or, if present in a mixture with oxides of thorium[2] or lanthanum[3], the oxidation of carbon monoxide. A catalytic activity of this oxide is also observed in the homomolecular isotopic exchange of oxygen, ^{16}O—^{18}O, if a simultaneous gamma irradiation[4] or a preliminary gamma irradiation at temperatures below 0°C (ref.[5]) is applied.

The aim of the present work was to examine the catalytic properties of cerium dioxide in mixtures with nickel oxide and to seek how these catalytic properties are changed if the catalyst has been exposed to ionizing radiation. Similarly as in our previous work dealing with mixed oxides in which the two components affect each other, decomposition of hydrogen peroxide was employed as a model reaction for testing the catalyst properties.

EXPERIMENTAL

The mixed oxides of cerium and nickel were prepared by mixing solutions of nickel nitrate and cerium ammonium nitrate *p.a.* (1 mol l^{-1}) in proportions such that the samples obtained covered the entire region of 0—100% of each component. The solutions were evaporated on a water bath and the residues were calcinated in air in an electric furnace at 200°C for 1 h and at 400°C for 3 h. Samples of the catalysts were taken for chemical analysis; they were allowed to dissolve in concentrated hydrochloric acid for 24 h in an autoclave at a temperature of 150°C. Cerium was determined iodometrically after oxidizing the trivalent form with ammonium persulphate, nickel was determined chelatometrically while cerium was masked in a carbonate complex. The crystal structure of the catalysts was examined by X-ray diffraction on a TUR M 62 instrument with a goniometer, using the K_α radiation of a copper anode. The size of the coherent regions in the catalyst was calculated based on the broadening of the selective reflections. The specific surface are of the samples was determined by the method of low-temperature $((N_2)_l)$ adsorption of nitrogen from a nitrogen–hydrogen mixture (1 : 3). The values obtained were compared with those of titanium dioxide measured by the BET method. The surface of the samples was also examined on a scanning electron microscope (Jeol) at magnifications of 100—3 000 x. The oxidation power of the catalyst surface was determined iodometrically according to Weller and Voltz[6]. Prior to the testing, some of the samples were thermally treated for 1 h in air in an electric furnace at 500°C, or reduced with hydrogen on a thermobalance at 350°C. Also, portions of all of the catalysts examined were exposed to gamma radiation in air at room temperature using a ^{60}Co source so that the total dose was 100 or 500 kGy, and to fast neutrons from a ^{252}Cf source with an energy of 2·1 MeV applying a dose of 400 Gy. The catalysts were tested in the decomposition of hydrogen peroxide immediately after their irradiation in conditions identical with those applied to the testing with the nonirradiated samples. The kinetics of the test reaction was investigated by monitoring the rate of liberation of oxygen, the volume of which was measured with a gas burette at constant temperature and pressure. The initial concentration of the hydrogen peroxide solution was 1·2 mol l^{-1}, the catalyst was used in amounts of 100 to 200 mg. The tests were carried out at four different temperatures, *viz.* 25, 30, 35, and 40°C, their overall error lay in the region of ±0·5 to ±2%.

RESULTS

Physical Properties

The results of chemical analysis of the catalysts prepared are given in Table I. The X-ray diffraction patterns only showed the cubic structure of nickel oxide and cerium dioxide, the parameters of which agree with the tabulated data. The size of the coherent regions of nickel oxide lies in the range of 300—700 nm, whereas for cerium dioxide the size is only 100—160 nm. The size of particles (crystallites) detected by electron microscopy at a 3 000-fold magnification diminishes with increasing content of nickel oxide in the sample. The specific surface area of the catalyst depends markedly on its composition, exhibiting a maximum for 50 mol% NiO (Table I). By heat treatment this quantity is 1·5—3 times lowered for all the samples except for catalyst No 5 (9·1 mol% NiO), where no change is observed, this catalyst also displays a relatively high oxidation power per unit surface area (the normalized oxidation power) (Fig. 1, curve *1*). A less pronounced, still observable maximum on the dependence portrayed in Fig. 1 also appears for catalyst No 15, containing 96·7 mol% NiO.

TABLE I

Catalyst composition, specific surface area S, relative increase in the oxidation power on the irradiated sample by a dose of 500 kGy, Δ_A, average apparent activation energy of the test reaction E_a, and the average relative changes in the catalyst activity on irradiation Δ_k

Sample No	NiO % (m/m)	CeO_2 % (m/m)	NiO % mol	S $m^2 g^{-1}$	Δ_A %	E_a kJ mol^{-1}	Δ_k %
1	0·00	98·25	0·00	4·4	390·4	60	9·1
2	1·97	96·02	2·01	4·6	476·8	72	18·5
3	2·87	95·36	2·91	2·0	424·2	73	13·6
4	5·32	92·77	5·42	1·8	195·9	65	−7·9
5	8·99	89·37	9·14	2·2	203·4	83	1·8
6	19·21	78·42	19·68	11·0	232·2	60	−36·8
7	30·87	67·11	31·51	17·8	169·7	59	12·9
8	41·12	56·40	42·17	19·3	192·0	49	2·4
9	49·02	48·12	50·50	36·5	161·3	47	6·2
10	58·08	39·74	59·37	31·8	200·4	52	−6·7
11	68·73	29·02	70·31	22·0	189·3	58	2·9
12	80·15	18·70	81·08	17·9	157·1	60	−3·3
13	90·46	7·21	92·62	16·2	92·3	60	−7·1
14	91·26	6·83	93·04	13·0	206·0	79	4·1
15	95·17	3·22	96·73	8·2	84·7	80	−34·3
16	97·09	1·50	98·48	13·2	73·7	75	−31·6
17	98·70	0·00	100·00	10·8	60·0	62	−50·1

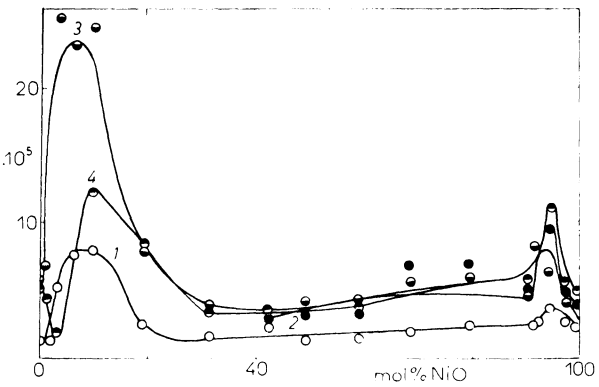

FIG. 1

Dependence of the normalized oxidation power A (g O^{2-}/m^2) on the catalyst composition. *1* Nonirradiated samples, *2* samples exposed to gamma rays in doses of 100, *3* and 500 kGy, *4* samples exposed to fast neutrons

Unlike the above properties, the oxidation power of the surface is appreciably affected by a previous exposition of the contact to ionizing radiation. The irradiation, either by gamma rays (in two different doses) or by fast neutrons, invariably leads to an increase in this quantity, the character of the dependence being preserved (Fig. 1, curves 2–4). The per cent increase, $\Delta_A = 100(A^* - A)/A$ (A^* and A are the normalized oxidation powers of the irradiated and the nonirradiated samples, respectively), is constant for the various ways of irradiation within the limits of error of its determination, the values for the gamma irradiation by a dose of 500 kGy are given in Table I. The oxidation power (with respect to iodide) is increased by the irradiation most for samples with high contents of cerium dioxide (about 430% for samples with 0–3% NiO), less for samples in the region of 5–94 mol% NiO (180% in average), and least for samples containing NiO as the dominant component, 97–100 mol% (70%).

Catalytic Activity

No dissolution of the catalyst takes place during the decomposition of hydrogen peroxide. The reaction proceeds in the kinetic region, its course was monitored up to a high degree of conversion, 80%, and was found to correspond to a 1st order process. The activity of the catalysts remained unchanged even after a time of several months. Also, the heat treatment of the catalysts had no appreciable effect on their activity as characterized by the 1st order rate constant normalized with respect to the surface area (the k_s constant).

The Arrhenius relation was found valid for all of the samples. Within the limits of error the obtained apparent activation energy of the reaction was unaffected by a previous irradiation of the catalyst. The average values of all measurements (Table I) indicate that the composition of catalyst has no marked effect on this parameter either, only in the region of approximately equal proportions of the components a slight minimum, nearly on the limit of measurement error, is observed.

The activity of the contact, characterized by the 1st order rate constant k_s normalized per unit surface area, depends substantially on the catalyst composition (Fig. 2), the dependence exhibits two maxima, an expressive one for 9·1 mol% NiO (sample No 5) and a less marked but reproducible one for 96·7 mol% NiO (sample No 15). The character of the dependence is the same for the nonirradiated and the irradiated samples. The effect of irradiation on the catalyst activity is expressed quantitatively by the value $\Delta_k = 100(k_s^* - k_s)/k_s$, where k_s^* and k_s are the normalized rate constants on the irradiated and the nonirradiated samples, respectively. The Δ_k data in Table I indicate that the irradiation does not affect the catalyst activity to a considerable extent, samples with a high content of nicekl oxide ($\geq$86·7 mol%), particularly pure nickel oxide, are exceptions, their exposition to any of the radiations applied leading to a reduction in their activity.

The rate constant of the test reaction normalized per unit catalyst mass (k_m) for sample No 5 (9·1 mol% NiO) is virtually unaffected by its partial (up to 60% of the theoretical mass loss) or complete reduction (Table II), and within the limits of measurement error the apparent activation energy of the hydrogen peroxide decomposition can also be regarded as constant. For both extents of reduction, however, the treatment brings about an approximately fifteenfold increase in the specific surface area, hence, the specific activity characterized by the rate constant k_s is lowered by the same factor. Other catalysts exhibit similar effects, the changes, however, are less pronounced (for instance, the specific surface area of samples No 3 and 6 increased by factors of seven and two, respectively).

TABLE II

Rate constants k_m and k_s at 25°C, apparent activation energy of the test reaction E_a, and the specific surface areas S for sample No 5 prior to its reduction (*A*) and after its partial (*B*) and total (*C*) reduction

Sample	k_m $1\,g^{-1}\,min^{-1}$	E_a $kJ\,mol^{-1}$	S $m^2\,g^{-1}$	k_s $1\,m^{-2}\,min^{-1}$
A	6·4	74	2·2	3·0
B	6·7	58	33·9	0·2
C	6·6	55	32·9	0·2

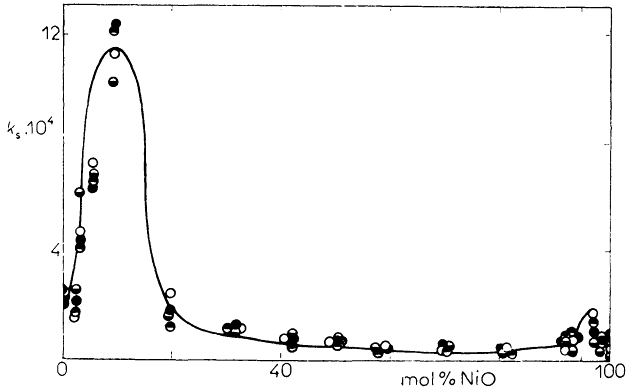

FIG. 2

Dependence of the normalized rate constant k_s (1 min^{-1} m^{-2}) at 40°C on the catalyst composition. Irradiation as in Fig. 1

DISCUSSION

Physico-Chemical Properties

The changes observed in some of the physical properties give evidence that the system does not represent a mere mechanical mixture of the two oxides involved; clearly, the oxides affect each other on the very structural level. For instance, a markedly nonmonotonic dependence on composition is observed for the specific surface area. The fact that the highest values are found for samples with approximately equal proportions of the two components may be explained in terms of the interface area, which is here highest and which obviously contributes appreciably to the total surface area. This is borne out by the fact that the specific surface area does not correlate in a simple manner with the size of the coherent regions of the two oxides or with the size of the crystallites observed with the electron microscope. As the observations indicate, the coherent regions of the system are not identical with the crystalites of the catalyst, the size of which decreases monotonically with increasing content of nickel oxide in sample. Heat treatment of the catalysts at 500°C for 1 h brings about a reduction in the specific surface area of all of the samples, probably as a result of sintering processes. In sample No 5, which is an exception, the surface structure is apparently highly stable; this may be a consequence of a deeper interaction between the two oxides, which may appear also in other properties of this catalyst, similarly as was the case with the nickel oxide–chromium sesquioxide system[7].

The last-mentioned assumption was confirmed by measurements of the oxidation power of the catalyst with respect to iodide ions, which again is highest for sample No 5 (Fig. 1, curve *1*). The less expressive maximum observed for sample No 15 (96·7 mol% NiO) indicates a significant interaction of the two oxides in the range of a high abundance of nickel oxide. The fact that exposition of the catalyst to radiation brings about an appreciable increase in the quantity in question while preserving the shape of the dependence (Fig. 1, curves *2–4*) suggests that the oxidation power is associated with defects induced in the catalyst by the ionizing radiation. The defects are probably of charge nature, as has been found for nickel oxide[8] or for oxides of rare earth elements[9,10] (La_2O_3, Y_2O_3) exposed to gamma radiation or to neutrons. The dependence discussed (Fig. 1, curve *1*) agrees qualitatively with that established for the nickel oxide–copper(II) oxide system[11]. Therefore, analogously as for the latter system, it is reasonable to assume that the oxidation power of the catalyst surface is related with the chemisorbed oxygen, according to the multiplet theory of catalysis, the dissociative adsorption of oxygen on the system under study requires a simultaneous action of a pair of centres. For nickel oxide, these are apparently Ni^{2+}–Ni^{2+} centres, which on the chemisorption (an acceptor reaction) are transformed into Ni^{3+} ions (which are in equilibrium with the chemisorbed oxygen and can be detected by an iodometric reaction). For cerium dioxide, the centres are obviously Ce^{3+}–Ce^{3+} pairs (whose presence in cerium dioxide is conceivable[3]), which on the chemisorption are transformed into Ce^{4+} ions detectable iodometrically. Within the scope of this concept it can be assumed that over a definite concentration region of the two-component system where the conditions of the dispersity and the geometrical factor are favourable, mixed sorption centres of Ni^{2+}–Ce^{3+} ion pairs can appear, and these are transformed on the oxygen chemisprotion into Ni^{3+}, Ce^{4+} ions, detectable by the iodometric method. These mixed adsorption centres are likely to be responsible for the maxima observed in the dependence under discussion (Fig. 1) in the side regions of composition, because the probability of occurrence of such centres increases with increasing content of the minor component up to a certain value and then decreases again, probably owing to the decreasing dispersity of the minor component. The increase in the oxidation power of all samples on irradiation can be ascribed to the radiation oxidation of Ni^{2+} and Ce^{3+} ions. A similar affect has been observed for nickel oxide[12] and copper(II) oxide[13] and their mixed systems[11]. The process is markedly dependent on the system composition (Table I) and may be associated with the way of deposition of the energy and its amount in the trace of the ionizing ray.

Catalytic Activity

The fact that the dependence of the specific catalytic activity on the system composition (Fig. 2) exhibits maxima for the same samples (9·1 and 96·7 mol% NiO) as the dependence of the normalized oxidation power seems to suggest that the activity is governed by the oxidation power, hence, in the model adopted, by the surface concentration of Ni^{3+} and Ce^{4+} ions formed as a result of chemisorption of oxygen. However, this hypothesis is contradicted by the fact that the ratio of the catalytic activity to the oxidation power is not constant for the various samples, hence, Ni^{3+}–Ce^{4+} ion pairs (or Ni^{3+}–Ni^{3+}, Ce^{4+}–Ce^{4+} pairs) do not act as the catalytic centres in the reaction under study.

Now, let us confront this conclusion with the conclusions following from the concept of bivalent catalytic centres[14]. It can be taken for garanted that the activity of nickel oxide is determined by the surface concentration of Ni^{3+} ions; this applies to the decomposition of hydrogen peroxide on the pure oxide[8,12] or on a mixed catalyst[11] as well as to other redox reactions such as the oxidation of nitrogen oxide on a nickel oxide–samarium sesquioxide system[15]. From the standpoint of the above concept it can be assumed that in nickel oxide, Ni^{3+}–Ni^{2+} ion pairs operate as the catalytic centres, Ni^{3+} ions being the minor (determining) centres. In view of the fact that cerium dioxide is an n-semiconductor, this property being probably due to overstoichiometric cerium[3] (Ce^{4+}, Ce^{3+} ions in interstitial positions), it can be supposed that similarly as in zinc oxide[16], in cerium dioxide the reaction occurs on centres constituted by Ce^{4+}–Ce^{3+} ion pairs, the surface concentration of the minor Ce^{3+} ions determining the catalyst activity. Thus in terms of the concept in question, the phenomena participating in the decomposition of hydrogen peroxide on pure nickel oxide can be written as

$$H_2O_2 \rightleftarrows H^+ + HO_2^- \qquad (A)$$

$$Ni^{2+} \rightarrow Ni^{3+} + e^- \qquad (B)$$

$$H^+ + e^- \rightarrow H \qquad (C)$$

$$HO_2^- \rightarrow HO_2 + e^- \qquad (D)$$

$$Ni^{3+} + e^- \rightarrow Ni^{2+} \qquad (E)$$

For pure cerium dioxide the processes are analogous, only reactions (*B*) and (*E*) are replaced by

$$Ce^{3+} \rightarrow Ce^{4+} + e^- \qquad (B')$$

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad (E')$$

Reactions (*B*), (*C*) and (*B'*), (*C*) constitute the acceptor process on the donor Ni^{2+} and Ce^{3+} centres, reactions (*D*), (*E*) and (*D*), (*E'*) described the donor process on the acceptor Ni^{3+} or Ce^{4+} centres; the (*B*), (*E*) and (*B'*), (*E'*) pairs express the equilibrium between the donor and the acceptor centres.

In the concentration region of the two-component system where the two oxides can exert a charge interaction (about 9 and 96 mol% NiO), the mixed Ni^{2+}–Ce^{4+} and Ce^{3+}–Ni^{3+} centres can be also assumed to operate in addition to the Ni^{2+}–Ni^{3+} and Ce^{3+}–$C\varepsilon^{4+}$ centre pairs, the elementary processes thus being

$$H_2O_2 \rightleftarrows H^+ + HO_2^- \qquad (A)$$

$$Ni^{2+} \rightarrow Ni^{3+} + e^- \qquad (B)$$

$$H^+ + e^- \rightarrow H \qquad (C)$$

$$HO_2^- \rightarrow HO_2 + e^- \qquad (D)$$

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad (E')$$

$$Ni^{2+} + Ce^{4+} \rightleftarrows Ni^{3+} + Ce^{3+} \qquad (F)$$

or

$$H_2O_2 \rightarrow H^+ + HO_2^- \qquad (A)$$

$$Ce^{3+} \rightarrow Ce^{4+} + e^- \qquad (B')$$

$$H^+ + e^- \rightarrow H \qquad (C)$$

$$HO_2^- \rightarrow HO_2 + e^- \qquad (D)$$

$$Ni^{3+} + e^- \rightarrow Ni^{2+} \qquad (E)$$

$$Ce^{3+} + Ni^{3+} \rightleftarrows Ce^{4+} + Ni^{2+} \qquad (G)$$

The reaction pairs (*B*), (*C*); (*B'*), (*C*) and (*D*), (*E'*); (*D*), (*E*) have the meaning as above, the reactions (*F*) and (*G*) ensure the equilibrium of the catalytic centres of the two kinds. Similarly as in the chemisorption of oxygen, the probability of occurrence of the mixed centres will increase with increasing concentration of the minor component up to a state where — probably owing to the low dispersity of one or the other component — the mixed centres will cease to play a part in the reaction and the catalyst activity will drop virtually to the initial values (Fig. 2). However, in contrast to the chemisorption of oxygen which probably is bonded *via* the Ni^{3+}–Ni^{3+}, Ce^{4+}–Ce^{4+}, or Ni^{3+}–Ce^{4+} centres, it is the Ni^{3+}–Ni^{2+}, Ce^{3+}–Ce^{4+}, Ni^{2+}–Ce^{4+}, and Ni^{3+}–Ce^{3+} centres that are involved in the catalytic reaction. This then accounts for the fact that the catalyst activity is not related in a straightforward way with the oxidation power of the surface.

The above concept is borne our also by a quantitative comparison of the maxima shown in Fig. 1 (curve *1*) and Fig. 2. The specific activity of catalysts with 9·1 and 96·7 mol% NiO (No 5, No 15) is about 8·9 and 5·7 times, respectively, higher than that of samples where no mutual interaction of the components takes place, whereas the normalized oxidation power is higher by factors of 6·6 and 1·6, respectively. Hence, the specific catalyst activity of the samples No 5 and No 15 and oxidation power of the sample No 5 is raised to a considerably greater extent than the normalized oxidation power of the sample No 15. The increase in the catalytic activity can be interpreted so that with increasing concentration of the minor component the abundance of the Ni^{2+}–Ce^{4+} pairs increases rapidly because the Ni^{2+} and Ce^{4+} ions are the major ones in nickel oxide and in cerium dioxide, respectively. A similar explanation can be applied to the oxidation power of sample No 5, the concentration of the minor Ce^{3+} centres in the region of excess cerium dioxide being rather high and the concentration of Ni^{2+}, the major ions in nickel oxide, also growing rapidly with increasing concentration of this oxide, so the probability of occurrence of the Ni^{2+}–Ce^{3+} adsorption centres increases significantly. For sample No 15 the increase in the oxidation power is considerably lower because the introduction of cerium dioxide brings about a low increase in the concentration of Ce^{3+} ions (the minor centres), so that the relative increase in the probability of occurrence of mixed Ni^{2+}–Ce^{3+} adsorption centres is rather low.

It can be thus concluded that the higher catalyst activity for these samples (No 5, No 15) is primarily due to the enhanced surface concentration of the catalytic centres constitued by Ni^{2+}–Ce^{4+} ion pairs rather than Ni^{3+}–Ce^{3+} pairs, in accordance with the abundance of these ions in the catalyst. This implies that on the two samples the reaction proceeds predomintly *via* the third of the mechanisms suggested. And based on the relative abundances of the components in the catalyst it can be assumed that for sample No 5 (excess cerium dioxide) the activity is governed by the surface concentration of Ni^{2+} ions and the acceptor mechanism is involved, whereas for sample No 15 (excess nickel oxide) Ce^{4+} ions are the minor centres and the decomposition of hydrogen peroxide proceeds here as a donor process.

The dependence of the specific activity on the catalyst composition for the system under study can be compared with that for the nickel oxide–zinc oxide[17] and nickel oxide–cadmium oxide[18] systems (which are composed of *p*- and n-semiconductors) to find that the shape of the dependences is similar, particularly in the region of excess nickel oxide (in the reference systems, the maxima were observed at 6 mol% ZnO and at 13·5 mol% CdO, respectively). In the latter reference system, however, the maximum could only be observed in a longer time after the sample preparation (8 months), when the equilibrium between the donor and the acceptor centres had established. It can be inferred that in the nickel oxide–cerium dioxide system a steady equilibrium between the donor and the acceptor centres establishes rapidly, this is borne out by the results of tests performed with older or thermally treated catalysts. The fact that the specific catalytic activity was unaffected by the heat treatment at 500°C for 1 h is consistent with the insensitivity of the activity to heat treatment established previously for the two pure components[1,8]. The activity of cerium dioxide in the test reaction in question drops and vanishes only if the sample has been heated up to a temperature of 780°C (ref.[1]), this can be explained in terms of the oxidation of trivalent cerium, hence, of a decrease in the concentration of Ce^{3+} ions that according to the first of the mechanisms suggested constitute the minor centres.

The model suggested based on the concept of bivalent catalytic centres can also account for the effect of ionizing radiation on the activity. The radiation is thought to bring about ionization of Ni^{2+} or Ce^{3+} ions, which do or do not exert a catalytic effect according to whether they are part of the centres (*i.e.*, Ni^{2+}–Ni^{3+}, Ni^{2+}–Ce^{4+}, Ce^{3+}–Ce^{4+}, or Ni^{3+}–Ce^{3+} pairs) or they stand alone. While the normalized oxidation power of the catalyst surface is affected by the ionization in both above mentioned cases (the concentration of Ni^{3+} or Ce^{4+} ions is increased), the activity is only affected to the extent to which the radiation influences those ions that are involved in the pairs forming the catalytic centres. Since most probably the concentration of the isolated Ni^{2+} or Ce^{3+} ions on the surface exceeds that of the above catalytic centres, for most samples the irradiation induces an enhanced oxidation power while leaving the specific catalytic activity nearly unchanged. Only for pure nickel oxide or samples with a high excess of this oxide, the ionization of the Ni^{2+} ions in the Ni^{2+}–Ni^{3+} centres plays a part; due to the reaction $(Ni^{2+}\text{–}Ni^{3+}) \rightarrow (Ni^{3+}\text{–}Ni^{3+}) + e^-$, the concentration of these centres is decreased and consequently, the catalytic activity is reduced while the oxidation power is increased. This has actually been observed for the system under study (Table I) or for some catalysts examined previously[7,12,19,20].

So, in view of this explanation, the behaviour of the system with respect to its irradiation can be regarded as an evidence in favour of the concept of the bivalent catalytic centres.

The results obtained with samples that had been in part or totally reduced (Table II) indicate a high stability of the catalyst system. The observed enlargement of the specific surface area is probably due to re-oxidation of the reduced nickel by atmospheric oxygen, taking place even at room temperature and resulting in finely dispersed nickel oxide with a large specific surface area. This process clearly has no effect on the initial catalytic centres and only appears in a lowering of their surface concentration. However, it should be borne in mind that in addition to the catalytic centres formed by ions of the two metals, other centres (*e.g.* ones that are due to structure defects in the catalyst's crystal lattice) may contribute to the activity, and these may appear particularly in a reduced and subsequently re-oxidized catalyst. Such centres then can play a part even in the region of nearly equal proportions of the two components of catalyst, where a slightly lower apparent activation energy of the test reaction has been observed (Table I) similarly as for other two-component systems[11,21-25].

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