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

Viliam MÚČKA

Department of Nuclear Chemistry,
Czech Technical University, 115 19 Prague 1

Received June 27th, 1983

Physical characteristics of nickel oxide–cerium dioxide catalysts and their catalytic activity in the decomposition of hydrogen peroxide were studied over the entire region of catalyst composition. The systems under study, prepared from cerium(III) nitrate, were compared with those prepared previously from cerium(IV) ammonium nitrate, and the properties of the catalysts were found to be affected considerably by the nature of the precursor used. Nevertheless, in spite of the differences the catalytic reaction on the catalysts of the two series seems to proceed on catalytic centres of the same kind, the extent to which the centres operate being dependent on the catalyst composition. The changes in the catalyst activity brought about by sample ageing, heat treatment, or previous exposition to gamma or beta rays or fast neutrons can be accounted for, in terms of the bivalent catalytic centres concept, by interaction of the catalytic centres with oxygen or the radiation applied.

The activity of oxide-type catalysts has recently received systematic interest. In principle, the catalytic properties can be explained in terms of changes in the oxidation–reduction state of the catalytically active component[1]. From this point of view the catalytic properties can be conveniently studied on cerium oxide, in which cerium can occur in two stable valency states. The NiO–CeO_2 system has been studied previously using hydrogen peroxide decomposition as the test reaction, and the catalyst activity has been found to be governed by the valency state of both of the active components[2].

Numerous data[3–5] indicate that the activity of one-component catalysts depends on the way of their preparation. It was therefore of interest to examine how the catalytic properties of a NiO–CeO_2 catalyst differ from those of the same system prepared from different precursors. In the present work, NiO–CeO_2 catalysts were prepared from cerium(III) nitrate, and its properties were compared with those of the catalysts prepared previously[2] (henceforth referred to as series B) using cerium(IV) ammonium nitrate. In addition, the sensitivity of the catalysts to ionizing radiation of various kind was also investigated in this work with regard to the fact that the activity of rare earth oxide catalysts can be modified in this manner, as proved for a number or reactions[6–8] including the decomposition of hydrogen peroxide[2,9].

EXPERIMENTAL

The mixed oxides of nickel and cerium were prepared from nickel nitrate and cerium(III) nitrate of reagent grade purity. The solutions in a concentration of 1 mol l^{-1} were mixed in different proportions, for the final catalysts to cover the entire composition region. The preparation procedure was identical with that used previously[2] for catalysts of series B (evaporation, drying, calcination at 200 and 400°C). Nickel was determined chelometrically while masking cerium in carbonate complex, cerium was determined iodometrically after its complete oxidation with peroxosulphate. The specific surface area measurements, electron microscope surface examination, as well as the heat treatment of the samples and the partial (60%) or complete reduction of selected samples with hydrogen were performed in the same conditions as for series B. Prior to testing, portions of the catalysts were exposed, in air at room temperature, to gamma doses of 100 or 500 kGy from a ^{60}Co source, a dose of 285 Gy of fast neutrons from a ^{252}Cf source, or a beta dose of 9 kGy from a ^{90}Sr–^{90}Y source. Both the nonirradiated and irradiated samples were tested on the decomposition of an aqueous solution of hydrogen peroxide in a concentration of 1·2 mol l^{-1} at temperatures of 25, 30, 35, and 40°C in the same manner as in work[2].

RESULTS

Physical Properties

Chemical analysis revealed that all the samples were composed of nickel oxide and cerium dioxide solely (the sum of the two oxides made up 99% (m/m) of the catalyst) (Table I). The electron microscope photographs at a magnification of 3 000 document that the crystallite size decreases with increasing nickel oxide concentration, similarly as in samples of series B. The specific surface area falls within the wide region of 3·2–51·7 $m^2 g^{-1}$ and decreases with increasing nickel oxide concentration except for sample with a high excess of nickel oxide (97·3 mol%), where a local maximum is observed (Fig. 1, curve *1*). This parameter decreases slightly if the sample is exposed to a temperature of 500°C for 1 h, except for samples containing more than 77·6 mol% NiO (Fig. 1, curve 2). The oxidation power of the catalyst surface per unit surface area, as determined iodometrically, also depends on the catalyst composition in a nonmonotonic manner, exhibiting the maximum values for catalysts with 60·3, 94·6, and 100 mol% NiO (Fig. 2, curve *1*). This trend remains unchanged by 23 months' storing of the samples (Fig. 2, curve 2), the absolute values, however, increase considerably, particularly for contacts with high concentrations of cerium dioxide (Table I); as the nickel oxide concentration is increased, the difference drops virtually to zero. Practically the same increase can be attained by exposing the contacts to the 500 kGy gamma dose (Fig. 2, curve *4*), whereas the dose of 100 kGy has no measurable effect (Fig. 2, curve *3*). Irradiation of the samples by fast neutrons or beta radiation 23 months after their preparation has no measurable effect on the oxidation power of the contact surface.

Catalytic Activity

The catalysts do not dissolve in the hydrogen peroxide solution and no transport phenomena interfere in the kinetics of the reaction. The kinetics was followed up to the high degree of decomposition of 80% and was found to be one of the 1st order; only in the initial stage, the reaction conducted on samples with excess cerium dioxide department from this course in the sense of retardation. The catalyst activity thus could be characterized by the 1st order rate constant of the reaction normalized with respect to the contact surface (specific catalytic activity k_s). The temperature dependence of this constant was consistent with the Arrhenius relation. The apparent activation energy of the reaction was evaluated to be between 45–80 kJ mol^{-1}; in dependence on the catalyst composition this energy exhibits a slight minimum in the range of approximately equal proportions of the two constituents and somewhat higher values in the region of excess nickel oxide (Table I). Within the error

TABLE I

Composition of the catalysts, apparent activation energy of the test reaction E_a, and relative change in the normalized oxidizing power of the catalyst surface ΔO_t resulting from the catalyst storage for 23 months

Sample No	NiO % (m/m)	CeO_2 % (m/m)	NiO % mol.	E_a kJ mol^{-1}	ΔO_t %
1	0·0	98·6	0·0	59	259
2	2·2	97·0	5·0	61	554
3	4·0	94·7	8·8	56	350
4	6·2	93·0	13·3	75	252
5	8·3	90·6	17·5	52	134
6	10·4	88·7	21·3	48	105
7	19·5	79·8	36·0	54	218
8	29·4	69·3	49·4	54	89
9	39·2	59·6	60·3	54	93
10	48·3	51·1	68·8	45	126
11	59·8	39·7	77·6	60	46
12	68·2	31·1	83·5	76	75
13	78·0	21·2	89·5	56	39
14	87·5	11·4	94·6	71	30
15	89·8	9·4	95·8	68	51
16	93·7	6·1	97·3	77	96
17	94·9	4·7	97·9	71	65
18	97·0	2·5	98·9	80	−23
19	99·7	0·0	100·0	73	− 1

of measurement the values remain unaffected by heat treatment or by ionizing radiation.

In contrast to the apparent activation energy of the test reaction, the specific catalytic activity k_s depends on the catalyst composition in a markedly nonmonotonic manner, exhibiting three maxima for samples with 17·5, 60·3, and 94·6 mol% NiO; the value for pure nickel oxide is also relatively high (Fig. 3, curve *0*). This trend did not change if the samples were stored for 4 months or thermally treated at 500°C for 1 h in air. On the ageing, only the activity of catalyst containing 60·3 mol% NiO (sample No 9) decreased by 32% and that of pure nickel oxide decreased by 27% (Fig. 3, curve *t*). The heat treatment had a similar effect: the activity of sample No 9 and of pure NiO decreased by 30 and 68%, respectively, and moreover, the activity of sample No 14 with approximately 95 mol% NiO decreased by 66% (Fig. 3, curve *T*). Qualitatively the shape of the dependence remains preserved for samples exposed to any of the radiations applied, the modification manifesting itself in an activity decrease particularly for samples initially exhibiting a high activity (No 5, 9, and 14), where the decrease is 30–50% (Fig. 3, curves γ, β, *n*). The negative effect of gamma radiation increases with the dose applied (Fig. 3, curves γ and $\bar{\gamma}$), the activity decrease

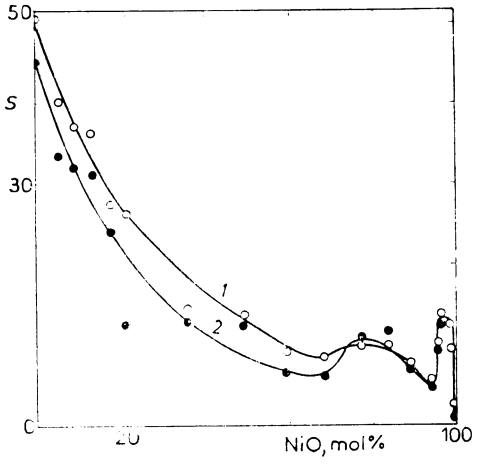

FIG. 1

Dependence of the specific surface area S ($m^2\ g^{-1}$) on the composition of initial *1* and thermally treated *2* samples

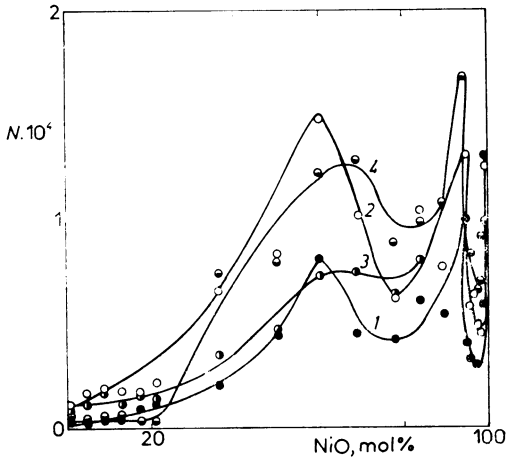

FIG. 2

Dependence of the normalized oxidation power N (g_{O_2}- m^{-2}) on the composition of the initial catalysts *1* and catalysts stored for 23 months (*2*), exposed to a 100 kGy gamma dose *3*, and exposed to a 500 kGy gamma dose *4*

for samples No 9 and 14 exposed to the 500 kGy dose being 63 and 84%, respectively. A positive effect (increase of about 50%) was only obtained for the pure oxides (or sample with a high fraction of NiO, 98·9 mol%) exposed to beta radiation (Fig. 3, curve β).

The effect of radiation can be regarded as being virtually removed by heat treatment at 500°C for 1 h; in fact, this treatment alone leads to approximately the same decrease in catalytic activity as the irradiation and the activity of the contact is unchanged by the successive heat treatment (Table II for sample No 5).

Gravimetric measurement on a thermobalance revealed that the catalyst reduction with hydrogen is followed by its surface reoxidation during the cooling. This process affects neither the specific surface area of the sample nor the apparent activation energy of the test reaction. The catalyst activity and, consequently, the specific

TABLE II

Specific catalyst activity $k_s \cdot 10^5$ (1 m^{-2} min^{-1}) at 35°C for nonirradiated, gamma-irradiated (γ), beta-irradiated (β) and neutron-irradiated (n) sample No 5 and the corresponding values for the samples thermally treated at 500°C for 1 h

Sample No 5	Nonirradiated	γ	β	n
Initial	5·3	3·5	3·3	4·3
Treated	3·2	3·7	3·3	3·4

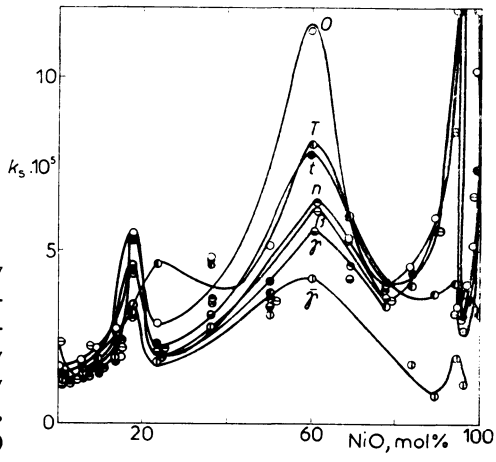

FIG. 3

Dependence of the specific catalyst activity k_s (1 m^{-2} min^{-1}) at 30°C on the composition of the initial catalysts (O) and catalysts stored for 4 months (t), thermally treated (T), and exposed to a 100 kGy gamma dose (γ), 500 kGy gamma dose ($\bar{\gamma}$), beta radiation (β), and fast neutrons (n)

activity, on the other hand, decrease considerably on the reduction (followed by the reoxidation). For instance, for sample No 5 in the initial state, in the state reduced to 60% of the theoretical weight loss, and in the completely reduced state the activity at 35°C was 14·3, 9·8, and 7·7 $l\,g^{-1}\,min^{-1}$, respectively.

DISCUSSION

The nonmonotonic trend of the dependences of the specific surface area of the samples and the normalized oxidation power of their surface on composition gives evidence that the components of the catalyst affect each other considerably. The shape of the dependences is qualitatively different from that obtained for samples prepared from cerium(IV) salt (series B), where the former dependence exhibited a pronounced maximum in the range of approximately equal proportions of the constituents and the latter dependence displayed two maxima in the side regions[2]. This shows that the precursor used for the preparation affects substantially the surface properties of the final catalyst. Another evidence follows from the fact that the heat treatment of catalysts of series B led to a reduction in their specific surface area as great as three times, whereas the same treatment of the catalysts studied in the present work (series A) brought about only a slight decrease in this parameter, hence, the latter samples exhibit a better stability with respect to sintering processes.

The two series of catalysts differ appreciably also in the sensitivity of the oxidation power of their surface to irradiation. In series A, this parameter increased on a 23 months' storage and on their irradiation by the 500 kGy dose (Fig. 2, curves *2–4*). In series B, this parameter was unchanged by the storage, whereas an increase was observed on the irradiation by gamma doses of not only 500 kGy, but also 100 kGy, and also by neutrons[2].

In agreement with the previous conclusions[2] the oxidation power can be regarded as determined by the surface concentration of Ni^{3+} ions and Ce^{4+} ions in their overstoichiometric amounts. Furthermore, it can be deduced that as a result of the interaction with oxygen gas during the storage the equilibria $Ni^{2+} \rightleftarrows Ni^{3+}$ and $Ce^{3+} \rightleftarrows Ce^{4+}$ are shifted forwards and the oxidation power increases. Probably, the irradiation of catalyst has an accelerating effect but the attained equilibrium cannot be further influenced by ionizing radiation, and so no radiation-induced effect appears with samples exposed to neutrons or β rays 23 months after their preparation.

The reduction and successive reoxidation of the samples studied (series A) has no effect on their specific surface area, whereas for samples of series B this parameter was observed to increase as much as fifteen times; this is another evidence for the role of the precursor used.

On the other hand, in addition to the fact that in both series the two components clearly affect each other, the specific surface area of samples A, too, seems to be in no simple relation to the size of crystallites as observed by electron microscopy.

The irradiation of the system studied also had no effect on the specific surface area, probably because the dose applied was too low.

Despite the differences in the physical properties of the two series of catalyst, the virtually identical values of apparent activation energy of the test reaction and the identical trends of the dependence of this quantity on the catalyst composition indicate that in both series the reaction proceeds on catalytic centres of the same kind. Hence, in the region of high excess of nickel oxide the catalytic centres, in terms of the bivalent catalytic centres concept[1], will be the Ni^{2+}–Ni^{3+} pairs and their concentration will be determined by that of the minority Ni^{3+} ions; in the region of high excess of cerium dioxide the catalytic centres will be the Ce^{4+}–Ce^{3+} pairs with the minority Ce^{3+} ions. This is borne out by the slowing down of the reaction observed in its initial stage on samples with excess cerium dioxide, which is due to the oxidation of trivalent cerium by the evolved oxygen or by hydrogen peroxide itself.

As the concentration of cerium dioxide in samples with a high excess of nickel oxide (100–97·3 mol% NiO) is increased, the nickel oxide holes (Ni^{3+}) will be occupied by electrons of cerium dioxide (n-semiconductor) and the concentration of the minority Ni^{3+} ions, and thereby of the Ni^{2+}–Ni^{3+} centres, will decrease. Really, in this region the oxidation power of the surface of samples A decreases in this direction and the catalyst activity drops rapidly too. For samples B, however, this trend has not been observed, which implies that no charge effect of cerium dioxide on nickel oxide takes here place.

If in the other side region the excess cerium dioxide were similarly affected by nickel oxide, *i.e.* if electrons passed from the Ce^{3+} ions to the Ni^{3+} ions, the specific catalyst activity would drop with increasing nickel oxide content of the system. This has not been actually observed, which implies that in the series under study, similarly as in series B, no such effect occurs. This may be accounted for by the relatively large size of the crystallites found in this composition region.

The expressive maxima of the specific catalyst activity found for samples containing 17·5 and 94·6 mol% NiO can be regarded as analogues of those found in series B for samples containing 9·1 and 96·7 mol% NiO. It is therefore again assumed that on these samples the reaction takes place on the mixed Ni^{2+}–Ce^{4+} and Ni^{3+}–Ce^{3+} ion pair centres, and the reaction mechanism of the decomposition of hydrogen peroxide is as suggested previously[2]. The ratio of the specific catalytic activity values for sample with 94·6 mol% NiO (maximum) to sample with 97·3 mol% NiO (minimum) is 3·5, the ratio of the oxidation power values is 3·7. The agreement between the two ratios points to an interrelation of the parameters in question. This can be due to the fact that in the 94·6 mol% NiO range the mixed Ni^{3+}–Ce^{3+} centres play a major role, the oxidation power being determined by the concentration of the Ni^{3+} ions constituting the centres. In the 17·5 mol% NiO range, no correspondence was established between the increased catalyst activity and the oxidation power of the surface, which indicates that responsible for the increased activity are

predominantly the mixed catalytic centres Ni^{2+}–Ce^{4+}; since Ce^{4+} ions are the stoichiometric ions of cerium dioxide, they cannot bring about an increased oxidation power of the catalyst surface similarly as observed with series B in both side regions[2]. In the extent of the role of the Ni^{3+}–Ce^{3+} centres the system under study differs from that of series B. This again may be a consequence of the fact that since one of the precursors of the present system was a salt of trivalent cerium, the surface can contain cerium(III) ions, and thus Ni^{3+}–Ce^{3+} pairs, in higher quantities.

The maximum of the specific catalyst activity observed for sample containing the two constituents in approximately equal proportions (60·3 mol% NiO) may be related with defects stabilized on the interface which is large in this composition region[1]. These defects can serve as the catalytic centres for the reaction in question and can also contribute to the oxidation power of the catalyst surface as indicated by the maximum of the normalized oxidation power established in this range. In series B the maxima were not observed, so the samples studied in the present work clearly are defective to a higher extent.

The centres in samples containing the constituents in approximately equal proportions differ from those in samples of the side regions also in that for the former the catalyst activity decreases slowly with the time of storage, probably due to the slow recombination of the defects, whereas for the latter no changes were observed in the specific activity of the stored catalysts. Since the catalyst ageing has a negative effect also on the activity of pure nickel oxide, on the surface of which the equilibrium concentration of Ni^{3+} ions establishes, it can be inferred that the systems involving the mixed catalytic centres possess a relatively higher stability. The stability of the catalytic centres with respect to oxidation is generally rather high; really, whereas the sample ageing results in an appreciable increase in the oxidation power of the surface particularly in the regions of excess cerium dioxide, the catalytic activity remains unchanged for the majority of samples. Hence, it is particularly the cerium ions not involved in the catalytic centres that undergo oxidation in the laboratory conditions.

The stable equilibrium of the defects in the sample with 60·3 mol% NiO or Ni^{3+} ions establishes more rapidly if the sample is subjected to heat treatment. In addition, however, this treatement affects considerably the extent to which the mixed centres operate in the reaction, and the specific activity drops particularly for catalyst with 94·6 mol% NiO, whereas the maximum occurring at 17·5 mol% NiO only shifts towards higher nickel oxide contents. This is consistent with the concept of Ni^{3+}–Ce^{3+} pairs playing the major role in the former sample and vanishing on the heat treatment because of the oxidation of trivalent cerium, and Ni^{2+}–Ce^{4+} centres occurring in the latter samples and being virtually insensitive to the heat treatment. This also is why in the samples of series B, where the mixed Ni^{2+}–Ce^{4+} are presumably the major centres, no change in the catalytic activity was observed on the sample ageing or heat treatment.

The catalytic system under investigation differs from that of series B also in its sensitivity to ionizing radiation. While in the latter series, sensitivity to gamma irradiation was only observed for pure or nearly pure nickel oxide, in the present series the irradiation by any of the radiations used leads to a lower specific catalyst activity, particulary for samples exhibiting a relatively higher catalytic activity (samples No 5, 9, 14). The cause may be in the different ways in which the absorbed radiant energy is stored in the two systems.

The negative effect of radiation on the catalytic properties, accompanied by increase in the oxidation power, can be explained as follows. The dominating process in the interaction of radiation with the catalyst is probably ionization. If the catalytic centres are Ni^{3+}–Ni^{2+}, Ce^{3+}–Ce^{4+}, Ni^{2+}–Ce^{4+}, and Ni^{3+}–Ce^{3+} ion pairs, then their ionization, hence, oxidation of Ni^{2+} and Ce^{3+} ions, can result in a negative radiation-catalytic effect as observed, the increased concentration of Ni^{3+} ions or overstoichiometric Ce^{4+} ions leading to the increased oxidation power. The fact that the lower gamma dose (100 kGy) only induces a lowered catalyst activity while leaving the oxidation power unchanged, whereas the higher dose (500 kGy) induces a drop in the catalyst activity and, at the same time, an increase in the oxidation power, can be explained so that whereas the electrons created on the ionization of the centres by the lower dose are completely trapped by the Ni^{3+} or overstoichiometric Ce^{4+} ions that do not create the mixed catalytic centres, the electrons produced by the higher dose are present in a concentration higher than that of the Ni^{3+}, Ce^{4+} traps, and an increased total concentration of the Ni^{3+} and Ce^{4+} ions and, consequently, increased oxidation power result.

The concept outlined implies that the activity of an irradiated sample cannot be restored by heat treatment because the treatment itself leads to oxidation of the catalytic centres by oxygen in air, hence, to processes of the same nature as those induced by the irradiation.

The substantially lower activity of the irradiated catalyst containing 60·3 mol% NiO, in which the catalytic centres presumably are stabilized defects of various kind, may be due to recombination interactions of the defects with the nonequilibrium charge carriers created in the ionization process.

The increased catalyst activity of beta-irradiated pure or nearly pure nickel oxide or pure cerium dioxide may be induced either by a partial ionization of the Ni^{2+}... ...Ni^{2+} or Ce^{3+}...Ce^{3+} pairs leading to the formation of Ni^{2+}–Ni^{3+} or Ce^{3+}–Ce^{4+} centres, or by the capture of the absorbed electrons by Ni^{2+} or Ce^{4+} ions, stimulating the formation of new catalytic centres such as Ni^{2+}–Ni^{0} or Ce^{4+}–Ce^{3+}. The latter of the mechanisms proposed is favoured by the fact that no such effect appeared on the gamma irradiation.

The change in the activity of catalysts which have undergone reduction followed by reoxidation, with the specific surface area unchanged, again documents the difference between series A and series B; in the latter, the reduction in the same condi-

tions resulted in a multiple increase in the specific surface area, the catalytic activity characterized by the rate constant, on the other hand, remained unchanged. The reduction–reoxidation process probably leads to a new equilibrium concentration of the catalytic centres, which seems to be highly sensitive to the conditions of formation of the catalyst surface layer. These conditions manifest themselves on a level deeper than the conditions determining the experimentally measurable specific surface area or dispersity of the catalyst.

REFERENCES

1. Múčka V.: This Journal *42*, 2074 (1977).
2. Múčka V.: This Journal *49*, 14 (1984).
3. Schwab G. M., Múčka V.: Z. Phys. Chem. (Wiesbaden) *93*, 77 (1974).
4. Múčka V.: This Journal *41*, 1717 (1976).
5. Múčka V.: This Journal *41*, 3504 (1976).
6. Sazonov L. A., Sokolskii V. D., Mitrofanova G. N.: Khim. Vys. Energ. *2*, 359 (1968).
7. Mitrofanova G. N., Sazonov L. A., Preobrazhenskaya L. V., Sokolskii V. D.: Kinet. Katal. *14*, 623 (1973).
8. Spitsyn V. I., Pirogova G. N., Korozteleva R. I., Sopina A. A., Stelmakh N. S.: Zh. Fiz. Khim. *54*, 2610 (1980).
9. Virmani V. P.: *Proc. Nucl. Rad. Chem. Symp.*, Bombay 1964, p. 134. Bombay 1965.

Translated by P. Adámek.