HYDROGEN PEROXIDE DECOMPOSITION
ON A TWO-COMPONENT NiO–Fe$_2$O$_3$ CATALYST

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Some physical and catalytic properties of the two-component nickel oxide–ferric oxide catalysts were studied using samples with different content of both components, covering the whole concentration range from 0 to 100% of one of the components. It was proved that these properties depend strongly on the preparation procedure of the catalyst of the desired composition and on the catalyst composition for the given preparation procedure; moreover, it was proved that the phase composition of the contact catalyst is not decisive for the catalytic activity of the given system. It seems probable that the valence state of the catalyst metal ions and their ability to form the reaction catalytic centers are the rate-determining factors. The results obtained lead at the same time to the assumption that these parameters change substantially with the catalyst composition. No changes of the catalytic activity were observed for catalysts irradiated by fast neutrons or accelerated electrons.

Previous studies[1] dealing with various two-component catalysts, tested by the decomposition of the aqueous solution of hydrogen peroxide, show that in most cases the two components of the catalyst interact so that the catalytic activity of samples with different content of both components are non-additive. The aim of this study was to investigate from this point of view the catalytic behaviour of the system nickel oxide–ferric oxide as a strong interaction of both components can be expected in this system, accompanied by the formation of the spinel structure NiFe$_2$O$_4$ similarly as in the system of ferric oxide and zinc oxide[2]. In addition the effect of ionizing radiation on this system was studied, too, as our previous studies[3–5] revealed that the catalytic activities of both nickel and ferric oxides can be changed by irradiation. All measurements were made with samples prepared by two different methods so that the effect of the two-component catalyst genesis on its properties could be studied because these effects are well known in nickel oxide[3,4], ferric oxide[5,6] and also in some other two-component catalysts as, *e.g.*, in the system nickel oxide–cerric oxide[7,8].

EXPERIMENTAL

The mixed oxides of nickel and iron were prepared from the nitrate solutions of both these metals (reagent grade purity) mixed in such ratios that the resulting samples would cover the whole

region from 0 to 100% of one component. In the first case (the catalyst series N) these solutions were evaporated to dryness, the product was calcinated in an electric furnace in air at 600°C for four hours and after grinding the resulting oxides of the grain size from 0·25 to 0·025 mm were used for further experiments. In the second case (series H) the nitrates of both metals were precipitated with the potassium hydroxide solution, the precipitate was repeatedly decanted with hot water, washed and after drying at 140°C for 4 hours it was calcinated at 450°C for 4 hours (it was verified by calorimetry that the temperatures applied were sufficient for the quantitative decomposition of the respective precursors). The same fraction of grains as mentioned above was used for subsequent experiments.

All catalysts were chemically analyzed by iodometric titration (determination of iron) and the content of nickel was determined by electrolysis. The specific surface area of the catalysts was measured by the low-temperature adsorption of nitrogen from the mixture $H_2 : N_2 = 5 : 1$, with the precision of $\pm 5\%$. The crystalline structure and the size of coherent regions of samples was determined by X-ray diffraction using the cobalt Kα line. The surface oxidation ability of the catalysts was determined by iodometric titration according to Weller and Voltz[9], with the precison of $\pm 15\%$. A part of the samples was irradiated by fast 2-MeV neutrons of the ^{252}Cf source with the dose rate of $7\cdot33 \cdot 10^{-5}$ Gy s^{-1} and with the total dose of 110 ($\pm 25\%$) Gy. Another part of samples was irradiated by 3 MeV electrons from the linear accelerator working in the pulse regime (pulse length 2·5 µs, pulse repetition rate 500 s^{-1}) with the mean current of 300 µA and with the total dose of 500 kGy. The irradiated samples were tested under the same conditions as the unirradiated ones. The decomposition of the aqueous solution of hydrogen peroxide (reagent grade) of the initial concentration of $1\cdot2$ mol l^{-1} that was used as the test reaction was measured at four different temperatures from 25 to 40°C. The measurements were done at the constant temperature and pressure with the overall error of $\pm 20\%$, the formed volume of oxygen per certain time period being the measured quantity. The catalytic activity of samples was then characterized by the test reaction rate constant taken per unit area of the catalyst surface (the specific catalytic activity k_s).

RESULTS AND DISCUSSION

Physico-chemical Properties

From the chemical analysis (Table I) it follows that both series of prepared catalysts cover the whole range of compositions and that all samples are — from the chemical point of view — composed only of ferric and nickel oxides (the sum of wt. % of both oxides is close to 100%). The difference between this sum and 100%, particularly in some samples of the series H, can be explained by the presence of water in the catalyst grains.

X-ray diffraction of the prepared catalysts confirmed that all samples are composed of the α-modification of ferric oxide and of nickel oxide. Moreover, in the samples of the series N with 83 — 15 wt.% of Fe_2O_3 (samples No 5 — 12) the existence of the spinel structure $NiFe_2O_4$ was unequivocally proved. From Table II it follows that the size of coherent regions of this structure does not change with the change of the catalysts compositions while the size of the coherent regions of ferric oxide decreases with the increasing content of nickel oxide and the size of nickel oxide coherent regions increases in the same sequence. Similar results were obtained also for the

samples of the series H, in which, however, the coherent regions are smaller than in the catalysts of the series N. This corroborates the idea of the substantial effect of the initial substances on the growth of the resulting catalyst crystals, similarly as it was observed[6], *e.g.*, in the case of the carrier catalyst $\alpha\text{-}Fe_2O_3/\gamma\text{-}Al_2O_3$.

It turns out from the measurements of the specific surface areas of the prepared catalysts (Fig. 1) that this quantity is strongly non-monotonous and non-additive not only for the samples of the series N (curve *1*) in which the presence of spinel was proved but also for the series H (curve *2*) in which the formation of spinel is strongly suppressed. It seems therefore evident that the non-monotonous character of this dependence (that is qualitatively different for the two series) is not directly connected with the crystalline structure of the catalyst components. Neither this interaction nor the absolute magnitude of the specific surface area can be affected by the irradiation of the catalysts under the given conditions.

The interaction of both components of the catalysts is also evident from the dependence of the oxidation ability of the catalyst surface (taken per the surface unit) on their composition (Fig. 2). In the case of nickel oxide this quantity indicates the surface concentration of Ni^{3+} ions, the presence of which is counterbalanced by chemisorbed oxygen[3,4]. Because ferric oxide is substoichiometric with regard

TABLE I

Chemical analysis of the samples under study

Sample	wt. %				Σ wt. %	
	Fe_2O_3		NiO		N	H
	N	H	N	H		
1	99·5	98·9	0·0	0·0	99·5	98·9
2	97·8	98·3	1·3	1·2	99·1	99·5
3	95·9	96·2	3·2	2·4	99·1	98·6
4	90·6	90·9	8·5	8·1	99·1	99·0
5	82·9	83·1	16·1	15·9	99·0	99·0
6	75·2	73·5	23·7	24·7	98·9	98·2
7	64·7	64·8	34·0	34·1	98·7	98·9
8	54·7	54·7	45·1	43·9	99·8	98·6
9	44·1	45·0	55·0	53·1	99·1	98·1
10	33·9	34·4	65·2	64·2	99·1	98·6
11	22·8	23·9	76·8	75·6	99·6	99·5
12	15·4	13·2	84·0	86·0	99·4	99·2
13	4·9	5·4	94·4	93·3	99·3	98·7
14	2·8	2·8	96·8	95·6	99·6	98·4
15	0·0	0·0	99·5	99·3	99·5	99·3

to oxygen (n-type semiconductor) it contains[10] a certain concentration of Fe^{2+} ions, about half of them is in the stable octahedral positions and the other half in the interstitial positions of the oxide lattice. These ions are able to chemisorb oxygen on the surface. Hence, Fe^{3+} ions are formed by the acceptor chemisorption. They are evidently less stable than the basic ions of ferric oxide in the octahedral configuration. It is therefore possible to identify these over-stoichiometric Fe^{3+} ions with the oxidation ability of the ferric oxide surface as determined by iodometric titration. Fig. 2 shows the steep decrease of the oxidation ability of the unit surface area of nickel oxide with the increasing content of ferric oxide. This is in agreement with the general theory of semiconductors because the oxide of higher valence state (Fe_2O_3) decreases the concentration of higher-valence ions (Ni^{3+}) of the lower-valence-state oxide (NiO). The decrease of this quantity in the region of Fe_2O_3 excess with a small addition of nickel oxide could be connected with the higher affinity of nickel oxide to oxygen (in comparison with the ferric oxide affinity). From Table III it is evident that the irradiation of the catalysts by neutrons as well as by electrons results in a decrease of their surface oxidation ability. This effect is more conspicuous in the

FIG. 1

Dependence of the specific surface area S ($m^2 g^{-1}$) on the content of Fe_2O_3 (wt. %) in the catalysts of the series N (1) and H (2)
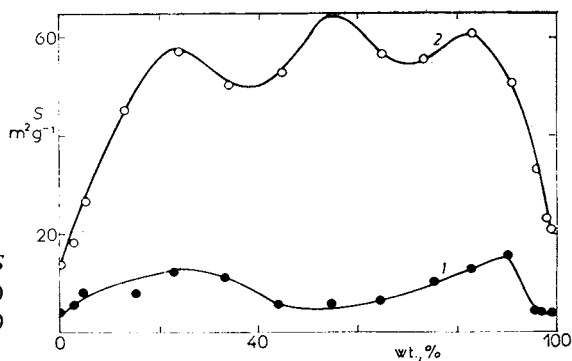

FIG. 2

Dependence of the normalized oxidation ability of the catalyst surface O (g_{O_2}- m^{-2}) of the series N (1) and H (2) on the content of Fe_2O_3 (wt. %)
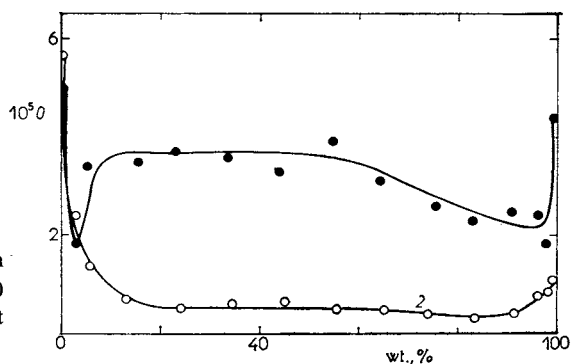
TABLE II

The size of coherent regions L (10^{-10} m) of nickel oxide, ferric oxide, and spinel $NiFe_2O_4$ in the series N samples

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
NiO	—	—	—	—	650	818	921	1381	1381	1052	936	1228	1300	1381	1578
α-Fe$_2$O$_3$	1674	1624	1209	1006	1088	1028	777	989	1065	—	—	—	—	—	—
NiFe$_2$O$_4$	—	—	—	—	694	742	544	633	648	523	578	708	—	—	—

TABLE III

The changes of the surface oxidation ability $\Delta_{O_2^-} = 100(O^* - O)/O\%$ (O^*, O — the oxidation abilities of irradiated and unirradiated surfaces, respectively) after the irradiation of the catalysts of both series (N, H) by neutrons (n) and electrons (e)

	Sample		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
N	n	−9	+16	−37	+6	−11	−17	−21	+21	−13	−37	−22	+7	−22	−23	−30
	e	−26	−10	−21	−56	−67	−21	−16	−22	−34	−4	−35	−9	−31	−4	−66
H	n	−72	−31	+15	−14	−57	−26	−14	+10	−5	−43	−39	−31	+10	0	−1
	e	−69	−71	−39	−42	−76	−38	−64	−37	−45	−38	−36	−25	−24	−22	−42

case of electron irradiation of the series H catalysts. Decrease of the oxidation ability, formerly observed[5] for ferric oxide samples prepared by different methods, is probably connected with the radiation reduction of nickel and iron ions of higher valence (due to the electron capture in Ni^{3+} or Fe^{3+} traps).

Catalytic Properties

Analysis of the hydrogen peroxide decomposition kinetics over the prepared catalysts proved that this reaction proceeds according the (approximately) 1st order kinetics. The catalytic activity of all samples was therefore expressed by the 1st order rate constant that was — due to the non-monotonous dependence between the specific surface area and the composition of samples — normalized to this surface area (the specific catalytic activity k_s). From Fig. 3, curves *1* and *2*, it follows that the specific catalytic activity is a complex non-monotonous function of the composition of both series catalysts. Moreover, the shape of both dependences is qualitatively different and this fact indicates the substantial effect of the method and conditions of the catalysts preparation on their catalytic properties. These dependences can also serve as a proof of the fact that the catalytic activity of these catalysts is determined not only by the area of their surfaces but also by other parameters of the catalytic system.

The oxidation ability of the catalyst surface, *i.e.*, the surface concentration of Ni^{3+} ions in nickel oxide and of the overstoichiometric Fe^{3+} ions in ferric oxide, can be one of these parameters, because in the case of nickel oxide this correlation was already found[3,11]. This assumption is supported by the similarity of the dependences of k_s and O on the composition of the series H catalysts in the region of nickel oxide excess (Fig. 3, curve *2*, and Fig. 2, curve *2*). From the curve *3* of Fig. 3 it turns out that the catalytic activity of the series H samples normalized to their surface oxidation ability is in fact only very little dependent on the catalyst

FIG. 3

Dependence of the reaction rate constant at 40°C normalized to the catalyst surface area k_s ($l\,m^{-2}\,min^{-1}$) and to the catalyst surface oxidation ability k_{O^2-} ($l\,g_{O^2-}^{-1}\,min^{-1}$) on the content of Fe_2O_3 (wt. %) in the catalysts *1* k_s, series N; *2* k_s, series H (○ unirradiated samples, ◑ samples irradiated by electrons, ◒ samples irradiated by neutrons); *3* k_{O^2-}, series H
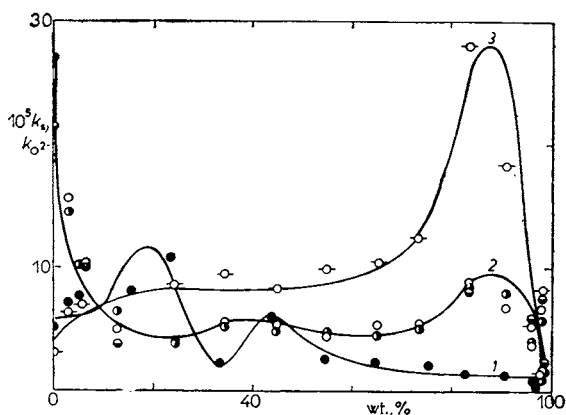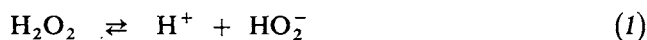
composition over a rather broad region of composition (up to about 65 wt.% of Fe_2O_3). It can be therefore assumed that in this region the catalytic activity of the series H samples is determined by the surface concentration of Ni^{3+} ions. The fact that the curve *3* of Fig. 3 exhibits a maximum in the region of ferric oxide excess excludes the possibility of the catalytic activity of the samples from this composition region being determined by the surface concentration of Fe^{3+} (or Ni^{3+}, respectively) ions. This is in agreement with the previous conclusions[2,5] that the surface concentration of Fe^{2+} ions is probably decisive for the catalytic activity of ferric oxide. The qualitatively different shape of the dependences of k_s and O on the composition of the series N samples (Fig. 3, curve *1*; Fig. 2, curve *1*) eliminates completely the possibility of a direct connection between the catalytic activity of these samples with their surface oxidation abilities. The catalytic activity changes of these samples with their composition cannot be explained even by the existence of the $NiFe_2O_4$ spinel phase that was found in this series of samples in the region of $15-83$ wt.% of Fe_2O_3 (Table II). In analogy with $ZnFe_2O_4$ spinel[2] it would probably cause only a decrease of the ferric oxide activity.

In connection with the previous results that the nickel oxide catalytic activity is probably determined by the surface concentration of the $Ni^{2+} - Ni^{3+}$ ion pairs[3,4] and that the catalytic activity of ferric oxide is probably determined by the surface concentration of centers formed by the $Fe^{2+} - Fe^{3+}$ ion pairs[5,12] the dependence of k_s on the composition of the catalysts under study (Fig. 3, curves *1, 2*) can be qualitatively explained on the basis of bivalent catalytic centers assumed in other two-component oxide catalysts[13].

The concentration of Ni^{3+} ions in nickel oxide, that probably participate on the formation of $Ni^{2+} - Ni^{3+}$ catalytic centers in the series H samples, decreases due to the doping of nickel oxide by ferric oxide. The catalytic activity therefore sharply decreases with the increasing content of ferric oxide in nickel oxide (Fig. 3, curve *2*). In the case of the series N samples probably only a small portion of Ni^{3+} ions form the catalytic centers of the given type. The catalytic activity of pure nickel oxide of the series N is therefore substantially lower than the activity of the respective oxide of the series H and the catalytic activity of the series N samples does not decrease with the increasing content of ferric oxide (Fig. 3, curve *1*). However, in this case also the decrease of the catalyst surface oxidation ability is less conspicuous than in the case of the series H samples (Fig. 2).

In the marginal composition regions the catalytic activity of the samples under study reaches its maximum value in the region of the nickel oxide excess for the series N samples (Fig. 3, curve *1*) while for the series H samples this is observed in the region of the ferric oxide excess (Fig. 3, curve *2*). In agreement with the principle mentioned above, this fact can be explained by the acceptor – donor reaction mechanism[13] that proceeds not only on the catalytic centers of pure oxides ($Ni^{2+} - Ni^{3+}$ or $Fe^{2+} - Fe^{3+}$, respectively) but also on the mixed centers formed by the $Fe^{3+} - Ni^{2+}$

or $Fe^{2+} - Ni^{3+}$ ion pairs, *e.g.*, according to the following mechanism:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad (1)$$

$$HO_2^- \rightarrow HO_2 + e^- \qquad (2)$$

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

$$Ni^{2+} \rightarrow Ni^{3+} + e^- \qquad (4)$$

$$H^+ + e^- \rightarrow H. \qquad (5)$$

The concentration of these centers increases with the increasing content of the minor component of the catalyst up to certain value and then, probably due to the observed decreasing dispersion of this component, the concentration of bivalent centers decreases again. This results in a maximum catalytic activity at a certain composition of the two-component catalyst.

In the series N catalysts the specific catalytic activity has also a local maximum in the region of approximately equal concentrations of both components (Fig. 3, curve *1*). It seems possible that this maximum is connected with the fact that at this composition of the catalyst the area of the system interface, where the interaction of both components is most intense, reaches also its maximum.

The observed non-monotonous character of the specific catalytic activity dependence on the catalyst composition was reported[1] also for most two-component oxide catalysts studied up to now.

Assuming the validity of the discussed explanation of these dependences it can be concluded that the catalytic centers of samples with different composition are not different from the point of view of their energy because the value of the apparent activation energy of the testing reaction is practically independent of the catalyst composition and it reaches the values of about 70 kJ mol^{-1}.

The pre-irradiation of the series H catalysts by electrons or neutrons has no effect on the dependence of the specific catalytic activity on the catalyst composition (Fig. 3, curve *2*). At the same time even the specific catalytic activity of individual samples remains practically the same as before irradiation (the observed average changes amount to about 4%). Only in the case of pure nickel oxide irradiation by electrons a 40% increase of its activity was observed. Because the irradiation of this oxide decreases its surface oxidation ability (Table III), *i.e.*, it diminishes the surface concentration of Ni^{3+} ions, it is possible that two antagonistic processes proceed in the sample during the irradiation. The first one, *i.e.*, the radiation reduction of Ni^{3+} ions that do not form the catalytic centers for the reaction, decreases the oxidation ability, and the second one, *i.e.*, the ionization of Ni^{2+} ions followed by the

formation of $Ni^{2+} - Ni^{3+}$ centers leads to the increase of the oxide catalytic activity. In the mixed oxide samples the second process is suppressed by the presence of ferric oxide so that the catalytic activity of mixed oxides is not affected by irradiation. Moreover, particularly in samples with ferric oxide excess, the substantial lability of the radiation-catalytic effect that was observed[5] in the case of beta irradiation of pure ferric oxide, can play an important role and can be the reason of the apparent insensitivity of the catalysts under study towards the ionizing radiation.

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