

EFFECT OF THE IONIZING RADIATION ON THE KINETICS OF THE REDUCTION BY HYDROGEN OF NiO-Fe₂O₃ MIXED OXIDES OF VARIOUS GENESIS

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The kinetics of the reduction by hydrogen of two series of NiO-Fe₂O₃ mixed oxides of different composition was studied in the temperature range 320–410°C using thermogravimetry. Both series were prepared from different precursors that were thermally decomposed at different temperatures. The oxidizing ability of the surface (the content of chemisorbed oxygen) is the only parameter from all physico-chemical properties studied that changed significantly during the pre-irradiation of the system by ⁶⁰Co gamma radiation (dose 505 kGy), by fast neutrons from the ²⁵²Cf source (dose $D_n = 110$ Gy) and by accelerated electrons (3 MeV, dose 500 kGy). A positive radiation effect was observed in the first case while the irradiation by neutrons and electrons resulted in a negative effect. The magnitude of the effect depends on the composition and genesis of the system and it decreases in the sequence γ, e^-, n . The radiation induced changes in the reduction kinetics of mixed oxides change their magnitude and sign in dependence on the composition and genesis. Not only the increase by an order of magnitude of the rate of the initial phase of the reduction which was ascribed to the partial reduction of hematite to magnetite but also the acceleration of the second step (reduction of Fe₃O₄ to Fe) was observed after the exposure to photons or fast neutrons. The radiation changes induced by electrons are limited only to the surface of the irradiated solid and they affect only the first step of the reduction. The maximum positive effect was observed in the region of high excess of hematite and its magnitude decreases with the increasing content of nickel oxide. The radiation effects decrease with the increasing temperature of the reduction and at about 400°C the effect of irradiation is completely annealed.

In our previous paper¹ we have studied the effect of the catalyst genesis and of some of its physico-chemical properties on the kinetics of the reduction by hydrogen of two series of NiO-Fe₂O₃ mixed oxides of various composition. Depending on the genesis, preparation conditions, and composition the character and degree of mutual interaction of the individual components is significantly varied and this fact has also an effect on the reactivity of the oxide system during its reduction by the gas. The reduction of oxides and of multicomponent oxide systems is – along with the thermal decomposition of certain salts of heavy metals – one of the most important methods of the metal catalyst preparation. The kinetics of these topochemical reactions can be altered by the pre-irradiation of the solid phase by various types

of the ionizing radiation^{2,3}. The radiation modification of reactivity under otherwise identical conditions (type of radiation, absorbed dose) can result either in a positive effect (increase of the reaction rate) or in a negative one, as it had been proved in the case of the reduction by hydrogen of certain pure metal oxides of various "origin"^{4,5}. The aim of this study was to investigate the effect of several types of ionizing radiation on the properties of both genetically different series of two-component oxides NiO-Fe₂O₃ and on the kinetics of their reduction by hydrogen.

EXPERIMENTAL

Two series of NiO-Fe₂O₃ mixed oxides with various content of both components in the range from 0 to 100% were prepared by the procedures and under the conditions described in more detail elsewhere¹ (the series A by the thermal decomposition of mixed crystalline nitrates of both metals for 4 hours at 600°C and the series B by the calcination of coprecipitated hydroxides for 4 hours at 450°C in the presence of air). In both cases the grains of the size from 0.25 to 0.025 mm were separated by sieving and used in the experiments.

The content of nickel in the samples was determined electroanalytically, the content of iron by iodometry. The specific surfaces were measured by the selective adsorption of nitrogen at low temperatures, the morphology of the mixed oxides and of the reduction products was determined by the scanning electron microscope JEOL JSM-50. The microstructure of samples of both series and of the reaction intermediates were studied by the Debye-Scherrer method using the apparatus TUR M 62 (Zeiss) with a goniometer (Co anode). The average size of the coherent regions of the phases present in the samples was calculated from the broadening of the diffraction lines.

The samples were irradiated by ⁶⁰Co gamma radiation in the presence of air by doses ranging from 900 Gy to 1 640 kGy, by fast neutrons of the energy of 2.1 MeV from the ²⁵²Cf source (Radiochemical Centre, Amersham) by a dose of 110 Gy and by accelerated electrons of the average energy of 3 MeV from the high-frequency linear accelerator by the dose of 500 kGy. The content of ionogenic surface oxygen (the oxidizing ability of the surface) of the initial and irradiated samples was determined by iodometry⁶. The reduction kinetics was studied by thermogravimetry¹ in the temperature range 320–410°C for both series of the initial and radiation-modified mixed oxides.

RESULTS AND DISCUSSION

Physico-chemical Properties of the Mixed Oxides

From the results of the chemical analysis (Table I), microstructure X-ray diffraction, and from the DTA and infrared spectroscopy of both series of mixed oxides it follows that the system A, prepared by the calcination of the precursor at a higher temperature, is composed of the independent phases of NiO, hematite (α -Fe₂O₃), and spinel NiFe₂O₄, in which almost all nickel oxide is bound in the region of the stoichiometric ratio of both components¹. The samples of the hydroxide origin (series B) contain the phases of both oxides and water that is bound in the trace

admixtures of goethite (α -FeOOH). The effect of genesis and of the preparation conditions is demonstrated by the nonmonotonous and in both series different dependences of the specific surface area on the composition that can be correlated with the changes of the microcrystallites dispersion in the oxide phases and with the morphological changes of samples of different composition (the form and dispersion of grains and their aggregations, porosity, and structure of the surface).

The significantly non-monotonous dependence of the oxidizing ability of the surface on the composition¹ (of the surface concentration of the higher-valent ions of metals — Ni³⁺, Fe³⁺, the charge of which is counterbalanced by the chemisorbed oxygen) indicates a higher degree of the mutual interaction (epitaxial contact) of both components in the system A that is governed mainly by the temperature of calcination. The time dependence of the dynamical equilibrium between the surface and gas-phase oxygen during the long-term contact of samples with air results in the change of the absolute value of the oxidizing ability of the surface while the original different shape of the dependence of this quantity on the composition of both series of samples remains unchanged. This fact indicates the high stability of the degree and nature of the mutual interaction of both components of the mixed system of the

TABLE I

Notation and composition of mixed oxides NiO-Fe₂O₃ of the series A and B

Sample	Series A wt. %			Series B wt. %		
	Fe ₂ O ₃	NiO	Fe ₂ O ₃ + NiO	Fe ₂ O ₃	NiO	Fe ₂ O ₃ + NiO
1	99.45	0.00	99.45	98.93	0.00	98.93
2	97.84	1.31	99.15	98.34	1.18	99.52
3	95.94	3.23	99.17	96.23	2.43	98.66
4	90.63	8.54	99.17	90.86	8.13	98.99
5	82.93	16.12	99.06	83.05	15.87	98.92
6	75.17	23.72	98.89	73.49	24.68	98.17
7	64.67	34.02	98.69	64.76	34.11	98.87
8	54.67	45.13	99.80	54.71	43.85	98.56
9	44.05	54.95	99.00	44.96	53.11	98.07
10	33.85	65.17	99.02	34.41	64.19	98.60
11	22.80	76.78	99.58	23.89	75.56	99.45
12	15.40	83.95	99.35	13.22	85.98	99.20
13	4.92	94.38	99.30	5.40	93.27	98.67
14	2.75	96.76	99.51	2.82	95.63	98.45
15	0.00	99.54	99.54	0.00	99.30	99.30

given genesis. In agreement with the previous results^{7,8} the various types of the ionizing radiation in the dose range used cause no changes of the physico-chemical parameters of the mixed oxides except for the oxidizing ability of the surface.

The comparison of the effect of various types of radiation on the changes of the ionogenic oxygen content is expressed in Table II by the quantity Δ_x , defined by the formula

$$\Delta_x(\%) = (X^+ - X) \cdot 100/X,$$

where X^+ is the wt. % of oxygen O_2^- in the irradiated samples and X is the same quantity for the non-irradiated original samples. The data given in Table II demonstrate the positive effect of pre-irradiation by gamma rays with a dose of 505 kGy that results in the increase of the surface oxidizing ability. The positive effect in the series B oxides, higher by an order of magnitude, is evidently connected with the non-stoichiometry of the original non-irradiated samples¹.

Due to the high stoichiometry of the initial system and in the case of mixed oxides also due to the stabilizing effect of the spinel structure, several samples from the series A (samples 1A–4A) showed a zero effect and the values of Δ_x were within

TABLE II
Values of Δ_x (%) for the samples of the series A and B and for various types of ionizing radiations

Sample	Series A			Series B		
	Gamma 505 kGy	Neutrons 110 Gy	Electrons 500 kGy	Gamma 505 kGy	Neutrons 110 Gy	Electrons 500 kGy
1	+ 5	- 9	-26	+ 96	-72	-69
2	+ 17	+16	-10	+167	-31	-71
3	+ 8	-37	-21	+180	+15	-39
4	+ 8	+ 6	-56	+214	-14	-42
5	+ 39	-11	-67	+141	-57	-76
6	+ 15	-17	-21	+ 98	-26	-38
7	+ 52	-21	-16	+138	-14	-64
8	+ 31	+21	-22	+159	+10	-37
9	+ 64	-13	-34	+200	- 5	-45
10	+ 11	-37	- 4	+302	-43	-38
11	+ 43	-22	-35	+214	-39	-36
12	+ 29	+ 7	- 9	+301	-31	-25
13	+ 18	-22	-31	+105	+10	-24
14	+133	-23	- 4	+ 80	0	-22
15	+ 13	-30	-66	+ 46	- 1	-42

the limits of the experimental error ($\pm 15\%$). The dependence of Δ_x on the oxide composition is evidently non-monotonous for both series and it has maxima in rather narrow composition limits. The irradiation of samples either in the presence of air or in evacuated ampoules ($1.33 \cdot 10^{-4}$ Pa) shows the same increase of the surface oxidizing ability within the limits of experimental errors so that no adsorption of oxygen from the atmosphere can be assumed. The radiation oxidation is caused only by the shift of the equilibrium between various forms of surface oxygen. Electrons generated by ionization ($\text{Me}^{2+} \rightarrow \text{Me}^{3+} + e^-$) are trapped by a weakly bound neutral form of oxygen which yields an increase of the concentration of the ionogenic forms ($\text{O}_{2,\text{ads}}^0 + 2e^- \rightarrow 2\text{O}_{\text{ads}}^-$). From the dependence of Δ_x on the gamma dose (Fig. 1) it follows that the minimum threshold dose necessary for an observable effect depends not only on the composition but also on the genesis of oxides. The effect of recombination processes decreasing the final effect is observed in the region of high doses (curve 2).

Similarly as in other oxide systems containing nickel oxide⁹ the indirect interaction of neutrons with the electron orbitals of the solid phase atoms results — at the doses used — in a zero effect or negative effect that is more remarkable in the series B mixed oxides (Table II). The irradiation of certain samples by fast neutrons yields probably a partial destruction of the chemisorbed oxygen centers (the polishing effect) or, eventually, the radiation reduction of metal ions of higher valence states. Also in the irradiation of the system by accelerated electrons with a dose of 500 kGy the radiation reduction due to the direct interaction with surface ions in the higher valence state (Ni^{3+} , Fe^{3+}) and resulting in a substantial decrease of the surface oxidizing ability, can be assumed.

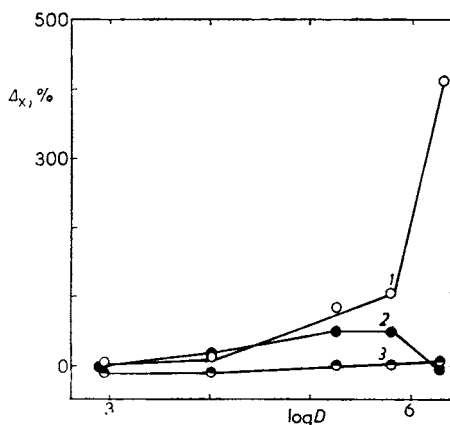


FIG. 1

Dependence of Δ_x (%) on the γ radiation dose. Sample: 1 1 B; 2 15 B; 3 1 A

Kinetics of the Reduction of Irradiated Mixed Oxides by Hydrogen

From the experimentally found weight decrease and also from the X-ray diffraction studies of intermediates and final products of the reduction of mixed oxides of both series it may be concluded that under the given conditions the system is completely reduced to the respective metals. The reduction of hematite proceeds in two steps (with magnetite as an intermediate); the formation of wüstite was not proved. The differences in the genesis of both series of mixed oxides are revealed also in the radiation modification of their reactivity in the reduction process (Fig. 2). The effect of gamma radiation on the reduction kinetics is in this figure expressed by the value of Δ_k , defined analogously as Δ_x , where instead of X and X^+ the reduction rate constants k and k^+ of the original¹ and pre-irradiated samples reduced at the given temperature, appear.

Reduction of the non-stoichiometric nickel oxide, the superstoichiometry of which is caused practically only by the strongly bound ionogenic form of oxygen formed by irradiation (sample 15B) proceeds by the same or lower rate in comparison with the unirradiated sample ($\Delta_k \cong 0$). In this case the slow donor chemisorption of hydrogen is the rate-determining step. This negative effect of radiation is counteracted by the competing positive effect, *i.e.*, by the formation of non-equilibrium charge defects or, eventually, point defects, accelerating the transport of electrons, the crystallochemical transformation of the reduced oxides and, in many cases, also the thermal decomposition of various solids³. If the both competing processes are in equilibrium the reduction rate is practically not influenced by irradiation (the region of NiO excess in the series B, Fig. 2, curve 1). In the same composition region of the series A, formed by nickel oxide of higher stoichiometry, the positive radiation effect dominates and the irradiated samples are reduced by a higher rate

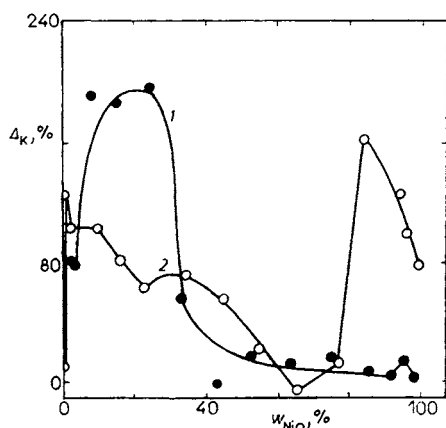


FIG. 2

Dependence of Δ_k (%) on the composition for the reduction of samples of both series, pre-irradiated by γ radiation, dose 505 kGy. 1 series B, T_r 350°C; 2 series A, T_r 320°C

than the original oxides and also faster than the oxides of the series B, including also pure nickel oxide (curve 2). With the increasing concentration of the other component the probability of the stabilization of formed defects on the present biographic lattice defects and on the boundaries of interacting phases increases so that the accelerating effect of irradiation reaches its maximum, the position of which depends on the degree of the epitaxial contact of both components. The subsequent steep decrease of the radiation effect is connected with the changes of the physico-chemical parameters of the system (the specific surface area and the dispersion of microcrystallites) and therefore also of the character of the interaction. The low value of the apparent activation energy of reduction indicates the effect of inner diffusion. With the increasing content of ferric oxide, nickel oxide is transformed into the spinel phase¹ and the magnitude of the positive radiation effect increases monotonously. The radiation activation of the spinel phase is probably caused by its partial radiolysis and by the catalytic effect of the produced metallic nickel, while in the unirradiated samples nickel oxide bound into spinel is not reduced under the given conditions. The reduction rate of pure hematite (sample 1A) remains therefore practically unaltered after irradiation.

The radiolytic decomposition of the constitutional water, catalyzed by the solid phase present¹⁰, and the activation of the surface yields a substantial positive effect, resulting in a 2–3 fold increase of the reduction rate of the samples of hydroxide origin with the excess of ferric oxide (10–25 wt. % of NiO, curve 1), *i.e.*, in the region in which the highest content of chemically bound water found in the unirradiated oxides was proved by infrared spectroscopy and by DTA¹. The irradiated pure hematite of the series B is completely reduced at 320°C to metallic iron, while in the unirradiated sample it is reduced only to the magnetite phase. At 350°C the radiation modified hematite is also reduced under otherwise identical conditions by a higher rate than the original sample.

Due to the two-step character of hematite reduction the rate constants k_1 of the initial stage of reduction, characterizing the partial reduction $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ (transformation degree $\alpha = 0-0.1$, *ref.*¹) was calculated for the samples of both series with the excess of ferric oxide. From Table III, where the effect of various types of ionizing radiation is expressed by means of the values of Δ_{k_1} , it turns out that the initial stage of reduction is also accelerated by pre-irradiation with gamma rays. In the series of the nitrate origin the maximum positive effect is found for the samples 4A and 5A, in which the (individual) spinel structure was evidently proved. This structure is destabilized by irradiation. The first reduction step of pure hematite is also accelerated (sample 1A). In the series B the radiation effect decreases monotonously with the increasing content of nickel oxide and for the samples 4B and 5B the values of Δ_{k_1} are already within the limits of errors (compensation of the positive and negative effects of pre-irradiation). Table III demonstrates also the decrease of the rate changes of the first reduction step with the increasing tempera-

ture, while the overall character of the dependence Δ_{k_1} vs composition remains unchanged. At the temperatures of 380–410°C the radiation effects are already undetectable due to the relatively fast recovering processes. In all cases the higher reduction rate after gamma irradiation is accompanied by the shortening of the induction period and by the decrease of the apparent activation energy in comparison with the values for the original non-irradiated sample.

The gamma dose dependence of the radiation induced effect is usually non-monotonous (Fig. 3) with maxima, the position of which depends on the genesis and composition of the sample. Fig. 3 indicates the higher sensitivity towards gamma radiation of the system prepared by calcination at a lower temperature (series B), in which the radiolysis of thermally non-decomposed admixtures (predominantly of water bound in the traces of present goethite) leads to a remarkable increase of the reduction rate, namely in the region of hematite excess. In agreement with our previous results⁸ the effect of applied gamma dose on the kinetics of pure nickel oxide reduction can be very well correlated with the dose dependence of the content of ionogenic forms of oxygen. Radiation induced changes of this parameter and also of the kinetics of nickel oxide reduction depend on the genesis of samples and on the conditions of their preparation.

From Table III it also follows that the initial stage of reduction is positively influenced also by the fast-neutron pre-irradiation. The interaction of neutrons

TABLE III
Values of Δ_{k_1} (%) for various types of ionizing radiation and for different reduction temperatures

Sample	Gamma 505 kGy		Fast neutrons 110 Gy		Electrons 500 kGy
	320°C	350°C	320°C	350°C	320°C
1 A	+ 62	+11	+108	+46	+ 2
2 A	+ 53	+13	+ 99	+48	+ 14
3 A	+ 47	+ 1	+ 46	+41	+ 24
4 A	+115	+50	+ 19	-11	+ 17
5 A	+ 77	+17	+ 15	+ 4	+ 10
6 A	+ 27	+ 5	+ 3	- 7	+ 18
7 A	+ 31	- 3	+ 5	- 9	+ 11
1 B	+100	+34	+140	+39	+131
2 B	+ 86	+18	+ 39	+ 2	+ 38
3 B	+ 46	- 2	+ 19	+ 2	+ 16
4 B	- 8	- 4	+ 1	- 6	- 9
5 B	- 9	- 3	+ 19	+16	+ 14

with nuclei (scattering interaction) results in the formation of point defects, increasing the reactivity of the solid. Recoil atoms induce a high density of ionizations and excitations so that the radiation effect is measurable at doses by an order of magnitude lower than for gamma radiation. The positive effect decreases with the increasing content of nickel oxide and — similarly as in the case of gamma radiation — with the temperature of reduction. In the intermediate and final stages of reduction, corresponding to the transformation of magnetite into iron, the radiation effect is reduced by half in comparison with the initial stage and it can be observed practically only at the lowest temperature of reduction. The character of the dependence of Δ_k on the composition is similar as in the case of gamma radiation (Fig. 2).

From Table III it can be also concluded that the relatively lowest positive radiation effect is observed after pre-irradiation of the system with electrons, even with doses comparable with those used in gamma irradiation. In spite of the basically identical mechanism of the radiation energy absorption in both cases, differences in the effect (*i.e.*, in the catalytic activity) were found for the practically equal doses even in the heterogeneous oxide catalysts modified by the two types of radiation¹¹. Along with the different values of the average energies of accelerated electrons and of the secondary Compton- and photoelectrons in the irradiation by cobalt gamma rays also the different spatial distribution of the radiation energy absorption can have an effect on the final radiation effects. It can be assumed that the distribution of the primary radiation changes induced in the bulk of the irradiated material by gamma radiation will be more homogeneous whereas the accelerated electrons will deposit a higher portion of their energy in the near-surface layers where a relatively higher concentration of charge defects will be formed. This assumption can be corroborated by the fact that in many reactions proceeding on the surface of solids the radiation catalytic effect observed after the irradiation of the catalyst by electrons

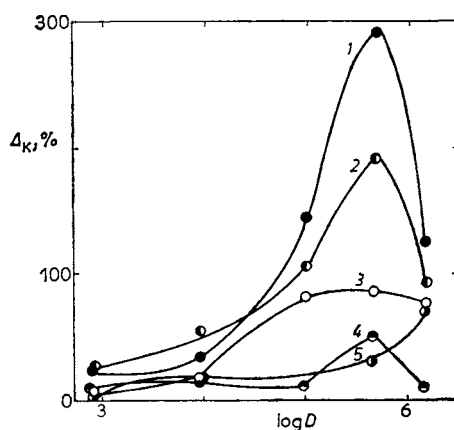


FIG. 3

Dependence of Δ_k (%) on the γ radiation dose for certain samples from both series. Samples: 1 1 B, T_r 350°C; 2 5 B, T_r 320°C; 3 12 A, T_r 320°C; 4 5 A, T_r 320°C; 5 1 A, T_r 320°C

was found to be higher than after gamma irradiation¹². In the topochemical solid-gas reaction under study a substantial positive effect of gamma radiation was proved both for the initial stage (Table III) and for the subsequent stages of reduction that proceed already in the subsurface layers (Fig. 2). On the other hand the higher concentration of surface reaction centers formed by electrons manifests itself only in a slight rate increase of the initial stage of reduction (Table III). The values of A_k characterizing the effect of accelerated electrons on the rate of the intermediate and final stages of reduction lie already within the limits of experimental errors, even for the lowest reduction temperatures.

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