

THE EFFECT OF ORIGIN AND PHYSICO-CHEMICAL PROPERTIES ON THE KINETICS OF REDUCTION OF MIXED NiO-Fe₂O₃ OXIDES WITH HYDROGEN

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We investigated the effect of origin and some physicochemical parameters on the kinetics of reduction with hydrogen of two series of mixed NiO-Fe₂O₃ oxides differing by their composition, the character of their precursors (mixed crystalline nitrates and coprecipitated hydroxides) and their decomposition temperature. This effect manifested itself by different magnitudes of specific surfaces of the mixed oxides and coherent regions of present phases as well as by different oxidizing abilities of the surface and differences in morphology and phase composition of corresponding samples in both series investigated. Nonlinear or nonmonotonous composition dependences of physico-chemical parameters investigated point to a mutual influence of individual components, which is also a function of the system origin and which modifies its reactivity during its reduction with hydrogen. The kinetics of the reduction was studied thermogravimetrically at 320–410°C. The reduction of oxides of the hydroxide origin is catalytically accelerated by primarily reduced nickel, whereas in corresponding samples of the nitrate series, the total NiO is bound to the spinel phase and the reduction is delayed. Experimental IR spectra, the effect of preliminary annealing and DTA of the mixed oxides point to an inhibitory effect of water, which is constitutionally bound in trace admixtures of the goethite phase, on the kinetics of reduction of samples in the hydroxide series.

In connection with the recent development of nonempirical methods of preparation and production of catalysts, still more attention is being paid to the research of all partial processes leading from precursors to a final form of catalysts of different types. The reduction of metal oxides or of multicomponent oxide systems with hydrogen often represents the last stage of the preparation or activation of catalysts based on metals, alloys or metals on an oxide carrier.

The effect of origin and conditions of preparation, which modify substantially not only the reactivity of oxides during their reduction, but also properties of products of the reduction – metal catalysts – has been so far most thoroughly investigated in the case of two oxides, namely nickel¹ and ferric² ones, which differ from each other by the mechanism of reduction. On the other hand, insufficient attention has been paid to multicomponent oxide systems, whose behaviour during the reduction also depends on the above given factors³. In our work we studied some physico-chemical properties in two series of mixed NiO-Fe₂O₃ oxides of different compositions prepared from different precursors and we tried to find correlations between these

properties affected by different origin and by the kinetics of the reduction of the system with hydrogen.

EXPERIMENTAL

Mixed oxides of different composition in series *A* were prepared by annealing of mixed nitrates. Aqueous 2 mol dm⁻³ solutions of AR grade Ni(NO₃)₂·6 H₂O and Fe(NO₃)₃·9 H₂O were filtrated and then mixed together in required ratios. The product was evaporated to dryness and then annealed in an electric furnace in air for 4 h at 600°C, ground in an agate mortar and finally the mesh fraction of 0.25–0.025 mm was separated.

The hydroxide series samples (series *B*) were prepared from the same original nitrate solutions of both metals mixed together in the same ratio and then further precipitated during an intensive agitation with a 10% stoichiometrical excess of aqueous 6 mol dm⁻³ solution of KOH. After repeated decantation with hot distilled water at 80°C, washing and filtration, the precipitate was dried for 4 h at 140°C. Since the temperature of the thermal decomposition of ferric and nickel hydroxides is not sharply defined, conditions of their quantitative decomposition — 4 h at 450°C — were determined from a preliminary investigation of samples of the precursor by the method of differential enthalpic analysis (DSC). Calcination products were also ground and the same mesh fraction was selected as in the case of series *A*.

The nickel concentration was determined electroanalytically whereas the iron concentration was found iodometrically. The microstructure of mixed oxides in both series was studied by the Debye-Scherrer method on a TUR M 62 apparatus (Zeiss) with a goniometer (Co anode). The magnitude of coherent regions of present phases was calculated from the broadening of diffraction lines. Specific surfaces were measured by selective adsorption of nitrogen at low temperatures with an error of ±5% and the morphology of mixed oxides and reduction products were investigated by an JSM-50 Jeol electron scanning microscope. The content of chemisorbed oxygen, resp. the oxidizing ability of surface of samples from both series was determined iodometrically⁴ with an error of ±15%. The reduction proceeded at 320–410°C at exactly same conditions for both series compared. The reduction kinetics was investigated thermogravimetrically⁵ at a hydrogen flow rate of 56 ml/min and the amount of the sample of 50 mg. At these conditions, the time course and the rate of the sample reduction at arbitrary composition are independent of the flow rate of the reducing gas.

RESULTS AND DISCUSSION

Physico-chemical Properties of Mixed Oxides from Both Series

It follows from results of the chemical analysis (Table I) that the thermal decomposition of precursors used leads in both cases to the formation of a two-component NiO-Fe₂O₃ oxide system. Due to a lower annealing temperature, samples from series *B* exhibit a higher deviation from the stoichiometry (0.5–2.0%) expressed by the difference from 100 wt.%. An orientation study of IR spectra of selected samples from this series and DTA showed that this deviation is brought about above all by constitutional water bound to the goethite phase, whose transformation temperature $\alpha\text{-FeOOH} \xrightarrow{-\text{H}_2\text{O}} \alpha\text{-Fe}_2\text{O}_3$ depends on origin and magnitude of crystals and lies in the range 190–380°C (ref.⁶). With our samples, this transformation depended on

composition and it proceeded at 200–330°C. The microstructural analysis also confirmed the presence of individual phases of both oxides, NiO and α -Fe₂O₃ (haematite). Mixed oxides from series *A* prepared by annealing at higher temperatures contain also an NiFe₂O₄ spinel phase which, in the region of the stoichiometric ratio of both components, binds almost all NiO.

In comparison with oxides from series *B*, the effect of higher annealing temperatures of the precursor, when system *A* passes during its preparation through the stage of a homogeneous melt, manifests itself by decreasing magnitude of specific surfaces of final oxides (Table I), lower dispersity of microcrystallites of present oxide phases (Fig. 1 and Table II) and a different character of the composition dependence of these parameters. Specific surfaces of samples from series *B* lie in the range 13 – 65 m² g⁻¹, whereas in series *A* they are in the range 4–16 m² g⁻¹. The minimal values of the specific surface correspond in both cases to the pure components, whereas the maxima are achieved in both series at different ratios of both components. The magnitudes of specific surfaces correlate well with the dispersity of microcrystallites of both components, especially in the hydroxide series. The initial sharp decrease in the magnitude of NiO microcrystallites (Fig. 1) corresponds to a significant in-

TABLE I

The notation, composition (wt.%) and magnitudes of specific surfaces (S , m²g⁻¹) of mixed NiO–Fe₂O₃ oxides

Sample	Series <i>A</i>				Series <i>B</i>			
	Fe ₂ O ₃	NiO	Fe ₂ O ₃ + NiO	S	Fe ₂ O ₃	NiO	Fe ₂ O ₃ + NiO	S
1	99.45	0.00	99.45	4.2	98.93	0.00	98.93	21.1
2	97.84	1.31	99.15	4.1	98.34	1.18	99.52	23.3
3	95.94	3.23	99.17	4.1	96.23	2.43	98.66	33.2
4	90.63	8.54	99.17	15.9	90.86	8.13	98.99	50.7
5	82.93	16.12	99.06	12.6	83.05	15.87	98.92	60.6
6	75.17	23.72	98.89	10.0	73.49	24.68	98.17	55.8
7	64.67	34.02	98.69	6.6	64.76	34.11	98.87	56.8
8	54.67	45.13	99.80	5.7	54.71	43.85	98.56	65.6
9	44.05	54.95	99.00	5.5	44.96	53.11	98.07	53.2
10	33.85	65.17	99.02	10.7	34.41	64.19	98.60	50.6
11	22.80	76.78	99.58	12.0	23.89	75.56	99.45	57.1
12	15.40	83.95	99.35	7.8	13.22	85.98	99.20	44.9
13	4.92	94.38	99.30	8.0	5.40	93.27	98.67	26.8
14	2.75	96.75	99.51	5.5	2.82	95.63	98.45	18.6
15	0.00	99.54	99.54	4.0	0.00	99.30	99.30	13.6

TABLE II
The magnitude of coherent regions (L , nm) of individual phases of mixed oxides from series A

Sample	NiO	α -Fe ₂ O ₃	NiFe ₂ O ₄
1	—	167.4	—
2	—	162.4	—
3	—	120.9	—
4	—	100.6	—
5	65.0	108.8	69.4
6	81.8	102.8	74.2
7	92.1	77.7	54.4
8	138.1	98.9	63.3
9	138.1	106.5	64.8
10	105.2	—	52.3
11	93.6	—	57.8
12	122.8	—	70.8
13	130.0	—	—
14	138.1	—	—
15	157.8	—	—

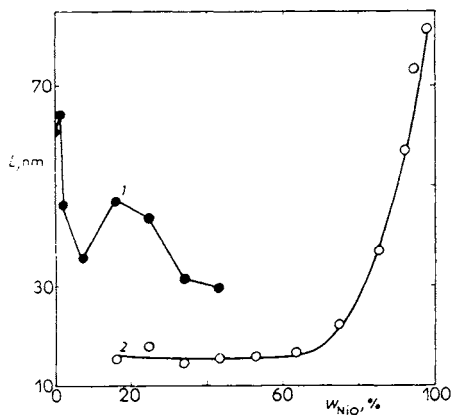


FIG. 1

The composition dependence of the magnitude of coherent regions L , (nm) in NiO and α -Fe₂O₃ for samples from series B. 1 α -Fe₂O₃, 2 NiO

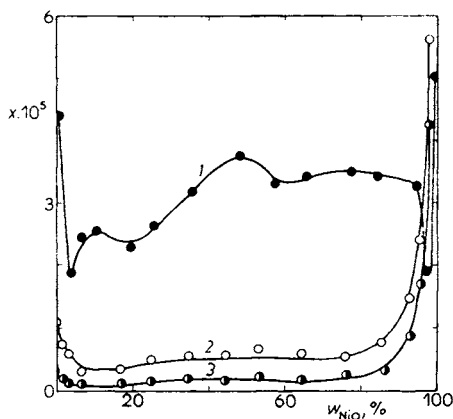


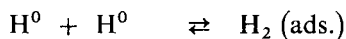
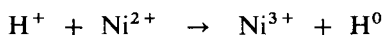
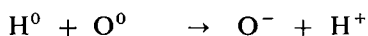
FIG. 2

The composition dependence of the specific oxidizing ability of the surface of mixed oxides, X ($\text{g O}^{2-} \text{m}^{-2}$). 1 ser. A, 2 ser. B, 3 ser. B stored for 18 months after the preparation

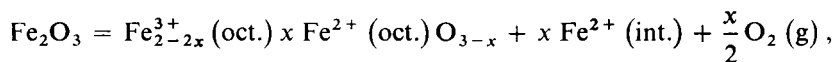
crease in specific surfaces (Table I). In the concentration region of 15–70 wt.% NiO, no substantial changes of both quantities occur. Similarly, the dispersity of haematite microcrystallites increases with increasing concentration of the second component when the magnitude of the specific surface also increases.

It was also shown by investigating the morphology (the shape and dispersity of grains and their agglomerates, roughness of the surface) of samples of the same composition from both series compared that the magnitude of the specific surface of mixed oxides from series *A* is above all determined by the geometric shape and the particle surface resulting from the manner of their preparation, whereas in oxides from series *B* also the structure and surface of pores become relevant.

Fig. 2 illustrates the composition dependence of the specific oxidizing ability of the surface of mixed oxides. This quantity represents the concentration of metal cations with higher valence (Ni^{3+} , Fe^{3+}), whose charge is compensated by ionogenic (chemisorbed) oxygen, related to unit surface. The maximum excess of oxygen over its stoichiometric ratio was observed in pure NiO in agreement with its *p*-semiconductor character. Besides strongly bonded forms which can be detected by methods employed in our work, the main part of this excess oxygen is formed by a weakly bonded form. A 50% increase in the oxidizing ability of the surface observed in a sample of pure NiO placed into flowing hydrogen at room temperature, when not even the surface reduction can be assumed, can be explained by an interaction of hydrogen with this latter form of oxygen. This interaction leads to an increase in the Ni^{3+} concentration compensated by ionogenic oxygen and it can be represented by the following elementary processes:

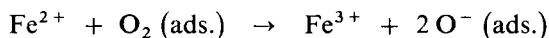


The non-zero content of ionogenic oxygen in *n*-semiconductive ferric oxide with the ratio $\text{O}/\text{Fe} < 1.5$ is compensated by decreased concentration of Fe^{2+} ions in the surface layer, that means by the surfacial nonstoichiometry with respect to the bulk concentration of oxygen. It follows from the defective haematite structure⁷, which can be illustrated by the equation



that interstitial positions of haematite contain a certain amount of Fe^{2+} ions, whereas all Fe^{3+} ions occupy only stable octahedral holes. Fe^{2+} ions in the surface layer can be oxidized by adsorbed oxygen to form $\text{Fe}^{3+} - \text{O}_2^-$ pairs. Fe^{3+} ions created in this

manner differ from octahedral ones by a lower stability and they react selectively during their determination. The actually four times larger specific oxidizing ability of pure Fe₂O₃ from series *A* (Fig. 2) can be related to a higher annealing temperature in this series, which leads to an increase in the concentration of Fe²⁺ ions, which serve on the surface of Fe₂O₃ as donor centres for the dissociative adsorption of oxygen:



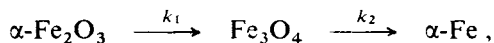
In the region of a high excess of NiO, a small addition of ferric oxide leads to a sharp decrease in the oxidizing ability of the surface in accordance with the theory of homogeneous semiconductors. An admixture of higher valency ions (Fe³⁺) into NiO brings about a decrease in the concentration of minority Ni³⁺ ions and, consequently, also in the content of ionogenic forms of oxygen. The dynamic equilibrium between the adsorbed and air oxygen, or among different forms of already adsorbed oxygen, changes with time as it follows from a comparison between curves 2 and 3 in Fig. 2 illustrating the concentration dependence of the normalized content of chemisorbed oxygen in oxides from series *B*. The first case (curve 2) corresponds to freshly prepared samples, the second case (curve 3) to the same oxides which were kept for 18 months after the finished preparation in contact with atmosphere. The fact that the course of this dependence remained unchanged may serve as a proof of the degree and the character of the mutual interaction between both components of the mixed system.

In contrast to series *B*, a higher degree of the interaction and the epitaxial contact in oxides from series *A* caused by their origin and a higher annealing temperature manifests itself by a significant non-monotonic dependence of the normalized oxidizing ability of the surface (curve 1). Similarly to the first case, no changes in the character of this dependence have been observed after a prolonged exposure of samples to the atmosphere, only the absolute amount of ionogenic oxygen has changed. After an initial sharp decrease in the oxidizing ability of the surface with a small addition of the second component in both boundary composition regions, this quantity increases up to a maximum which is achieved at approximately same concentrations of both components. This behaviour is probably due to an increase in the concentration of mixed catalytic centres (ionic pairs Fe²⁺-Ni²⁺), where a dissociative adsorption of oxygen occurs⁸ during which metal ions are oxidized into their higher valency states.

Kinetics of the Reduction of Mixed Oxides

Values of mass losses found experimentally and results of the microstructural analysis of reaction products from both series confirmed the assumption stating that at the given conditions both oxides reduce totally to the corresponding metals. From the character of kinetic curves of the reduction ($\alpha = f(t)$) of samples with the prevailing

content of Fe_2O_3 and from the phase analysis of intermediate products, the following two-stage course of the haematite reduction may be deduced



and, simultaneously, no individual wuestite phase has been observed in accordance with results of other authors⁹. Taking into account a different mechanism of the expansion of the reaction from the surface inside the grain during the one-stage reduction $\text{NiO} \rightarrow \text{Ni}$ in comparison with the multistage haematite reduction and considering different rate-determining steps of the reduction of both oxides¹⁰, the kinetics of the reduction of the mixed system was characterized by an empirical rate constant according to Delmon¹¹ and determined with respect to the total error of our measurements with an error of $\pm 10\%$. The slope of the pseudolinear part of the time dependence of the degree of reduction was evaluated by methods of the linear regression and correlation analysis. The scatter of points around the regression straight line was expressed by the correlation coefficient, which was in the range 0.9–1.0. For samples with the prevailing content of Fe_2O_3 (approx. 100–70 wt. %), both rate constants corresponding to both partial reductions of haematite were evaluated; k_1 for the degree of conversion α from the range 0–0.1 (the theoretical value for the reduction $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ is $\alpha = 0.11$) and k_2 for the range $\alpha = 0.1–0.9$. For the remaining samples, only one rate constant k was evaluated, which corresponds to the total reduction rate of the mixed oxide in the range $\alpha = 0.1–0.9$.

Fig. 3 illustrates the composition dependence of this constant and it shows an apparent effect of origin and a significant effect of temperature on the kinetics of reduction of mixed oxides investigated. In accordance with earlier results⁵, the reduction of pure nonstoichiometric NiO from series B proceeds at a higher rate and

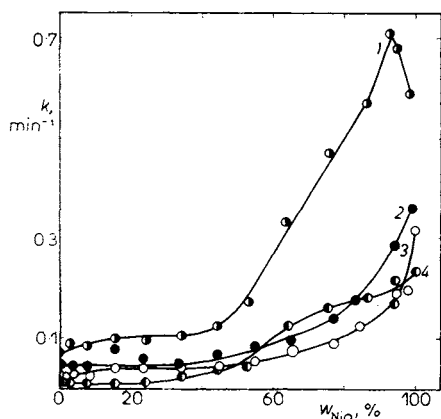


FIG. 3
The composition dependence of the reduction rate constant, k (min^{-1}). 1 ser. B, 410°C; 2 ser. A, 380°C; 3 ser. A, 350°C; 4 ser. B, 320°C

with a shorter induction period in comparison with the oxide from series *A*. The non-sigmoidic character of the kinetic curve of the reduction points to a rapid chemisorption and to the formation of nuclei on the grain surface. The maximum rate of reduction is then achieved at a considerably lower degree of conversion (Table III) and this maximum rate shifts to lower values of α with increasing temperature. On the other hand, the reduction curve for the reduction of NiO from series *A* with higher stoichiometry possesses a sigmoidic shape typical of nucleation-controlled processes. With increasing concentration of thermodynamically more stable Fe₂O₃, the reduction rate of mixed oxides from series *A* in the region of excess on NiO decreases monotonously. Considering a higher degree of interaction between both components in this series (more perfect epitaxial contact), this decrease in the reduction rate may be caused by the retardation of the donor chemisorption of hydrogen due to the addition of *n*-semiconductive haematite to *p*-semiconductive nickel oxide.

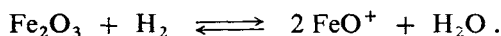
Oxides from series *B* possess an analogous course of the composition dependence of *k* only at lower temperatures of reduction (Fig. 3, curve 4). A pronounced rate maximum (curve 1) due to an increased magnitude of the surface and to its thermic activation appears on these curves at low amounts of Fe₂O₃ and at increased temperatures. The constitutionally bound water retards the reduction of NiO by checking its active centres for the chemisorption of hydrogen and, due to small dimensions of the pores, its thermic desorption and the consequent activation of its surface occurs only at higher temperatures. The transformation of goethite with its dehydration proceeds parallelly with the reduction of the majority nickel oxide. The inhibitory effect of water is particularly obvious at a high excess of haematite and at lower reduction temperatures, which follows from the composition dependence of the specific rate constant k_1^s (normalized to unit surface) of the initial stage of the reduction (partial reduction of haematite to magnetite, Fig. 4). Since no significant changes in the specific surface occur during the first stage of the haematite reduction (Fig. 5) and considering also results of other authors¹² who found a proportionality between the initial reduction rate of ferric oxides and the initial magnitude of the specific surface, this normalization of the rate constant k_1 to unit surface is justifiable in the case of oxides with the prevailing content of Fe₂O₃.

TABLE III

The temperature dependence of the degree of conversion α of samples 15*A* and 15*B* corresponding to the maximum reduction rate

<i>t</i> , °C	320	350	380	410
α , 15 <i>A</i>	0.70	0.65	0.57	0.56
α , 15 <i>B</i>	0.43	0.35	0.34	0.33

Curves in Fig. 4 point to a lower reduction rate of samples from series *B* containing hydrated ferric oxide. The largest difference between the reduction rates was found for samples of pure haematite from both series compared. The retardation effect of water can be explained by reaching the equilibrium of the process which represents according to some authors¹³ the elementary stage of the haematite reduction:



In this equation, FeO^+ ions are active molecules of ferrous oxide which do not create the lattice. Small additions of NiO accelerate the haematite reduction (curve 2) due to the catalytic effect of reduced nickel. Its effect manifests itself also in the achieved degree of the haematite reduction. At the given conditions and at 320°C , pure haematite is reduced only to magnetite, whereas the mixed oxide containing approximately 1% NiO is reduced totally to metallic iron. In the same composition range for samples from series *A*, entire nickel oxide is bound in the spinel phase, whose presence decreases the reduction rate as it has also been confirmed for other two-component oxide systems¹⁴. The apparent activation energy of reduction of these samples is higher than that of mixed oxides containing already free nickel oxide.

It follows from Fig. 6 that the reduction reactivity of haematite is affected also by its preliminary annealing. Its effect on the reduction rate may be expressed by

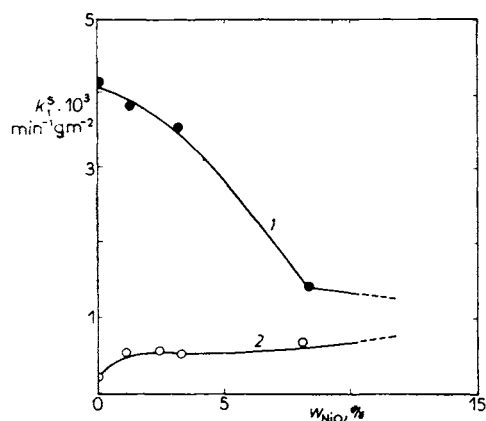


FIG. 4

The composition dependence of the specific rate constant of the initial stage of the reduction, k_1^s ($\text{min}^{-1} \text{g m}^{-2}$); reduction temperature 320°C . 1 ser. *A*, 2 ser. *B*

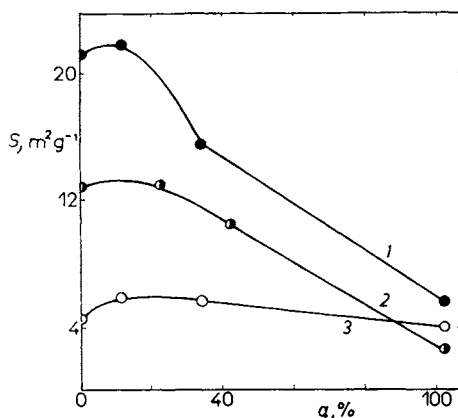


FIG. 5

The dependence of the specific surface S ($\text{m}^2 \text{g}^{-1}$) on the degree of reduction α ; reduction temperature 380°C . 1 sample 1B, 2 5A, 3 1A

quantity Δ_k defined by the relation: $\Delta_k\% = (k^+ - k)/k \cdot 100$, where k^+ is the reduction rate constant of the annealed sample and k is the corresponding quantity for the original sample. A much more positive effect (acceleration of the reaction) in the second stage of the reduction of sample 1B in comparison with the oxide from series A ($\Delta_{k_2}(1B) = 129\%$, $\Delta_{k_2}(1A) = 83\%$) can be related mainly to the dehydration and activation of the reaction interface. For oxides of the nitrate origin (1A), the positive effect comes mainly from the desorption of strongly bound forms of oxygen. It is obvious from a comparison of the time course of the reduction of ferric oxide from both series (curves 1 and 2) that the properties of both samples after annealing at 800°C become uniform and differences in the reduction kinetics disappear.

A negative effect of sintering during the initial stage of the process in both cases leads to a deactivation of the surface due to a decreased concentration of centres of chemisorption of hydrogen and nucleation. It is obvious from a comparison of magnitudes of the prolongation of the induction period of reduction of both samples investigated that this deactivation affects much more the initial stage of the reduction of sample 1B and that it eliminates entirely the total positive effect. During the annealing of mixed oxides with a haematite excess, the spinel phase forms also by a direct reaction in the solid phase, which leads to a decrease in the initial reduction rate of samples of the same composition in both series (*e.g.*, $\Delta_{k_1}(5A) = -48\%$, $\Delta_{k_1}(5B) = -58\%$). With a further increasing content of NiO, the deactivation sintering effect starts to prevail over the positive dehydration effect. The reduction rate of annealed samples is lower in the whole range of the degree of conversion and it depends on the concentration and on the actual ratio of different forms of stoichiometrically excessive oxygen in this oxide, which is a function of the annealing temperature and which determines its reactivity.

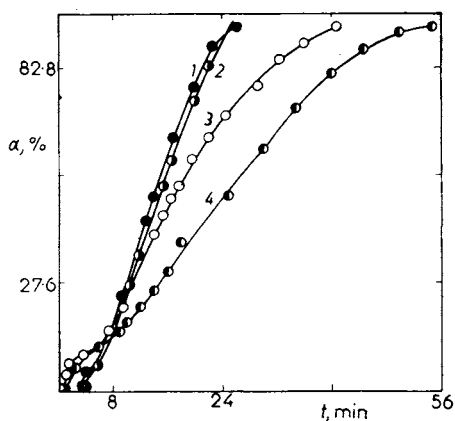


FIG. 6

The effect of annealing (1 h at 800°C in air) on the time course of the reduction at 380°C. 1 sample 1B annealed, 2 1A annealed, 3 1A not annealed, 4 1B not annealed

CONCLUSIONS

It may be concluded from our results that the character of original precursors employed for the preparation of two-component NiO-Fe₂O₃ oxides affects significantly their physico-chemical properties, their phase composition, the degree of mutual interaction of present components as well as composition changes of these parameters as long as the mixed oxide system has been prepared by a low-temperature annealing (up to approximately 500°C) of the given precursor. Due to a dependence on these properties, the origin of oxides modifies also their reactivity during the reduction with hydrogen. If the final oxide system is additionally annealed or if the precursor is annealed directly at higher temperatures (at $t \geq 500^\circ\text{C}$), the properties of the system become uniform and specific differences in the reduction kinetics due to different origins disappear.

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