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EFFECT OF GENESIS ON THE PROPERTIES AND HYDROGEN REDUCIBILITY OF NiO–ZnO MIXED OXIDES

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Abstract

The physico-chemical properties and reactivity tested by hydrogen reduction have been studied for two series of NiO–ZnO mixed oxides of various composition. The solid nickel oxide or zinc oxide in interaction with the solution of nitrate of the second component were used as the precursors in each series. The differences in some physico-chemical parameters of the samples in both series were correlated with their reduction behaviour, followed both in iso- and non-isothermal regime. Moreower, the influence of various factors modifying the reactivity of mixed oxides was also investigated and the results were compared with those obtained from earlier studied analogous systems of quite different origin.

Keywords: hydrogen reduction, NiO–ZnO mixed oxides, physico-chemical properties

Introduction

Within the framework of systematic research of the effects of genesis and various treatments on the reactivity of two-component oxide catalysts tested by their reduction with hydrogen the NiO–ZnO mixed system has been investigated. Different physico-chemical properties as well as differences in reduction kinetics were observed with mentioned mixed oxides of various composition prepared by thermal decomposition of crystalline nitrates of both metals [1], by calcination of coprecipitated basic carbonates without [2] or with incorporated radionuclide ^{65}Zn [3] or by decomposition of precursors in different combinations. In the last case the properties and reduction behaviour of two series of NiO–ZnO mixed oxides were compared [4]. The precursor of the first series (denoted as series N) arised by evaporation of suspension of the basic nickel carbonate with $Zn(NO_3)_2$ solution to dryness and vice versa the precipitates of basic zinc carbonate were mixed with nickel nitrate solution during the preparation of the second series (series Z). In all above mentioned cases the high degree of mutual interaction of both components in the final mixed oxide systems was proved.

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It was found that in the series N containing basic nickel carbonate as a component of the precursor, its decomposition leads to the formation of higher nickel oxides with variable composition in the range from $NiO_{1.33}$ to $NiO_{1.50}$. Their presence is connected with variable content of the different bound residual water [5]. The influence of basic amorphous carbonate in mixed precursors manifests itself by higher values of surface areas of final oxides i. e. with pure nickel oxide of series N including mixed samples with its prevailing content and with pure zinc oxide of series Z including mixed samples containing an excess of ZnO [4]. Analogously the content of chemisorbed oxygen was found to be substantially higher with the mixed samples of series N containing an excess of nickel oxide including pure NiO as compared with the same samples of series Z. This finding is in full accordance with *p*-semiconducting character of NiO. The presence of Ni^{3+} ions is compensated by ionogenic forms of super-stoichiometric oxygen. With zinc oxide the defects formed by interstitial Zn^{+} ions and by oxygen vacancies determine its *n*-semiconductivity. Therefore the content of chemisorbed oxygen with the samples of both series containing an excess of ZnO including pure zinc oxide was found to be zero [4].

The samples with nickel nitrate precursor (series Z) contain practically stoichiometric nickel oxide. Therefore the sum of mass% of both oxides of stoichiometry NiO and ZnO achieves nearly 100% over the whole range of composition. Contrary to series N with these samples the changes in the amount of chemisorbed oxygen induced by irradiation appear to be negligible. For both series the formation of solid solution during the decomposition of precursors appears to be characteristic but the dependencies of NiO lattice parameter (a_{NiO}) on composition are quite different. For the samples of series N this quantity intensely increases up to 30% content of ZnO. With its further increasing content the rise of a_{NiO} is very slow. With series Z a_{NiO} achieves at 30% of ZnO a maximum and then decreases. The increase of the lattice parameter of metallic nickel (a_{Ni}) with increasing content of ZnO and the formation of a new cubic structure of Ni–Zn alloy as a result of partial reduction of ZnO were observed with the reduced samples of both series N and Z [4].

The samples of series N containing a high excess of nickel oxide assign the highest reactivity whereas the reduction rate of the samples of series Z is substantially lower and monotonously decreases with increasing content of ZnO. The degree of partial reduction of zinc oxide achieves its maximum at about 20% of ZnO for series N, for series Z this maximum lies at 80% of ZnO. In the present paper the analogous systems precursors of which consist of the pure oxide of one component in interaction with the salt of the second component have been investigated. Therefore one series of NiO–ZnO mixed oxides of various composition was prepared from the precursors containing nickel oxide of carbonate origin and solution of zinc nitrate (denoted series A), whereas the precursors of the other series consist of zinc oxide (carbonate origin) and solution of nickel nitrate (series B). In addition to the physicochemical properties the influence of various factors modifying the reactivity of both systems was also studied.

Experimental

Two series of mixed oxides with various proportions of the components in the range 0–100% were prepared by thermal decomposition of the precursors for 4 h at 450°C in air. The starting solutions of AR grade nickel or zinc nitrate (1.5 mol L^{-1}) were precipitated during intensive agitation with a 15% stoichiometric excess of aqueous Na_2CO_3 solution. A carefully washed and dried precipitates of basic nickel (zinc) carbonates were calcinated for 4 h at 450°C and pulverized by grinding. For the preparation of the precursors of series A the powdery nickel oxide was then mixed with required volumes of the solution of zinc nitrate. These suspensions formed were evaporated on the water bath to dryness at 120°C. Before the final decomposition the products were homogenized by grinding in an agate mortar. An analogous procedure was used for the preparation of the precursors of series B in which the powdery ZnO oxide was mixed with the solution of nickel nitrate.

The content of both metals in the mixed oxides was determined chelatometrically in combination with atomic absorption spectroscopy. The microstructure of the samples was investigated by X-ray diffraction using a TUR M62 generator with goniometer. Nickel-filtered CuK_α radiation was used. Specific surface areas were measured by low temperature selective adsorption of nitrogen from a N_2/H_2 mixture and the morphology of the mixed oxides and the products of their reduction was investigated using a JSM 840A (Jeol) scanning electron microscope. The content of chemisorbed oxygen (its ionogenic forms expressed as the surface concentration of O^{2-} ions) was determined by iodometric titration.

Selected samples of different composition were heat-treated for 4 h at 600, 750 and 900°C in air and at 600°C for 2 h in oxygen or helium atmospheres. The samples treated in this manner were, prior to use, cooled down to room temperature in the same atmosphere. Part of the samples prepared were further irradiated with ^{60}Co gamma rays in air and by accelerated electrons of an average energy of 4 MeV from a high-frequency linear accelerator using a dose of 3 MGy. The chemical modification of the reactivity was performed by impregnation of various samples from both series with 2% aqueous solution of H_2PtCl_6. After three-day storage of suspension the liquid phase was removed by drying at 80°C up to a constant mass. The activated samples were either directly reduced with hydrogen or preliminary heat-treated in air and then reduced with hydrogen at the same temperatures. The reduction kinetics were studied partly by isothermal thermogravimetry in the range of 350–440°C and partly in the non-isothermal regime (temperature programmed reduction) at a heating rate of 10°C min^{-1} up to 440°C. The reduction took place in hydrogen flowing at 60 mL min^{-1} using a 50 mg mass of the sample.

Results and discussion

Physico-chemical properties of mixed nickel and zinc oxides

Structure, morphology

From the results of chemical and X-ray analyses follows that both systems under study consist of the separate phases of cubic nickel oxide and hexagonal zinc oxide. Contrary to the earlier studied series Z some of first samples of both series A and B contain non-stoichiometric nickel oxide. With further increasing content of ZnO the sum of both oxides of stoichiometry NiO and ZnO approaches 100% (Table 1). In contrast with the samples of pure nitrate or carbonate origin [1, 2] as well as with the series N or Z [4] no changes in the lattice parameter of NiO with increasing content of the second component were observed. The absence of the solid solution of both oxides in the whole range of composition demonstrates the lower degree of the mutual influence of components determined by the origin of both systems. Analogously the size of NiO microcrystallites in the present studied series A and B appears to be independent of composition (Table 1) and this parameter is by two orders of magnitude higher than that with the series N or Z [4].

The interaction of both components in the systems under study results in a non-additivity of the specific surface areas and non-monotonous dependence of this parameter on the composition (Fig. 1), especially with the samples of series A. These dependencies are in accordance with the results of morphological investigation of the samples and correlate with the different origin of both series. During the preparation only one precursor (corresponding nitrate) undergoes the decomposition which proceeds very rapid under temperature used. Therefore the last stage of this operation ap-

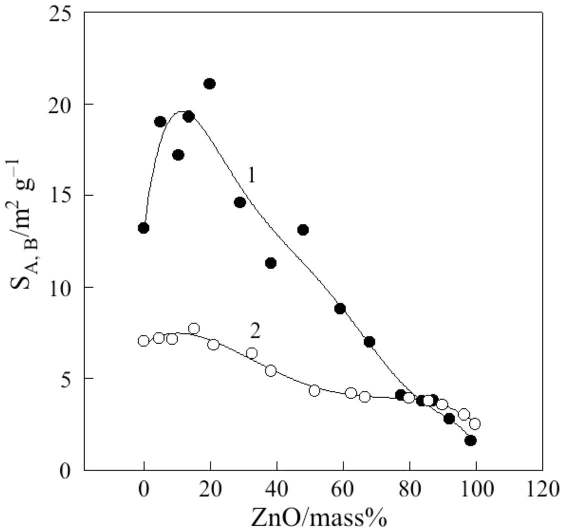

Fig. 1 Dependences of the specific surface areas (*S*) on composition. 1 – series A; 2 – series B

Table 1 Notation, composition and size of coherent regions (L) of NiO–ZnO mixed oxides of the series A and B

Sample	Mass/%			L/nm	
	NiO	ZnO	NiO+ZnO	NiO	ZnO
1A	93.95	0.00	93.95	350.7	
1B	94.93	0.00	94.93	165.3	
2A	91.35	4.98	96.33	295.8	
2B	90.63	4.46	95.09	150.8	
3A	86.66	10.40	97.06	427.2	
3B	86.13	8.59	94.72	189.6	
4A	82.60	13.57	96.17	450.4	
4B	81.08	15.03	96.11	190.8	
5A	77.53	19.84	97.37	340.5	
5B	75.67	20.98	96.65	120.4	
6A	69.83	28.95	98.78		
6B	63.78	32.65	96.43	130.5	
7A	60.45	38.28	98.73		
7B	60.24	38.38	98.62	120.2	
8A	51.14	47.92	99.06		
8B	48.03	51.53	99.56	140.9	
9A	40.23	59.13	99.36		
9B	36.77	62.44	99.21	146.4	
10A	31.80	68.10	99.90		1347.5
10B	33.18	66.65	99.83		242.4
11A	21.62	77.36	98.98		1285.9
11B	20.01	79.93	99.94		198.5
12A	14.17	83.70	97.87		1250.6
12B	11.85	85.78	97.63		294.5
13A	10.53	87.12	97.65		1087.4
13B	9.59	89.89	99.48		205.4
14A	5.55	92.14	97.69		900.5
14B	3.18	96.49	99.67		320.8
15A	0.00	98.49	98.49		831.5
15B	0.00	99.50	99.50		194.3

pears to be only the heat treatment of final mixed oxides determining their morphological properties. The samples of series A are more resistant towards sintering processes owing to the lower dispersity of their microcrystallites (Table 1) as compared with the series B. Therefore the resulting grains are formed by smaller agglomerates with rugged surface so that the overall surface areas appear to be higher than those with series B, virtually in the whole range of composition. The abrupt decrease of this parameter with the samples containing more than 20% of zinc oxide distinctly shows the influence of increasing concentration of nitrate precursor. During its decomposition a melt is created so that the final oxides possess very low surface areas. As can be seen from Table 2, the additional heat treatment when the temperatures exceeded the calcination temperature (450°C) leads to the pronounced decrease of the surface areas with the samples of series A. On the contrary with the series B, where the majority portions of microcrystallites and agglomerates were sintered already during the preparation, the decrease of this parameter and the effect of sintering processes at the additional heat treatment is substantially lower. With the earlier studied series N and Z the degree of mutual interaction of both components is higher owing to the simultaneous decomposition of mixed salts (amorphous basic carbonate with crystalline nitrate). Hence the effect of nitrate, decreasing the final surface areas appears to be still higher [4].

Table 2 Decrease of the specific surface areas with the samples of series A and B after their heat treatment at different temperatures

Series	Mass/% ZnO	Decrease of S/%	
		600°C	750 and 900°C
A	10.4	80	90
	28.9	80	86
	59.1	70	75
	83.7	50	50
B	8.6	50	70
	20.9	44	60
	38.4	47	50
	62.4	50	50

Chemisorbed oxygen, effect of pre-irradiation

In the preparations of all series the different dependencies of the content of ionogenic chemisorbed oxygen normalized to unit surface area of the samples on composition were also compared. From the presence of a maximum of the freshly prepared samples in the region of an excess of nickel oxide with the series B (Fig. 2, curve 1) it can be deduced, similarly to the series N or Z, that the dissociative chemisorption of molecular oxygen takes place both on the dominant $Ni^{2+}–Ni^{2+}$ centres and on the mixed $Ni^{2+}–Zn^{+}$ centres. In comparison with the series N the second maximum in the middle of series was not observed and the amount of oxygen further monotonously decreases with increasing content of zinc oxide. From Fig. 3, curve 1, it can be seen that with the freshly prepared samples of series A no additional mixed centres enhancing the chemisorption of oxygen are created so that the content of surface oxygen monoto-

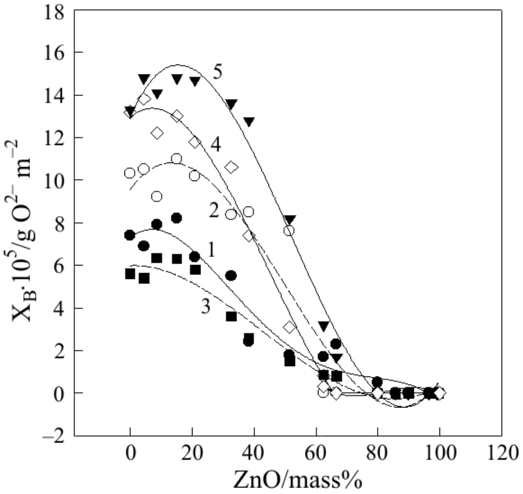

Fig. 2 Dependence of the content of superstoichiometric oxygen normalized to unit surface area X (series B) on the composition. 1 – freshly prepared samples; 2 – samples after two years storage; 3 – samples after three-years storage; 4 – samples irradiated by accelerated electrons, 3 MGy; 5 – samples irradiated by gamma rays, 3 MGy

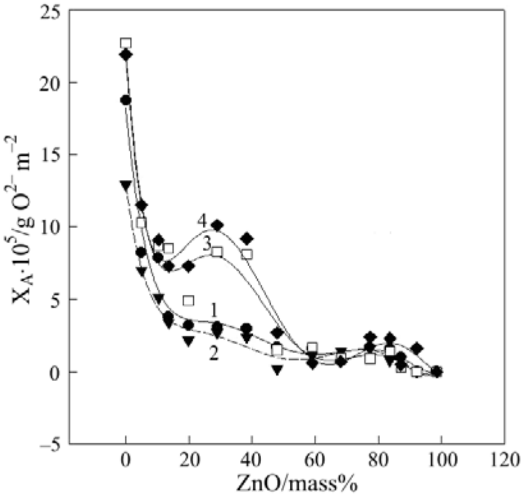

Fig. 3 As in Fig. 2 but for the series A. 1 – original samples; 2 – samples after two years storage; 3 – samples irradiated by gamma rays; 4 – samples irradiated by accelerated eletrons

nously decreases with decreasing content of nickel oxide in the whole range of composition. This behaviour is in accordance with above mentioned semiconducting character of both pure oxides. Curves 2, 3 (Fig. 2) and 2 (Fig. 3) also show that the dynamic equilibrium between surface and atmospheric oxygen changes with time during storage of the samples. These changes appear to be positive or negative, but the character of the dependence remains unchanged. Analogously as it was found earlier [4], that the higher content of super-stoichiometric oxygen in pure nickel oxide of series A compared with the same sample of series B which may be probably determined predominantly by the different morphologic character of decomposed precursors – basic nickel carbonate or crystalline nickel nitrate. On the contrary, the distinctive influence of the temperature of precursor decomposition, mentioned in paper [6] is out of question in our case due to the same values of this parameter.

The pre-irradiation both by gamma rays and accelerated electrons results in a pronounced increase in the amount of chemisorbed oxygen with the samples containing an excess of nickel oxide in both series (Fig. 2, curves 4 and 5, Fig. 3, curves 3 and 4). The unchanged character of the dependence for the series B (Fig. 2) gives evidence, that in this case and in this region of composition the increase in concentration of surface oxygen can be attributed predominantly to the shift of equilibrium between various forms of oxygen sorbed on the already existing centres in favour of the strongly bound ionogenic form. In addition to this effect with the series A a new maximum of given dependence after irradiation (Fig. 3) proves that the subsequent chemisorption of oxygen from the atmosphere on the new centres created by ionization takes place. Figure 4 represents the dependence of the quantity ΔX on composition for both series. This quantity is expressed by the relation $\Delta X(\%)=100(X^*-X)/X$, where X^* and X denote the normalized content of chemisorbed oxygen of the irradiated and original samples, respectively. Whereas no considerable differences between the effect of gamma rays or accelerated electrons on the samples of series A were found, the mixed oxides in the middle of series B appear to

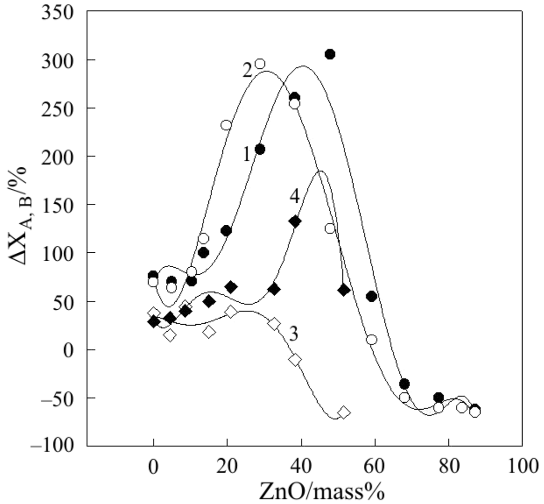

Fig. 4 Plot of quantity ΔX(%), defined in the text, *vs.* composition for the samples of both series. 1 – series A gamma irradiated; 2 – series A irradiated by accelerated electrons; 3 – series B irradiated by accelerated electrons; 4 – series B gamma irradiated. Doses 3 MGy

be much more sensitive to the irradiation with gamma rays (curve 4). Owing to the relatively high content of zinc oxide in this region of composition, the enhanced adsorption of atmospheric oxygen on mixed centres $Ni^{2+}–Zn^{+}+O_2 \rightarrow Ni^{3+}–Zn^{2+}+O^{2-}$ induced by gamma radiation can be assumed. In addition to that, this radiation may evoke, in contrast with accelerated electrons the migration of activated oxygen from bulk to the surface of particles [7].

The accelerated electrons induce in the central region of composition the opposite effect i.e. the radiation reduction of ions in higher valency states (Ni^{3+}, Zn^{2+}) which takes place also with the samples of series A containing an excess of zinc oxide regardless of the type of radiation. At the doses applied in this work such reduction may be caused by hydrated electrons resulting in radiolysis of the trace amounts of moisture [8]. The same effect was observed with the different mixed oxide systems irradiated directly in suspension with distilled water [9], or during the radiolytic reduction of metal ions in aqueous systems [10] already at substantially lower doses. The above mentioned role of genesis in connection with mixed centres for chemisorption of oxygen can be supported by the findings, that the high temperature treatment in air leads to the increase of normalized content of chemisorbed oxygen only with the mixed samples of series B containing an excess of NiO oxide. Up to 35% of zinc oxide the increase of this quantity averages 20% (treatment at 750°C) or 75% (treatment at 900°C). With further increasing ZnO content the amount of oxygen monotonously decreases up to zero. With the mixed samples of series A under the same conditions only the decrease of this quantity was observed regardless of the atmosphere used. The high temperature treatment of pure nickel oxide leads to the gradual loss of super-stoichiometric oxygen and two processes may be assumed. With increasing temperature the neutral weakly bound oxygen may be desorbed [6] or transformed to the ionogenic forms like O_2^-, O^-, O^{2-} owing to the facilitation of electron transfer [11]. These ionogenic forms then may be partially incorporated into the lattice due to its increased mobility or desorbed from the surface. At about 800–900°C fully stoichiometric nickel oxide is formed [9].

Reduction of mixed oxides

Kinetics and degree of hydrogen reduction

As it follows from Fig. 5 the maximum reduction rate (V_{max}) monotonously and non-linear decreases with increasing content of thermodynamically more stable zinc oxide in the whole range of composition for both series. A similar course was found also for the dependence of the same quantity normalized to the unit surface area (specific maximum reduction rate, $V_{max,\,s}$) on composition. This course appears to be different from that in the earlier studied systems N and Z [4], where the strongest mutual influence of both components was observed in the region of occurrence of solid solution. Above the concentration level of 25–30 mass% the zinc oxide formed a separate phase and its effect on the quantity V_{max} was practically negligible. Moreover with the series N the extremely high reactivity of the system manifested itself by a local maximum of the dependence under discussion at about 10% of ZnO oxide. It was found that this behaviour is connected with the presence of very finely dispersed nickel ox-

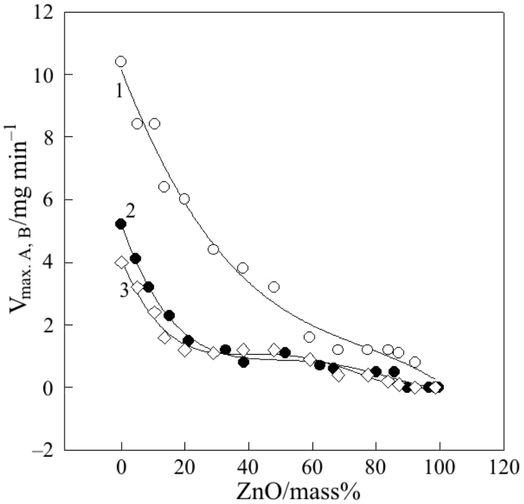

Fig. 5 Dependence of the maximum reduction rate V_{max} on composition at different temperatures. 1 – series A, 440; 2 – series B, 440; 3 – series A, 350°C

ide (microcrystallite size about 3 nm) of super-stoichiometry which was created predominantly by weakly bound forms of oxygen making very rapid sorption of hydrogen and subsequent surface nucleation of the reduction product possible [4]. Even though the analogous effect was not observed with the systems A and B, the higher reactivity of the samples of series A in the whole range of composition is also evident from Fig. 5 as well as from the dependencies of the apparent activation energy on composition. With the series A this quantity increases monotonously wits increasing amount of ZnO up to its 20% content from 40 to 100 kJ mol^{-1} and then remains unchanged. With the series B in the region of 0–30% ZnO this quantity rises from 60 to 150 kJ mol^{-1}. The lower values of the apparent activation energies of reduction calculated for the samples containing an excess of nickel oxide including pure NiO oxide give evidence for the participation of transport processes. Owing to the higher surface areas as well as resistance to the sintering and therefore more porous texture with the samples of series A the transport of water vapour may be facilitated. This leads to the acceleration of reduction and lowering of the activation energy [12].

The different reactivity of the samples of both series A and B follows also from Fig. 6. This figure shows that the degree of reduction over the theoretical value, corresponding to the total reduction of NiO, increases monotonously with increasing content of ZnO oxide in the series A only, containing the nickel oxide of carbonate origin. A sharp maximum of this dependence was reached at 80 mass% of zinc oxide. At the same reduction temperature the excess of reduction with the series B reaches only 30% in the region of prevailing content of nickel oxide. The X-ray analysis of the samples reduced at this temperature proved that the partial reduction of the second component (ZnO) takes place in both series up to the different degree depending on their origin and composition. The same dependences for the earlier studied se-

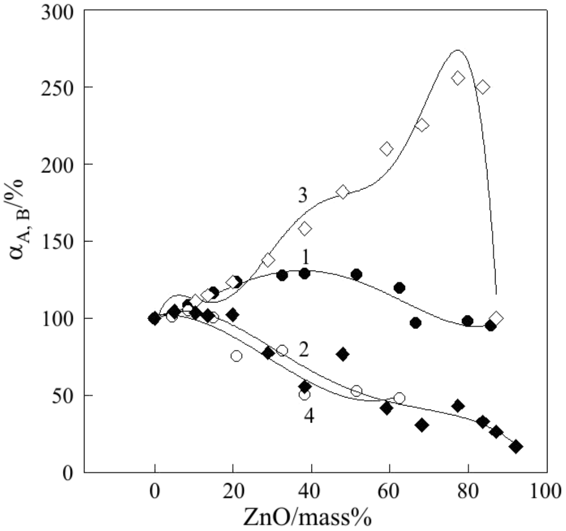

Fig. 6 Dependence of the percentage reduction at different temperatures over the theoretical value corresponding to the total reduction of NiO on the composition. 1 – series B, 440; 2 – series B, 380; 3 – series A, 440; 4 – series A 380°C

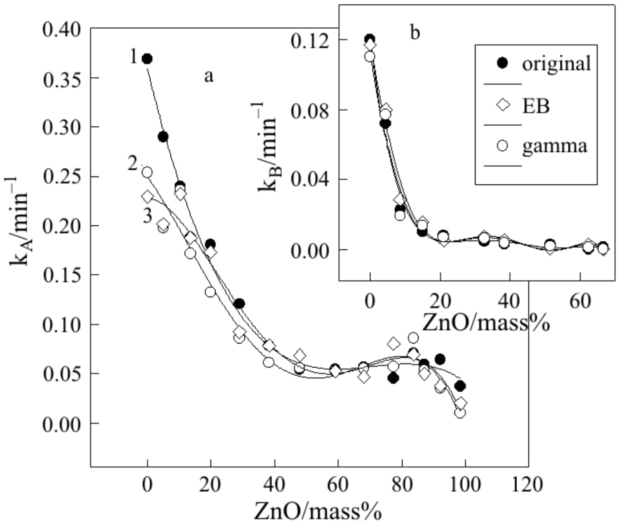

Fig. 7 Dependence of rate constants *k* of the reduction on composition for the original and irradiated samples of a – series A reduced at 440°C and b – series B reduced at 380°C. 1 – original samples; 2 – irradiated by gamma rays, dose 3 MGy; 3 – irradiated by accelerated electrons, dose 3 MGy

ries N and Z showed more distinctive differences [4]. This effect may also be related to the different size distribution of grains and their agglomerates [13]. The kinetics of reduction of both series A and B can be quantitatively described in conformity with the shrinking unreacted-core model by the equation: $1-(1-\alpha)^{1/3}=kt$, where α is the degree of reduction in time t and k is the rate constant. As can be seen from Fig. 7 the rate constant of the reduction for both series decreases monotonously with increasing content of ZnO similarly as the quantity $V_{\max}$.

Effect of pre-irradiation

In contrast with the series B, the samples of series A appear to be sensitive towards pre-irradiation. This manifests itself by the decrease of the reduction rate especially with irradiated pure nickel oxide and the mixed samples containing its distinctive excess. Analogous effect was observed with the earlier studied series N [4]. However in contrast with this series no inversion of negative radiation effect to the positive one (acceleration of the reduction) was proved with the irradiated samples of series A containing an excess of zinc oxide. This gives evidence for very low concentration of lattice perturbations and local boundaries of interacting phases making possible the capture and stabilization of radiation-induced charge defects especially quasi-free electrons accelerating the decomposition processes [14]. As it follows from Fig. 8, both quantities characterizing the reduction rate ($V_{\max}$, respectively, $V_{\max,\,s}$ and k) may be affected in an opposite manner. With the selected mixed samples of series B containing an excess of nickel oxide the value of rate constant decreases with increasing temperature of heat pre-treatment whereas the quantity $V_{\max,\,s}$ increases. This gives evidence for the activation of surface centres by removal of bound water and

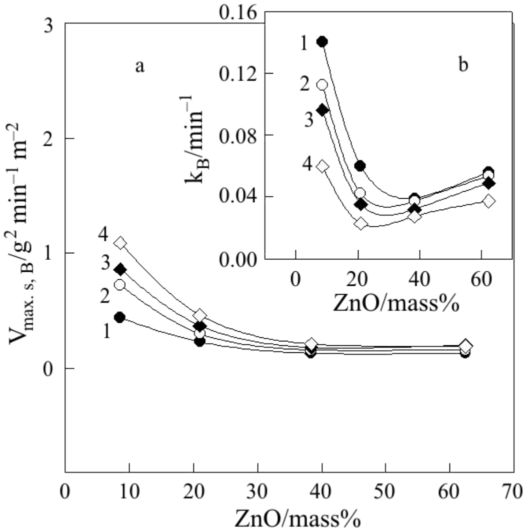

Fig. 8 Plot of specific maximum reduction a – rate $V_{\max,\,s}$ and b – rate constant k *vs.* composition for the selected samples of series B, heat treated at different temperatures and reduced at 440°C. 1 – original non-treated samples; samples treated at 2 – 600; 3 – 750 and 4 – 900°C

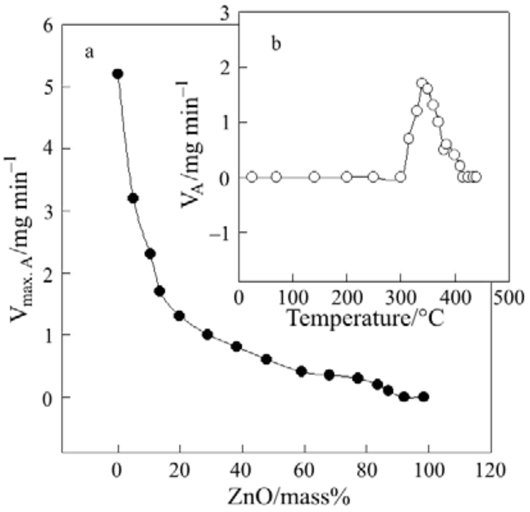

Fig. 9 Dependence of the maximum reduction rate V_{max} for the samples of a – series A measured in non-isothermal regime on composition and b – temperature-programmed reduction profile of sample 4, series A

desorption of gaseous impurities. In addition to the observed increase in ionogenic forms of oxygen retarding the donor chemisorption of reducing hydrogen, the enhanced adsorption of weakly bound, easily reducible neutral oxygen can be assumed during the cooling of the samples treated in air. In contrast with the rate constant, the quantity $V_{max,\,s}$ characterizes the reaction on the surface or in the near sub-surface layers of the grain. From Fig. 9b showing the dependence of the instantaneous reduction rate on the temperature, measured in a non-isothermal regime (temperature programmed reduction profile) it is evident that in accordance with the above mentioned kinetic model the maximum reduction rate is attained in the initial stages of the reduction. The same character exhibit the dependences of the instantaneous reduction rate on the reduction degree, measured in an isothermal regime for both series. However with increasing content of zinc oxide the quantity V_{max} is shifted towards higher values of reduction degree. As it follows from the comparison of Fig. 5, curves 1 and 3 (samples of series A) with Fig. 9a the courses of the dependencies of quantity V_{max} on composition appear to be similar both for the non-isothermal and for the isothermal regime of measurement.

Effect of chemical modification of surface

Reactivity of the samples in both series may be substantially enhanced by surface impregnation with a platinum activator. Figure 10 shows the dependence of rate constants of the reduction on composition for the samples of series B impregnated with the solution of H_2PtCl_6 and measured by different ways. Selected samples were thermally pre-treated in air at 350°C up to the constant mass loss and then reduced by hy-

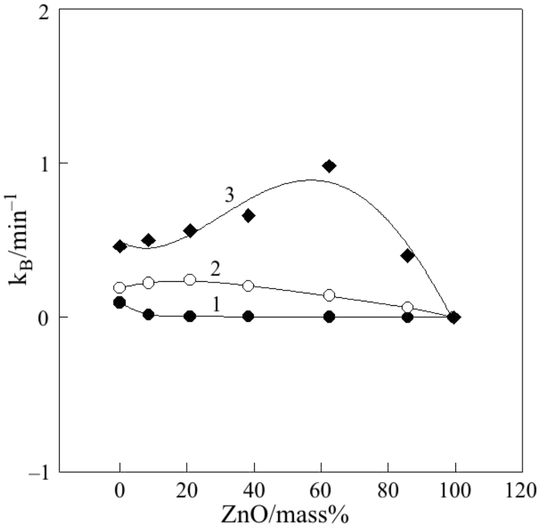

Fig. 10 Dependence of the rate constants of reduction on composition for selected samples of series B activated with platinum and reduced at 350°C. 1 – original samples; 2 – hydrogen reduction after pre-decomposition of activator (H_2PtCl_6) in air; 3 – reductive decomposition of the impregnated samples directly in hydrogen

drogen at the same temperature (curve 2). In subsequent experiments the same impregnated samples were directly reduced by hydrogen (reductive decomposition, curve 3). Both processes took place without observable induction period. As compared with the original non-modified samples (curve 1) the reduction is accelerated, however the activation appears to be much more effective in the case of reductive decomposition. In the former case it may be assumed that the thermal decomposition of the activator takes place according to the equation

$$H_2PtCl_6+1/2O_2 \rightarrow H_2O+Pt+3Cl_2$$

In addition to that the pre-treatment in air leads to the reaction in surface layers

$$NiPtCl_6+1/2O_2 \rightarrow NiO+Pt+3Cl_2$$

Therefore the following reduction appears to be facilitated predominantly by platinum due to the spill-over effect. More reactive species (atomic hydrogen) can migrate by surface diffusion from Pt catalyst to reduced oxide and the reaction is accelerated even though both phases (Pt/oxide) are gradually separated by creating product-metallic nickel. As it was found [15], only the fraction of platinum which is formed by the latter reaction substantially increases the rate of reduction whereas the catalytic activity of the platinum fraction originated according to the former reaction appears to be slight. During the reductive decomposition in hydrogen probably the reaction

$$NiPtCl_6+NiO+4H_2 \rightarrow 2Ni+Pt+6HCl+H_2O$$

takes place so that the positive effect of platinum simultaneously superimposes with the autocatalytic effect of reduced metallic nickel. The efficiency of the positive effect increases with increasing proportion of ZnO which probably acts as a transmitter of active hydrogen. Moreover in contrast with the non-impregnated samples in both cases the slow reduction of pure zinc oxide as well as its reduction in mixed samples was observed at low temperatures. The literature indicates that the temperature of reduction may be markedly reduced by small admixtures of platinum with various hardly reducible metal oxides, however in the limits of their thermodynamical stability [16]. Similar results were found with the impregnated samples of series A. In comparison with the series B the only difference lies in lower accelerating effect predominantly with the samples preliminary thermally treated and then reduced. It may be connected with different epitaxial contact of activator determined by different morphology and dispersity [15, 16].

Conclusions

The two series of NiO–ZnO mixed oxides of various composition prepared by calcination from solid nickel oxide of carbonate origin suspended in solution of zinc nitrate (series A) and from solid zinc oxide of carbonate origin mixed with solution of nickel nitrate (series B) consist of separate phases of both oxides. Although the degree of mutual interaction of the two components appears to be lower than that with earlier studied analogous systems precursors which were formed by mixed unsoluble or soluble salts, the series A and B compared widely differ both in their physicochemical properties and chemical reactivity tested by reduction with hydrogen.

The preparation of mixed oxides of both series resulted in differences in the dispersity of microcrystallites, their morphology, thermal stability, absolute values of specific surface areas and normalized content of surface chemisorbed oxygen as well as in character of the dependences of these parameters on composition.

The presence of thermodynamically more stable zinc oxide affects not only the reduction kinetics but also the overall degree of reduction achieved. Depending on the temperature the partial reduction of zinc oxide also takes place however with both series up to different degrees and in different regions of composition. The reduction kinetics of both series can be quantitatively described by the shrinking unreacted-core model. However the oxides of series A show the higher reactivity as well as the higher sensitivity towards pre-irradiation both by gamma rays and by accelerated electrons.

The reduction can be substantially accelerated by the addition of platinum activator due to the spill-over effect and its superposition with autocatalytical influence of reduced nickel. The efficiency of the positive effect increases with increasing content of zinc oxide up to the maximum, however in the case when the initial form of activator (H_2PtCl_6) impregnated on the surface was reductive decomposed in the flow of hydrogen. The preliminary decomposition of the activator in air leads only to the slight acceleration of following hydrogen reduction. Owing to the different epitaxial contact this positive effect appears to be higher with the samples of series B. In the presence of activator the thermodynamically more stable zinc oxide undergoes reduction at lower temperatures.

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