STUDY OF THE REDUCTION OF MIXED NICKEL AND ZINC OXIDES BY HYDROGEN

M.POSPÍŠIL and J.CABICAR

Department of Nuclear and Physical Engineering,
Czech Technical University, 115 19 Prague 1

Reduction of mixed nickel and zinc oxides of different composition by hydrogen has been studied by means of thermogravimetry. The oxides were prepared by calcination of the coprecipitated basic carbonates of the two components at 400°C in air. The reduction proceeds in the temperature interval of 320—430°C under kinetic regime. In the temperature range of 430—500°C the rate of the reaction is affected by internal transport processes. In addition to the total reduction of nickel(II) oxide also zinc(II) oxide is partially reduced, particularly at higher temperatures. The system studied is formed in the region up to 30 mol% ZnO by a homogeneous solid solution of both components; over this concentration also the phase of pure zinc oxide is present. The reduction rate depends on the composition, decreasing steeply with increasing content of ZnO till the above mentioned concentration is attained. Kinetics of the reduction can be described by an equation derived for a zonal model of decomposition of solid substances. The dependences found are qualitatively in accordance with the concepts of the electron theory of adsorption and catalysis on semi-conductors. The effect of different genesis of the oxides on the process of reduction has been demonstrated by comparing some properties of the studied oxides and experimental results with the earlier published study on the reduction of the same system, however, prepared by decomposition of mixed nitrates.

In the previous publication[1] the reduction of a two-component oxide system NiO.ZnO was studied by flow method with thermal conductivity detection. Samples of various composition were prepared by thermal decomposition of mixed crystalline nitrates at 340°C in air. It is well known[2] that the conditions of preparation and of the genesis of the starting oxide affect the kinetics of the reduction as well as the catalytic properties of the final metal obtained by reduction. The aim of the present work was therefore to investigate the reduction of a similar system of oxides, however, in this case prepared by calcination of coprecipitated basic carbonates of both components and to compare the results for both types of mixed oxides of different "origin".

EXPERIMENTAL

Preparation of samples: Mixed oxides of various ratios of both components in the range of 0—100 mol% were prepared by calcination of basic carbonates, formed by precipitation of the solution of nitrates of both metals with the solution of potassium carbonate in 15% excess with

respect to stoichiometry. Concentration of all solutions was 1 mol l^{-1}; all chemicals were of reagent grade purity. Precipitation was performed at 20°C under vigorous stirring so that all three solutions were added dropwise into 200 ml of redistilled water. The precipitate was repeatedly decanted and washed on filter with distilled water till no nitrates could be detected. The precipitate was dried at 20°C for 24 h, then for another 3 h at 120°C and finally was calcinated in air at 400°C for 6 h. To study the effect of calcination temperature on the course of reduction, several samples of different composition were prepared beside the fundamental series prepared in the above mentioned way. These samples were prepared so that parts of the precipitate were calcinated under otherwise identical conditions at 300, 600 and 700°C. The content of metals in these oxides was determined complexometrically. The notation of the samples, their composition and specific surface areas, measured by adsorption of nitrogen at low temperatures, are summarized in Table I.

Measurement and working procedure. Reduction of mixed oxides was studied using the previously described[3] thermogravimetric apparatus, in the temperature range of 320—500°C. Conditions were established under which the rate and the course of the reaction does not depend on the flow rate of hydrogen for any arbitrary composition of the sample, the standard weight of the sample being 50 mg. This region can be, in the given arrangement, guarranteed at the hydrogen flow rate 56 ml/min which was employed in all experiments.

The starting mixed oxides and reduction products were studied by means of microstructure X-ray analysis[4]. The superstoichiometric oxygen in nickel(II) oxide was determined iodometrically[5].

RESULTS

Effect of Temperature and Composition

The dependence of the time course of the reduction on temperature was followed for all samples of the series. As can be seen in Fig. 1, the reduction rate decreases with decreasing temperature, whereas the time of induction period increases. Samples of carbonate "origin" are reduced faster than samples of the nitrate series[1] of the same composition, beginning from 320°C. Samples 13 and 14 (Table I) showed no weight losses even at 500°C. The apparent activation energy was calculated from the temperature dependence of the reduction. In the temperature range of 500 to 430°C the mean value of this quantity is 4·5 ± 3 kcal/mol over the whole range of composition and in the interval 430—320°C it is 22·8 ± 1 kcal/mol, independing on the degree of reduction. The analysis of the experimental results, based on the criteria taken from the literature[2], indicates that the reduction proceeds in the region of lower temperatures 430—320°C as a pure kinetic process.

The effect of composition on the time course of the reduction can be seen in Fig. 2. This effect is similar for both series of oxides which are of different "origin". With increasing content of zinc(II) oxide the reduction rate decreases and the induction period becomes longer. The effect of zinc(II) oxide is most pronounced up to its content 20—30%, when the reduction rate decreases very steeply. Further increase of the ZnO content results only in a slow decrease of the reduction rate or it even has practically no effect (nitrate series).

Principal difference of the nitrate and carbonate series concerns their specific surface areas and the dependence of this quantity on composition. In neither of these cases this dependence can be expressed as the sum of specific surface areas of the two pure components. This non-additivity indicates a higher degree of interaction and of mutual influence od both oxides, than might be expected with a simple mechanic mixture. As follows from the comparison of the S

TABLE I

Denotation and Composition of Samples of Mixed Oxides NiO.ZnO and Values of Their Specific Surface Areas S

| Sample	Weight%		Weight%		Weight%	Mol.%		S
	Ni	Zn	NiO	ZnO	NiO + ZnO	NiO	ZnO	m²/g
1	74·98	—	95·42	—	—	100·0	—	28·39
2	70·67	6·08	89·93	7·57	97·50	94·30	5·70	22·72
3	68·25	6·84	86·85	8·52	95·37	91·52	8·48	30·18
4	60·61	13·78	77·13	17·09	94·22	83·10	16·90	45·77
5	52·94	22·14	67·37	27·56	94·93	72·75	27·25	48·40
6	43·07	31·56	54·81	39·28	94·09	60·40	39·60	51·38
7	36·53	38·23	46·49	47·58	94·07	51·48	48·52	50·73
8	29·12	45·64	37·12	56·80	93·92	42·20	57·80	55·02
9	22·70	51·43	28·89	64·02	92·91	32·95	67·05	59·92
10	18·61	54·83	23·69	68·25	91·94	27·46	73·54	72·94
11	11·44	63·19	14·55	78·65	93·20	16·78	83·22	66·87
12	6·07	69·17	7·72	86·10	93·82	8·89	91·11	51·29
13	0·98	75·09	1·25	93·48	94·73	1·13	98·87	37·78
14	—	78·54	—	97·76	—	—	100·00	19·34
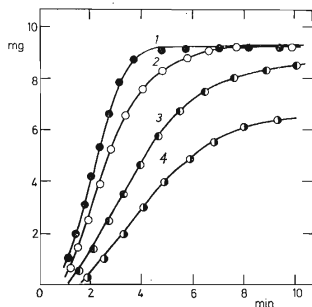
FIG. 1

Time Course of the Reduction of Sample 3 at Various Temperatures
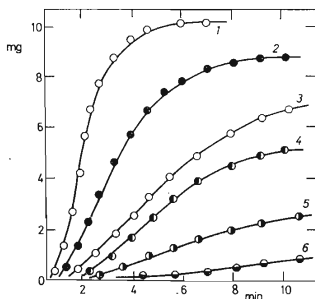
1 450, 2 400, 3 350, 4 320°C.

FIG. 2

Time Courses of the Reduction of Samples of Various Composition (Table I) at 350°C

1 Sample 1, 2 2, 3 4, 4 6, 5 8, 6 12.

values (Table I) with the data reported in paper[1], specific surface areas of the samples of the carbonate series are practically by one order of magnitude higher than those of the nitrate series at the same composition. In view of this fact the reduction rate was referred to unit surface, in order to check the validity of the measured dependences. In this manner the reduction rates of different samples can be compared regardless of their genesis. As can be seen from Fig. 3 where the specific maximum reduction rate is plotted vs composition a steep decrease of the reduction rate occurs in the region up to 30 mol% ZnO.

Interrupted Reduction

The existence of induction period as well as the reduction course characterized by the increase of the rate up to a maximum values, is an evidence of the autocatalytic character of the process which usually is taken as connected with the catalytic effect of the already reduced metal phase[6]. To prove the character of the process, it was interrupted in its initial phase by stopping the hydrogen input. The reduction went on for some time with decreasing rate till a constant weight loss was achieved. This means that a certain amount of the product was formed at the phase boundary. It cannot be expected that under the given conditions its crystallo-chemical transformation into final form will be accomplished[7]. The reduction was then resumed almost immediately after reaching the constant weight loss by letting in hydrogen. The pre-reduced samples were almost instantly reduced further, at a higher rate and to a very high degree of reduction.

Effect of Water Vapour and of Partial Tension of Hydrogen

Water is the gaseous product of the reduction by hydrogen and therefore its effect on the reduction course was studied. In the range of $p_{H_2O} = 17 \cdot 5 - 31 \cdot 8$ Torr the reduction is not in the least affected by water vapour. At higher partial pressures only an increase of the induction period and a slight decrease of the reduction rate was observed in the initial phase of the reduction. Selected samples were further reduced with a nitrogen–hydrogen mixture at a constant flow rate 56 ml/min. In the range of low partial pressures of hydrogen the reduction rate increases linearly with p_{H_2}, whereas at high partial pressures it is independent of p_{H_2}. The ranges of the two regions can be seen in Fig. 4.

Reduction of Reoxidized Samples

This reduction process was studied in a way similar as in the previous work[1]. After primary reduction the samples were oxidized with air directly in the apparatus and then reduced again. The secondary reduction proceeds at a higher rate than the primary one under otherwise identical conditions. All the oxide formed by oxidation of metal with air is reduced again. With increasing content of zinc(II) oxide in the samples the degree of oxidation and consequently also of the secondary reduction increases, whereas the metallic nickel, formed by primary reduction of pure NiO (samples No 1, Table I) is oxidized only negligibly. The rate of the secondary reduction of the reoxidized pure nickel oxide is, contrary to the mixed samples, comparable with the rate of primary reduction. The attained degree of reduction is, however, the lowest of all the samples. Sample No 3 is oxidized and secondarily reduced to 68% with respect to the original oxide, sample No 9 to 79%, the temperature of all processes being 410°C. An X-ray record, obtained using the method of back beam, showed distinct lines of nickel and a weak reflection of NiO in the reoxidized sample 1. The mixed sample reoxidized under identical conditions showed only selective reflections of nickel(II) oxide. Simultaneously a decrease of the lattice parameter a_{NiO} in the

mixed reoxidized sample was observed as compared with the original sample. Besides, reoxidized samples have lower specific surface areas than the original oxides; the difference diminishes with increasing content of zinc(II) oxide.

The Effect of Thermal Treatment

Selected samples were heated, prior to reduction, in argon atmosphere to 150, 300, 500, 700, and 1000°C for 1 h and then reduced at various temperatures in the interval 350—440°C. Thermal treatment at 150 and 300°C is without any effect on the reduction course. Samples, heated to 500°C showed an increase of the reduction rate. Simultaneously (in the case of samples 4, 6, 8, 9, 10) also an increase of the value of apparent activation energy of the reduction was observed to the value 28.4 ± 2 kcal/mol. However, thermal treatment at 500°C causes already a decrease of specific surface areas (e.g. sample 9 from 59.92 to 38.4 m^2/g). Specific maximum reduction rate increased after thermal treatment at 500°C approximately to double of its original value. In view of the possible thermal decomposition of ZnO at higher temperatures[8] total weight losses of the samples were measured after one-hour treatment in an inert atmosphere. The samples
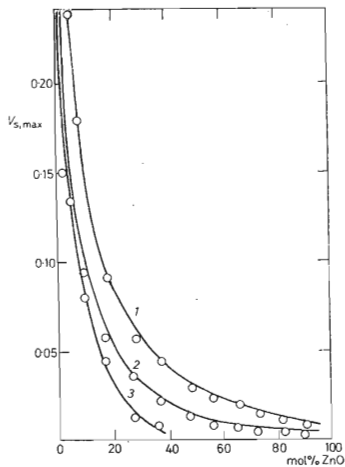

FIG. 3

Dependence of the Specific Maximum Reduction Rate (mg/min m^2) at Various Temperatures on Composition

  1 380°C, 2 350°C, 3 samples of the nitrate series[1], 350°C.
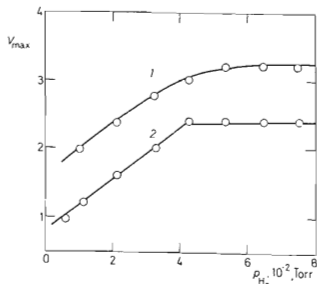

FIG. 4

Dependence of the Maximum Reduction Rate (mg/min) at 440°C on the Partial Pressure of Hydrogen

  1 Sample 8, 2 sample of the nitrate series[1] of the composition 64.1 mol% NiO and 35.9 mol% ZnO.

were first dried to constant weight at 300°C and a precisely weighted amount was then thermally treated. It has been proved experimentally that in the non-reducing atmosphere no decomposition occurs up to 500°C. At 1 000°C the weight loss in dependence on composition attains the average value of 1% of the original weight for samples of the nitrate series and 3% for carbonate series. Only with further increasing temperature the weight loss increases abruptly and the decomposition of the zinc(II) oxide sets in. Thermal treating at 700 and 1 000°C results in the lengthening of the induction period of the reduction and in a considerable sintering of the surface. With samples treated at 1 000°C even after 30 min the reduction did nor proceed with a measurable rate.

Maximum weight losses (degrees of reduction) attained in the reduction of all samples of the series were compared with the theoretical values. Samples 13 and 14 (Table I) showed no reduction in the temperature range up to 500°C. Therefore the theoretical values of the weight loss for the given amount weighted of the samples and for the given compositions were calculated assuming that the only component of the system that is reduced is nickel oxide, similarly as it is with the samples of the nitrate series[1]. These values were compared with the weight losses obtained at the temperature of reduction 500°C when practically constant degrees of reduction were attained with all samples within the times of measurement. As can be seen from Fig. 5, the samples are reduced at this temperature to a higher degree than would correspond to the theoretical values. This deviation (in per cent) increases with increasing content of ZnO up to a maximum at 70% ZnO. The dependence of the excess reduction on composition in the nitrate series has
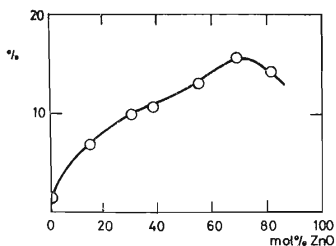

Fig. 5

Dependence of the % of Reduction at 500°C over the Theoretical Value, Corresponding to Total Reduction of NiO, on the Composition
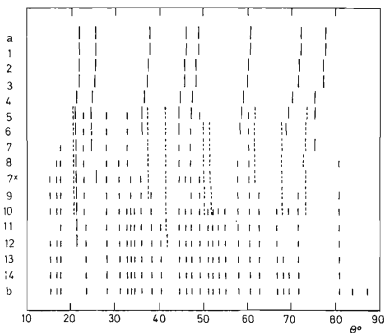
Fig. 6

Debyegrams of Samples (Table I) after Reduction with Hydrogen for 3 h at 400°C

a Theoretical lines of Ni, b theoretical lines of ZnO, × sample 7 prepared by calcination at 600°C, | selective reflection of Ni, | selective reflection of ZnO, ⋮ selective reflection of new structure of Ni–Zn alloy.

the same course as compared with the theoretical values, however, the maximum is lower and does not exceed 5%.

Determination of the Content of Super-Stoichiometric Oxygen

With respect to the fact that even sample 1 (pure NiO) was reduced to a higher degree than corresponds to stoichiometry, the content of the superstoichiometric oxygen was determined in this sample. The value found iodometrically was 0·15 weight% and the value calculated from thermogravimetric measurements was 2·5 weight % of super-stoichiometric oxygen. Pure nickel oxide of the nitrate "origin" contains only half of this concentration of super-stoichiometric oxygen.

Sample 1 was then further treated at 600, 800 and 1 000°C for 1 h and under the same conditions in argon atmosphere. The amounts of super-stoichiometric oxygen determined iodometrically in these samples are summarized in Table II. From it is evident that these amounts decrease with increasing temperature of heating and at high temperatures (800—1 000°C) especially when heated in an inert atmosphere, nickel(II) oxide becomes stoichiometric. Iodometry does not yield satisfactory results in the case of mixed NiO.ZnO oxides. The cause is a considerable effect of composition on the solubility of the samples and the resulting impossibility to attain standard conditions for all samples. The found values increase with increasing solubility of the sample. With pure zinc(II) oxide of both nitrate and carbonate series (these samples were completely dissolved) no super-stoichiometric oxygen was found, according to expectation.

Effect of Calcination Temperature

The rate and the degree of reduction decreases with increasing temperature of calcination, which is accompanied by sintering of the samples and by diminishing of the specific surface area. Samples prepared by calcination at a temperature lower than was used in the basic series (400°C) are reduced at a higher rate. Curves of the time course of reduction of these samples are characterized by a steep onset part with a delay. This course indicates the presence of a further component in the system, *i.e.* of undecomposed carbonates which are then decomposed during reduction. The first step is the formation of oxide which is further reduced[9]. The presence of carbonates in these samples was also proved analytically, in contrast with the samples of the basic series. Thus the calcination temperature 400°C which was employed in the preparation of the basic series can be taken as the optimum, in accordance with the literature[10].

DISCUSSION

The difference in the specific surface areas of the samples of the two series of different "origin" is in agreement with the literature data[11]. In all cases a many times lower value of the specific surface area was found with various oxides, prepared by thermal decomposition of the respective nitrates as compared with the oxides prepared from carbonates. The validity of this rule can therefore be extended also for two-component systems. According to Dreyer[12] coprecipitation of nitrates of metals by alkali metal carbonates results in the formation of basic amorphous carbonates. Assuming that the calcination temperature is sufficient to make possible the decomposition to oxides and if no considerable sintering of the samples occurs, the system can retain to a great extent the surface properties of the starting substance,

irrespective of the fact that a new structure of the final oxide is formed[13]. In our case these conditions are fulfilled, including the optimum temperature. If we take into account that in the nitrate series the initial system of mixed crystalline nitrates underwent the stadium of a homogeneous melt[1] prior to proper decomposition, then the found difference in the values in the specific surface areas of the two oxides can be explained. The different genesis is evident even from the habitus of the sample. Oxides of the carbonate series form a loose powder, whereas samples of the nitrate series are of microcrystallinic structure throughout.

The results of microstructural analysis of the oxides of both series[4] show that in both cases the system consists in the region up to c. 30 mol% of ZnO of homogeneous solid solution of both components. Over this concentration a two-phase system exists, formed by solid solution and free zinc(II) oxide. Up to the mentioned concentration ZnO is incorporated into the nickel(II) oxide lattice under simultaneous increase of the lattice parameter. The end of this growth of a_{NiO}, whereby the cubic lattice of NiO is still preserved, is accompanied by the formation a new phase of the hexagonal ZnO. This means that in the region to 30 mol% of ZnO the interaction of both components is the highest which is manifested also by a maximum change of the reduction rate (Fig. 3). The change of the lattice parameter a_{NiO} attains its maximum value 0·86% for samples of the carbonate series and 0·53% in the nitrate series.

It is known[14] that thermal decomposition of nickel salts in air leads to the formation of nickel(II) oxide containing a higher amount of oxygen than corresponds to the stoichiometry of NiO. Iodometric and thermogravimetric determinations of this oxygen in pure NiO show that stoichiometry corresponding to Ni_2O_3 is not attained. It follows from re-oxidation experiments, that the affinity of nickel towards oxygen is strongly influenced, in positive sense, by the presence and amount of zinc(II) oxide. With respect to this and under the conditions of preparation of the whole series it can be assumed that mixed samples contain nickel(II) oxide with superstoichiometric oxygen, too. The results of analyses (Table I) indicate that in the carbonate series a system of oxides of the composition Ni_2O_3.ZnO might be formed in some samples in the region of high ZnO contents (the sum of weight% of both oxides, beginning with sample 6, would approach 100% of the Ni_2O_3 stoichiometry). Unlike this, with samples of the nitrate series the sum of weight% of both oxides is about 99% for the whole series[1] and for the stoichiometry of nickel(II) oxide calculated as NiO. The amount of superstoichiometric oxygen found iodometrically and thermogravimetrically in pure nickel(II) oxide of the nitrate series was half of the amount found for NiO of the carbonate "origin". Since the superstoichiometric oxygen in the mixed samples could not be determined quantitatively, the values of the weight losses of those samples of the carbonate series where the presence of Ni_2O_3 could be expected according to analysis were calculated under the assumption that the system is formed by Ni_2O_3 and ZnO, Ni_2O_3 being totally reduced. Comparison

of these losses with those experimentally found (at the highest reduction temperature 500°C) showed that the theoretical value is never attained. This finding proves unambiguously the absence of Ni_2O_3 in mixed samples and demonstrates that oxygen exceeding the stoichiometric value of NiO is not the only component that is responsible for the attained degree of reduction over the theoretical value for NiO (Fig. 5). According to the literature[3,15] the non-stoichiometric nickel oxide, prepared by decomposition of salts in air, contains mainly adsorbed water. It can be entirely removed at 300°C, as it was also found in our experiments. Besides, these samples contain chemically bound water, directly in the form of stable hydrates[15]. Temperatures necessary to remove last traces of water and to transform the oxide into stoichiometric NiO are reported to be as high[15] as 1000°C. During the crystallochemical change to the lattice of metallic nickel in the reduction process water is totally released, which is added to the weight loss and thus forms a further component participating in the attained degree of reduction to the value exceeding that for NiO. Release of —OH groups from the possibly present undecomposed basic carbonate can be excluded on the basis of experimental results. Only ionogennic forms o f the adsorbed super-stoichiometric oxygen[14] can be determined iodometrically (actually determination of Ni^{3+} ions). Thermogravimetry which allows to determine all present forms of this oxygen[14] yield results about twenty times higher[16]. This is caused just by the water present in the samples and participating in the total weight loss found, so that even this method is not satisfactory.

The results of microstructural analysis of the reduced samples indicate[4] that also a certain amount of zinc(II) oxide is reduced at higher temperatures. As can be seen from Fig. 6, the Debyegrams of samples after reduction in the region over 30 mol% of ZnO show selective reflections of nickel, non-reduced zinc(II) oxide and quite new lines that can be assigned to a hitherto not well determined structure of an alloy of both metals. The occurrence of this system of lines reaches its maximum about 70 mol% ZnO which is in accordance with the maximum in Fig. 5 Lower population of the reflexions of this alloy in the reduced samples of the nitrate series (reflexions of the weakest intensity are lacking) proves that the portion of the reduced ZnO and consequently also of the formed alloy is lower in this series. This result also agrees with experimental results. In the region up to 30 mol% of ZnO an increase of the lattice parameter of the reduced nickel was found which reaches its maximum 1·7% for samples of the carbonate series and 0·96 for those of the nitrate series. "Lengthening" of the nickel lattice is probably caused by the formation of metallic alloy with cubic lattice. A similar alloy was described by Rubinštejn[17] in his study of an analogous system.

Thus we can assume that the part of the ZnO which forms directly a solid solution, is reduced preferentially. Reduction of this zinc(II) oxide does not proceed as a parallel reaction since in a homogeneous solution the oxygen present cannot be unambiguously assigned to nickel or zinc. At higher reduction temperatures even a certain amount of ZnO may be reduced which forms the immediate phase boundary solid solution–ZnO. With gradual reduction of NiO its influence will become weaker so that after its total reduction also the reduction of ZnO will cease and a constant weight

TABLE II

Content (in weight%) of Superstoichiometric Oxygen in Sample 1, Treated for 1 h at Various Temperatures and in Various Atmospheres

Atmosphere	600°C	800°C	1 000°C
Air	4·05	0·06	0·03
Argon	0·12	0·00	0·00

loss will be attained which was also observed. The low value of the apparent activation energy in the temperature interval $430-500°C$ proves that internal transport processes in the sample phase are effective as the rate determining step. Reduced metals participate in the diffusion in different ways according to their degree of nobility[18]. According to paper[19] the reduction rate can in this case be expected to be independent of the partial pressure of the reducing gas which is in accordance with our experimental results.

The reduction of a certain portion of free ZnO is also supported by the finding that the degree of reduction over the theoretical value diminishes with decreasing temperature and equals zero at 380°C. If only ZnO present in the solid phase were reduced this excess degree of reduction should be constant over a wide temperature interval, provided a total reduction of the components of this phase takes place. In the same way, this quantity should be constant, independent of composition, beginning with the content 30 ml% of ZnO, when the amount of solid solution in the system is the highest. It is known[20] that reduction of ZnO is thermodynamically possible even at lower temperatures, if it is present in a two-component system in which the tensions of oxygen of both oxides are different. Reduction of zinc(II) oxide appear thus to be the third factor participating in the degree of reduction exceding the theoretical value for NiO. Simultaneously it makes impossible thermogravimetric determination of the superstoichiometric oxygen in nickel(II) oxide in the studied mixed system.

To describe the kinetics of the reduction in the system under study the experimental results were treated similarly as it was with samples of the nitrate series[1,2]. The results were in agreement with the Roginski's model of a zonal course of the reaction[21]. Reduction kinetics can be expressed by equation $1 - (1 - \alpha)^{1/3} = kt$, where $(1 - \alpha)$ is the non-reacted fraction in time t and k is a constant.

Recent papers, dealing with the reduction of poly-component semi-conducting oxides by gases, have also applied the assumptions of the electron theory of adsorption and catalysis on semiconductors to explain the effect of admixtures on the rate of reduction of the basic oxide[22]. According to the theory addition of a second component results in the change of the Fermi level on the semiconductor surface and thus its adsorption properties are also modified. In the region up to 30 mol% of ZnO where we have a homophaseous system and where we can except maximum

mutual influence of the electronic structure of both semiconductors a steep decrease of the reduction rate takes place. Nickel(II) oxide as p-semiconductor is characterized by a certain equilibrium concentration of the superstoichiometric oxygen whose prevailing part exists as neutral form 0° and a minor part[26] as ionogennic form O^-. The latter is compensated, to meet the condition of electroneutrality of the crystal as a whole, by an equivalent amount of Ni^{3+} ions. The incorporated zinc(II) oxide releases as a n-semiconductor free electrons which are localized in the main part in the defects represented by Ni^{3+} ions, and simultaneously reduces these ions to Ni^{2+}. At room temperature the equilibrium of the electron exchange between both forms of defects in the ZnO lattice, represented mainly by interstitial ions Zn^+ and Zn^{2+}, $Zn^{2+} + e^- \rightleftarrows Zn^+$, is shifted to the right hand side[23] so that in pure zinc(II) oxide practically only defects formed by Zn^+ ions or by oxygen vacances are present. The result of the electron transfer into nickel(II) oxide is an increase of the concentration of Zn^{2+} ions. Composition of both oxides will approach stoichiometry till the equilibrium state is achieved, according to equation $Ni^{3+} + Zn^+ \rightleftarrows$ $\rightleftarrows Ni^{2+} + Zn^{2+}$.

Consequently, incorporation of zinc(II) oxide leads essentially to a weakening of the p-semiconducting character of NiO by recombination processes of the major free charge carriers, positive holes, with the relaesed electrons. Lowering of the hole conductivity of the p-semiconductor results, according to the concepts of the electron theory, in a decrease of the adsorption capacity of the surface towards donor molecules and in a decrease of the reaction rate. In our case it means that with increasing content of ZnO adsorption of hydrogen which always is a donor sorbate is lowered and thus also the reduction rate decreases.

As has been shown[3], reduction of black superstoichiometric nickel(II) oxide is characterized by a high reduction rate as compared with the greenish-yellow stoichiometric oxide under identical reduction conditions. Accordingly, if an increase in the ZnO concentration causes formation of stoichiometric NiO, we can simultaneously expect a decrease of the reduction rate which is in agreement with experimental results. If we further assume that the carriers of active centers from which the reaction spreads according to the zonal model are those sites on the oxide surface which have higher content of superstoichiometric oxygen, then the concentration of these centers will decrease with increasing content of ZnO. In accordance with the zonal model also the maximum reduction rate will decrease and a single zone of the maximum surface area will be formed in deeper layers under the surface. This will be manifested by a shift of the V_{max} value towards higher degrees of reduction, α. This was really observed in the interval of $\alpha = 0.2-0.3$. In the region over 30 mol% of ZnO the assumptions of the theory of homogeneous semiconductors cannot be applied any more. The degree of interaction between the sodid solution present in maximum concentration and the formed phase of free zinc(II) oxide is lower so that the effect of increasing content of ZnO will be only negligible. The observed

slight decrease is probably connected with mechanic blocking of the active metal–oxide interphase boundary by the accumulating zinc(II) oxide[20].

Similarly as in the samples of the nitrate series[1] thermal treating in an inert atmosphere leads to an increase of the reduction rate which, however, can be observed in contrast to the samples of the nitrate "origin" only at 500°C. If a partial desorption of the superstoichiometric oxygen (mainly of the weakly bound neutral form $0°$ and partially also of the ionogennic form O^-, see Table II) takes place, then according to the above mentioned mechanism a decrease of the reduction rate should occur. If we neglect the possibility of a reaction in solid phase, thermal treating must result either in a direct destruction or in desactivation of the active centers, predominantly by sintering processes[13] or the opposite will occur, *i.e.* thermal activation or formation of active centers[24]. Desactivation in our conditions follows directly from the mechanism and from the found decrease of specific surface areas of the samples treated at 500°C. The increase of the apparent activation energy of the reduction of samples treated in this way demonstrates the activation or rather formation of new active centers. The number of factors deciding which of the counter-current processes will prevail is a complex function of the temperature of treatment, of oxide genesis and of their composition. Activation of samples by thermal treating may be caused by gradual desorption of the bound water which cannot be achieved by the short heating during adjusting the sample to the desired, relatively low, reduction temperature[3]. The degree of desorption of these last traces will increase with increasing temperature of treatment.

Higher reduction rate of re-oxidized samples (secondary reduction), the decrease of the size of NiO lattice parameter and of the specific surface of these samples as compared with the starting oxides prove that primary reduction results in destruction of the structure of mixed samples and in a lowering of the high degree of interaction of both components. Subsequent oxidation gives rise to a new system of oxides which, as to its properties, is more related to a mechanic mixture where the zinc(II) oxide plays only a role of an inert admixture in the reduction. The same type of reduction of re-oxidized samples has been found also with the oxides of the nitrate series[1].

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