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EFFECT OF DIFFERENT TREATMENTS ON THE REDUCIBILITY OF NiO–Y_2O_3 MIXED OXIDES BY HYDROGEN

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Abstract

Some physico-chemical properties and reactivity in their reduction with hydrogen of NiO–Y_2O_3 mixed oxides prepared in a dry way have been studied using isothermal thermogravimetry in the range of 320–410°C and temperature-programmed reduction. It was found that addition of small amounts of chloride and acetate anions retarded the reduction of nickel oxide and accelerated the reduction of mixed oxides. The presence of oxalate and formate ions manifests itself by a small positive effect. Introduction of platinum activator or heat treatment of the samples in various atmospheres led to a pronounced increase in the reduction rate. The efficiency of the spill-over effect increases with increasing proportion of non-reducible Y_2O_3. The pre-irradiation of the samples by accelerated electrons and gamma rays at a dose of 1 MGy results in a negative kinetic effect only with the samples containing an excess of nickel oxide.

Keywords: hydrogen reduction, NiO–Y_2O_3 mixed oxides, physico-chemical properties

Introduction

It is known that the conditions of preparation including the genesis and overall pre-history influence the reactivity of solids in their chemical reactions and transformations [1]. The rate of reduction of many binary mixed oxides with hydrogen was found not to be additive but, as a rule, it seemed to be rather determined by a mutual influence of the components in the mixed system. This conclusion is also valid for various mixed oxides where, for thermodynamic reasons, one of the components is not reduced or is reduced to lower oxidation state only [2, 3]. All systems of this type studied earlier were prepared in a wet way, i.e. by calcination of mixed crystalline salts obtained by the evaporation of mixtures of their starting solutions [4] or by calcination of coprecipitated insoluble salts [5]. This manner of preparation guaranteed a high degree of mutual interaction of both components in the final mixed oxide system. The aim of the present work was to study the physico-chemical properties and reactivity, tested by reduction with hydrogen, of an analogous system, but prepared in a dry way, i.e. by low-temperature (under 500°C) calcination of mechanically homogenized powdery mixture of the oxide and precursor (basic carbonate) of the sec-

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ond component. Moreover, the influence of various factors modifying the reactivity of mixed oxides in dependence on the ratio of the components was also investigated. NiO–Y_2O_3 mixed oxides of various compositions were chosen for this purpose.

Experimental

The series of mixed oxides with various proportions of the components in the range 0–100 wt% were prepared by thermal decomposition of the mixture of Y_2O_3 and basic nickel carbonate for 4 h at 450°C in air. Basic nickel carbonate was precipitated from the starting solution of AR grade $Ni(NO_3)_2 \cdot 6H_2O$ (1.5 mol l^{-1}) with a 10% stoichiometric excess of a solution of Na_2CO_3 (1.65 mol l^{-1}) under stirring at room temperature. The carefully washed and dried precipitate was pulverized by grinding in an agate mortar. This precursor was mixed with powdery AR grade Y_2O_3 (Merck) in the required ratios of the metals in an aqueous suspension with intensive agitation. After filtration and drying at 160°C, the mixture was again homogenized by grinding and then calcined. The optimum conditions of decomposition were preliminarily established by DTA measurement of the precursors.

The metals were determined in the mixed oxides by atomic absorption spectroscopy combined with chelatometry. The phase composition of the samples was investigated by X-ray diffraction using nickel-filtered CuK_α radiation. Specific surface areas were measured by low-temperature selective adsorption of nitrogen from a H_2/N_2 mixture and the morphology of the starting mixed oxides and the products of their reduction was investigated using a JSM 840 A (Jeol) scanning electron microscope. The content of ionogenic chemisorbed oxygen (oxidation ability of the oxide surface expressed as the surface concentration of O^{2-} ions) was determined by iodometric titration. For studying the effect of radiation on the reactivity, part of each sample was irradiated with ^{60}Co gamma rays in air or by accelerated electrons of an average energy of 4 MeV from a high-frequency linear accelerator using a dose of 1 MGy in both cases. The heat treatment of selected samples was performed in an inert (Ar) or oxygen atmosphere for 2 h at 600°C, and 3 h at 480°C. The samples treated in this manner were, prior to use, cooled down to room temperature in the same atmosphere.

The chemical modification of the reactivity was performed by impregnation of the samples with solutions of hexachloroplatinic acid and other acids. In the former case a suspension of the sample with 2% aqueous solution of H_2PtCl_6 was prepared and after a four-day storage, the liquid phase was removed by drying at 120°C to constant mass. The activated sample was either directly reduced with hydrogen or the time course of the thermal decomposition of the activator in air and the subsequent reduction with hydrogen at the same temperature were measured. In the latter case the suspension of the samples with solutions of hydrochloric acid (10^{-2} mol l^{-1}), oxalic acid (1 mol l^{-1}) as well as concentrated acetic and formic acids were prepared. After allowing to stand for twenty minutes, the suspension was filtered and, prior to measurement, either directly dried at 120°C to constant mass, or repeatedly washed with a hot distilled water and then dried under the same conditions.

The reduction kinetics was studied partly by isothermal thermogravimetry in the temperature range of 320–410°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 standard conditions of measurement used i.e. 50 mg samples and hydrogen flow rate of 60 ml min^{-1}, guaranteed the independence of the kinetics of sample reduction at an arbitrary composition of the flow rate of the reducing gas.

Results and discussion

Physico-chemical properties of NiO–Y_2O_3 mixed oxides

The chemical (Table 1) and X-ray analyses show that the system under study consists of the cubic phases of NiO and Y_2O_3 as the major components. In both marginal regions of composition the incorporation of the second component does not lead to the change of the lattice parameters of the majority oxide. The mutual inter-

Table 1 Composition, specific surface areas (S) of NiO–Y_2O_3 mixed oxides and surface oxidative ability (X) of the fresh samples (A) and after 6 months of storage (B)

Sample	Composition/wt.%			S/ $m^2\ g^{-1}$	$X/10^{-5}\ gO^{2-}\ m^{-2}$	
	NiO	Y_2O_3	NiO+Y_2O_3		A	B
1	0.00	97.92	97.92	6.7	0.0	0.0
2	2.16	96.65	98.81	8.8	0.0	2.3
3	2.41	95.38	97.79	8.6	0.0	2.3
4	5.46	92.33	97.79	8.5	0.0	1.2
5	7.49	89.15	96.64	9.0	0.0	2.2
6	8.76	88.26	97.02	10.3	3.9	0.9
7	17.02	80.26	97.28	11.5	4.3	2.6
8	25.65	70.61	96.26	12.5	4.0	3.2
9	31.75	64.77	96.52	16.8	4.8	3.6
10	44.19	51.94	96.13	19.3	6.7	4.1
11	56.51	41.02	97.53	18.2	4.4	3.8
12	62.99	34.42	97.41	21.0	5.7	3.8
13	73.78	24.26	98.04	20.6	6.3	3.9
14	86.36	12.83	99.19	15.5	5.8	3.9
15	87.88	11.05	98.93	13.5	6.7	5.2
16	89.02	10.41	99.43	13.0	5.4	3.8
17	92.71	4.83	97.54	10.2	6.7	5.9
18	96.26	2.67	98.53	13.2	4.5	3.8
19	97.28	0.00	97.28	10.3	4.9	4.8

action of both components is evident from the non-monotonous dependences of the size of microcrystallites (coherent regions) and specific surface areas on composition (Fig. 1 and Table 1). The values of specific surface areas changed from 7 to 21 $m^2 g^{-1}$ with a maximum in the central range of composition of the samples. These values may be correlated on the basis of a morphological investigation of the samples creating agglomerates with average size of about 5 μm without distinct porous texture. The reduction of the samples containing an excess of nickel oxide leads to the disintegration of spherical grains to particles with average dimensions smaller than 1 μm accompanied by a simultaneous decrease in surface areas. This quantity is also reduced by about 40 or 70% compared with the original mixed oxides thermally treated at 480 and 600°C owing to the microsintering processes occurring under the above given conditions.

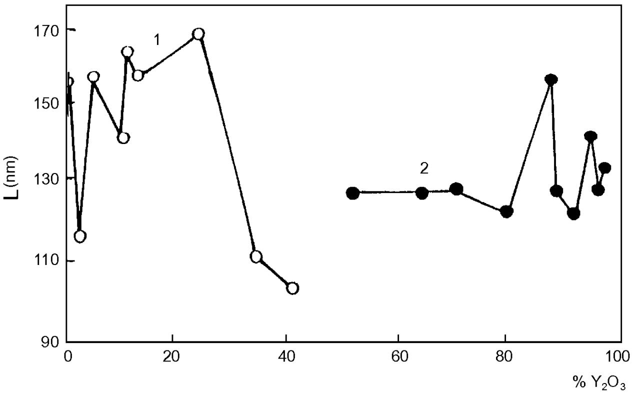

Fig. 1 Sizes of the coherent regions *L* (nm) of NiO (1) and Y_2O_3 (2) *vs*. composition

The surface oxidative ability changes with the sample composition achieving zero value in the region of a high excess of yttrium oxide, including pure Y_2O_3 (Table 1). After 6 months of sample storage in air at room temperature this quantity decreases with the exception of samples with predominant content of Y_2O_3. However, after 32 months of storage no further changes in the surface oxidative ability were found for the samples including the pure Y_2O_3 with permanently zero amount of chemisorbed oxygen. The low affinity of this oxide to oxygen is in accordance with its electrical properties. Y_2O_3 belongs to saturated compounds with fully occupied energetic band of metallic lattice ions ($4s^2$ $4p^6$) and behaves as an insulator [6] or weak *n*-semiconductor. The changes of the parameter under discussion during storage of the samples evidence the establishment of a new adsorptive equilibrium between the atmospheric oxygen and the surface of oxides containing *p*-semiconductive over-stoichiometric nickel oxide. The dissociative chemisorption of molecular oxygen probably proceeds in the whole range of compositions only on the centres created by the ionic pairs of Ni^{2+}–Ni^{2+}. These ions undergo a transition by the chemisorption of oxygen to higher oxidation states according to the equation:

$$Ni^{2+}–Ni^{2+} + O_2 \rightarrow Ni^{3+}–Ni^{3+} + O^{2-}$$

As it follows from Table 2, the surface oxidative ability can be affected by pre-irradiation under the above given conditions. The influence of irradiation on the change of this parameter was expressed by the relation

$$\Delta X/\% = 100\,\frac{X^{*}-X}{X}$$

where X^{*} and X denote the specific surface oxidative ability of the irradiated and original sample, respectively.

Table 2 Changes of the surface oxidative ability (ΔX) of mixed oxides due to accelerated electrons and gamma irradiation at a dose of 1 MGy

Sample	ΔX (%) due to accelerated electrons	ΔX (%) due to gamma rays
1	0	0
2	–100	–100
3	–100	–100
4	–100	–33
5	50	4
6	220	411
7	65	173
8	20	87
9	33	92
10	18	71
11	16	116
12	10	13
13	13	51
14	31	69
15	13	25
16	42	79
17	17	24
18	20	158
19	6	65

The quantity ΔX changes non-monotonously with the composition of the samples and beginning with sample 5 has only positive values. This gives evidence for the radiation-induced oxidation of low valency ions (centres Ni^{2+}–Ni^{2+}) both with the accelerated electrons and by the gamma rays. However, the mixed system under study appears to be more sensitive to the gamma rays as compared with the electron irradiation (higher values of the quantity ΔX). With pure Y_2O_3 the enhanced chemisorption of oxygen cannot be initiated by radiation, whereas with samples containing an excess of this oxide (samples 2–4) the minor Ni^{3+} ions are radiation reduced. These radiation-induced redox processes can be connected not only with the increased or decreased chemisorption of oxygen (the samples were irradiated in both cases in air) but also with the changes of the equilibrium between various forms (neutral or different ionogenic forms) of surface oxygen [7]. The thermal treatment of the samples in both atmospheres at two different temperatures, leads to the activation of the surface (desorption of residual gases and water) and to an increase in the chemisorption of oxygen.

Reduction of mixed oxides by hydrogen and effects of different treatments

In the temperature range studied only the last nine (at 320°C) or twelve (at 410°C) samples of the series with sufficient nickel oxide content are reduced at a measurable rate. The degree of reduction calculated by comparison of the theoretical and experimental mass losses is independent of the composition and shows that the nickel oxide present in the sample is totally reduced. The presence of the yttrium oxide as a thermodynamically more stable and under the given conditions non-reducible component conspicuously affects the reduction kinetics of the nickel oxide. As it follows from the dependences of the instantaneous reduction rate on the temperature (temperature programmed reduction) the maximum reduction rate (V_{max}) is attained with the samples containing an excess of NiO at about 320°C (T_{max}). With increasing Y_2O_3 content the quantity T_{max} is shifted towards higher values up to 380°C (Fig. 2). The segments corresponding to the constant reduction rate give evidence that the reduction is retarded not only by the transport barrier created by the solid reduction product, but also by the second non-reducible component blocking the reaction interface in the deeper layers of the grain. This is probably the reason why the apparent activation energy of the reduction decreased to about 20 kJ mol^{-1} for samples containing a high excess of Y_2O_3. A low value of this quantity gives evidence for the effect of transport processes. The dependences of the instantaneous reduction rate on the degree of reduction obtained in measurements in an isothermal regime also exhibit segments of constant reduction rate on their declining part for samples containing an excess of Y_2O_3. On the contrary, the first stage of reaction is autocatalytically accelerated up to the maximum rate as it follows from the last mentioned

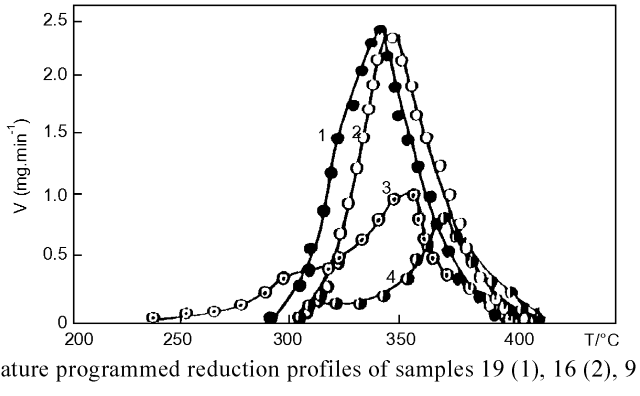

Fig. 2 Temperature programmed reduction profiles of samples 19 (1), 16 (2), 9 (3) and 6 (4)

dependences and the sigmoidal shape of the kinetic curves of reduction. This also provides evidence for the nucleation control of the reaction.

The mutual influence of both components results in a non-linear dependence of the maximum reduction rate normalized to unit surface area (specific maximum rate, $V_{s,max}$) and semiempirical rate constants of the reduction (k) on the composition of the mixed oxides (Fig. 3). This constant is given by the slope of the pseudolinear part of the integral kinetic curve of reduction [8]. The character of these dependences observed also for some other binary systems containing only one reducible component [9] provides evidence that the system prepared in a dry way by decomposition of the precursors at lower temperature (under 500°C) differs in its properties and reactivity from the simple mechanical mixture.

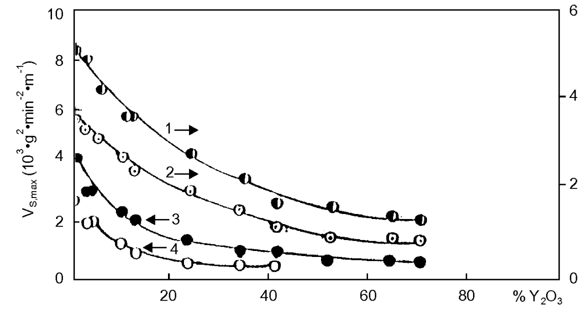

Fig. 3 Dependence of k (arbitrary units) and $V_{s,max}$ /g^2 m^{-2} min^{-1} on the composition

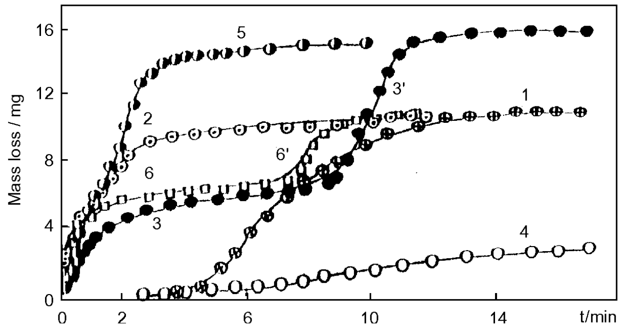

Fig. 4 Reduction by hydrogen of the original samples 18 (1) and 9 (4), their reduction after impregnation with H_2PtCl_6 and drying (sample 18–2, sample 9–5) and thermal decomposition of the activator in air (sample 18–3, sample 9–6) followed by reduction by hydrogen of the activated samples 18 (3’) and 9 (6’)

Figure 4 demonstrates the influence of platinum on the reactivity of two samples of different compositions during their reduction by hydrogen. Curves 1 and 4 represent the time course of reduction of the original samples 18 and 9, curves 2 and 5 belong to the reductive decomposition of the activator (H_2PtCl_6) and reduction of the corresponding activated oxides. Both processes occurred in dry hydrogen. From the small differences in the slope of the two parts of the curves it can be deduced that first the decomposition of activator accelerated by hydrogen proceeds, and in the second stage the reduction of oxides takes place.

Curves 3 and 6 represent the preliminary thermal decomposition of the activator in air. The subsequent reduction of the activated oxides by hydrogen is illustrated by the second parts of the curves (3' for sample 18 and 6' for sample 9). All processes took place at 320°C except the reduction of the original sample 9 which occurred at 350°C. It is evident from these dependences that the activation leads to a pronounced increase in the rate of reduction and shortening of the induction period. The spill-over or jump-over effects therefore positively influence all the phases of the reaction. Their efficiency increases with increasing proportion of Y_2O_3. This non-reducible oxide may probably act as a transmitter of active species (atomic hydrogen) transforming the jump mechanism (migration of activated hydrogen via the gaseous phase) to the spill mechanism (migration by surface diffusion).

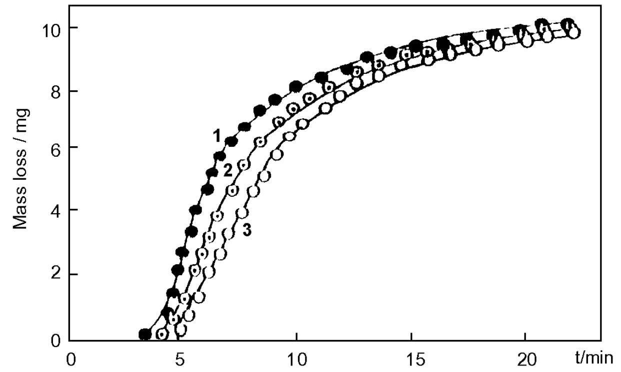

Fig. 5 Reduction by hydrogen of sample 16 at 320°C; 1 – original sample; 2 – sample after irradiation with accelerated electrons, dose of 1 MGy; 3 – after irradiation with gamma rays, dose of 1 MGy

It follows from Fig. 5 that the pre-irradiation of mixed oxides under study with gamma rays and accelerated electrons causes a decrease in the reduction rate in both cases. This negative effect, more pronounced with gamma rays, was found only for the samples containing an excess of NiO. In accordance with earlier results [3] the retardation of the reduction can be connected with an increase in the concentration of the ionogenic, strongly bound oxygen, leading to a decrease in the chemisorption of hydrogen. With increasing proportion of the second component the negative effect is compensated by the competitive positive one. The non-equilibrium radiation-induced charge defects may be stabilized on biographic lattice perturbations, the concentration of which increases on the reaction interface [10]. Hence, the reactivity during the decomposition reaction also increases.

The influence of the additives introduced by an impregnation of the samples on their reduction kinetics is demonstrated in Fig. 6 for pure NiO and in Fig. 7 for mixed oxide containing an excess of Y_2O_3. Treatment with hydrochloric acid leads to the formation of $NiCl_2$ which is practically completely removed by washing of the samples. This follows from the mass losses observed and the unchanged specific surface areas of these samples. Traces of Cl^- ions exhibit a pronounced negative effect, in accordance with the results of some authors [11]. No satisfactory explanation has yet been found for these effects. Some interpretations are based on the theory of homogeneous semiconductors and emphasize either an electronic factor (charge and point defects of the lattice) or the size of substituting ions [12, 13]. The fact that the presence of Y_2O_3 evokes the inversion of the effect i.e. the acceleration of the process including the shortening of the induction period supported the idea, that in our case the additive creates a separate phase retarding the nucleation of the reduced nickel on the oxide surface. The opposite of this effect, the nucleation is probably facilitated by Y_2O_3 which suppresses the sintering of metallic nickel. This follows from the morphological investigation of the treated original and partially reduced samples. Control experiments performed with pure Y_2O_3 show that the soluble yttrium(III) chloride possibly formed is removed by washing and does not contribute to the effects observed. Similar results i.e. a decrease in the reduction rate with pure nickel oxide (Fig. 6) and acceleration of the reduction with mixed oxides (Fig. 7) were found after treatment of the samples with acetic acid and their subsequent washing. The specific surface areas and mass losses during the reduction of these samples also remained unchanged as compared with the original values.

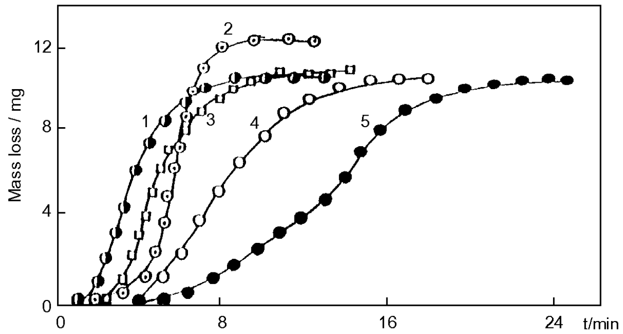

Fig. 6 Influence of various additives on the reduction kinetics of pure nickel oxide at 320°C, 1 – original sample; 2 – sample treated with $(COOH)_2$ and unwashed, 3 – or washed; 4 – sample treated with CH_3COOH and washed; 5 – sample treated with HCl and washed

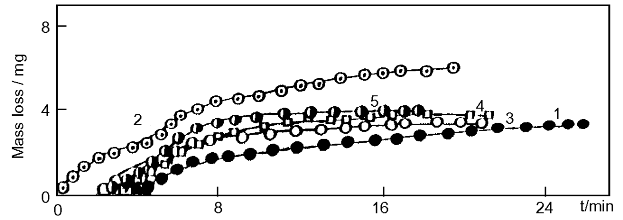

Fig. 7 Influence of various additives on the reduction kinetics of sample 9 at 320°C, 1 – original sample; sample treated with $(COOH)_2$ and unwashed (2) or washed (3); 4 – sample treated with CH_3COOH and washed; 5 – sample treated with HCl and washed

The action of oxalic acid results in a conversion of certain portions of both oxides to slightly soluble oxalates. It was accompanied by a decrease in specific surface areas attaining one half of their original values. However, this original value is restored after washing away major parts of the salts and thus uncovering the sub-surface layers of the grain. The reduction proceeds then virtually with the same kinetics as for the non-treated sample (Fig. 6). In the mixed system the residual part of oxalates is greater so that their reductive decomposition and the reduction of the oxides take place simultaneously in a hydrogen atmosphere (Fig. 7). With unwashed nickel oxide the very rapid reaction results in a greater mass loss and the kinetic curve does not permit separation of the two processes. On the contrary, from the kinetic curve of the reduction of the mixed oxide it is evident, that both reactions proceed consecutively and the decomposition process also includes the decomposition of yttrium oxalate. Analogously, the treatment of the samples with formic acid leads to the formation of a thick layer of formates on the surface of grains and their agglomerates. In all cases the dramatic decrease in the specific surface areas takes place (from 11.5 to 0.2 $m^2 g^{-1}$ for sample 7, from 16.8 to 1.1 $m^2 g^{-1}$ for sample 9, from 13.0 to 2.6 $m^2 g^{-1}$ for sample 16 and from 10.3 to 2.1 $m^2 g^{-1}$ for pure nickel oxide).

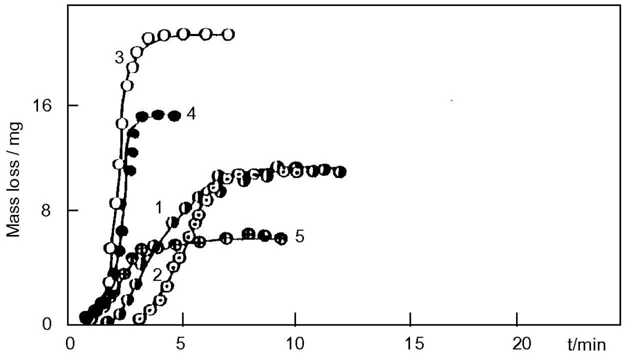

Fig. 8 Effect of treatment with formic acid on the reduction kinetics of pure nickel oxide at 320°C and the thermal decomposition of nickel formate in air followed by reduction with hydrogen of the treated sample, 1 – original sample; 2 – sample treated with HCOOH and washed; 3 – reductive decomposition and reduction of the unwashed sample; 4 – preliminary thermal decomposition of formate in air; 5 – reduction by hydrogen of treated unwashed sample after decomposition of formate

As it follows from Fig. 8 the presence of a slight amount of formate manifests itself by an insignificant increase in the reduction rate of washed (curve 2) pure nickel oxide. The mass loss observed was found to be indentical with that of the original non-treated sample (curve 1). The reduction of the washed mixed oxides containing an excess of Y_2O_3 and therefore a greater residual amount of the formates of both metals, appeared to be distinctly accelerated (Fig. 9). It is known [14] that the thermal decomposition of nickel formate in vacuum on the surface of nickel oxide leads to an artificial nucleation conspicuously increasing the rate of the subsequent reduction by hydrogen. Figures 8 and 9 depict the kinetic curves of the reductive decom-

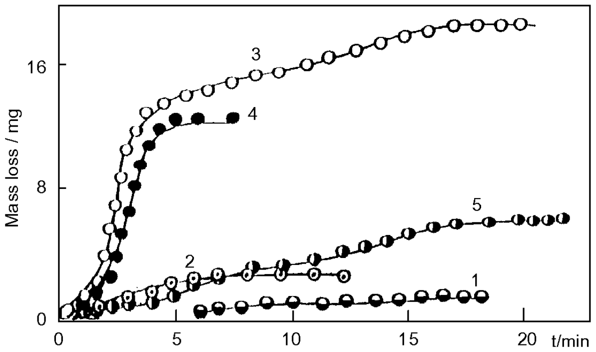

Fig. 9 Effect of treatment with formic acid on the reduction of sample 7 at 320°C and the thermal decomposition of formates in air followed by reduction of the treated sample with hydrogen; 1 – original sample; 2 – sample treated with HCOOH and washed; 3 – reductive decomposition and reduction of the unwashed sample; 4 – preliminary thermal decomposition of formates in air; 5 – reduction of treated unwashed sample by hydrogen after decomposition of formates

position and reduction of the unwashed samples (curve 3) in hydrogen and also the preliminary thermal decomposition of the deposited formates in air (curve 4) as well as the subsequent reduction by hydrogen of the treated oxides (curve 5). It is evident that there are only negligible differences between the kinetics of the reductive decomposition (in hydrogen) and the thermal decomposition in air (more precisely in the atmosphere of the gaseous products of decomposition). No differences between the reductive decomposition and sum of the mass losses observed during the thermal decomposition and subsequent reduction were found. Because the thermal decomposition did not affect the course of the following reduction of the treated oxide, it can be concluded that no nucleation proceeds in our case. Under the given conditions the decomposition therefore led to the formation of nickel oxide according to the equation $Ni(COOH)_2 \rightarrow NiO+2CO+H_2O$ and the reductive decomposition to the final metallic nickel. With yttrium formate the product of both these processes is the oxide which does not undergo reduction by hydrogen.

The heat treatment of the mixed oxides under the above given conditions leads to an activation of the surface centres. In addition to the enhanced chemisorption of oxygen, an increase in the reduction rate is observed especially in the initial stage. The quantity $\Delta V_{s,max}$ defined analogously to the quantity ΔX, where X and X^* are replaced by the specific maximum reduction rate of the original sample ($V_{s,max}$) and of the same sample after treatment ($V^*_{s,max}$) changes non-monotonously with the composition, attaining a value of about 840% for the samples containing a high excess of Y_2O_3. It may therefore be assumed that not only enhanced chemisorption of the ionogenic strongly bound forms of oxygen but also the sorption of neutral, more easily reducible oxygen proceed on the activated surface. Contrary to the ionogenic forms of oxygen, the sorption centres for the weakly bound neutral oxygen are not determined only by the presence of nickel oxide in the sample.

Conclusions

In the NiO–Y_2O_3 mixed oxide system the NiO appears to be the only reducible component, its rate of reduction by hydrogen being a non-linear function of the composition. Although influencing the reduction kinetics, the presence of the thermodynamically more stable Y_2O_3 oxide does not affect the degree of reduction achieved.

The reduction kinetics can be positively influenced by the addition of platinum activator due to the spill-over and jump-over effects. Their efficiency increases with increasing proportion of Y_2O_3 which acts as a transmitter of atomic hydrogen. Similarly, this oxide causes the transformation of the negative kinetic effect caused by the addition of chloride and acetate anions to a positive effect (acceleration of the reduction). Oxalate or formate ions result in an insignificant positive effect depending on the composition of the samples. Heat treatment of the oxides in an Ar or oxygen atmosphere leads to an increase in the reactivity of the system during reduction as a result of surface activation.

Except samples with predominant content of Y_2O_3 the reduction rate is decreased by the pre-irradiation of the system with accelerated electrons and gamma rays at a dose of 1 MGy. This negative effect was found to be correlable with an increasing content of the strongly bound ionogenic oxygen retarding the donor chemisorption of reducing hydrogen. All of the physico-chemical parameters followed were found to be insensitive to pre-irradiation of the samples except the concentration of surface ionogenic oxygen. This quantity changes after irradiation non-monotonously with the composition and also with the age of the samples.

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