

EFFECTS OF GENESIS AND IONIZING RADIATION ON THE KINETICS OF REDUCTION OF NiO–CeO₂ MIXED OXIDES WITH HYDROGEN

M. Pospíšil

DEPARTMENT OF NUCLEAR SCIENCE AND PHYSICAL ENGINEERING,
TECHNICAL UNIVERSITY OF PRAGUE, 115 19 PRAGUE 1, CZECHOSLOVAKIA

(Received June 27, 1983)

The reduction of mixed oxides NiO–CeO₂ of various composition with hydrogen was studied at 290–470° by means of thermogravimetry. Some physicochemical properties of the system were also investigated and compared with earlier studied analogous samples of different "origin". The degree of mutual interaction of the two components, the reduction kinetics and the sensitivity to the different sorts of radiation (gamma-rays, fast neutrons and electrons), applied in different doses, are strongly affected by the "pre-history" and by the composition in both compared series of mixed oxides.

In our previous paper [1] the reduction of mixed oxides NiO–CeO₂ with hydrogen in the temperature range 260–500° was studied by means of thermogravimetry. Samples of various composition were prepared in air by thermal decomposition of mixed crystalline nitrates, obtained by evaporation of solutions of mixtures of the starting salts Ce^{IV}(NH₄)₂(NO₃)₆ · 6 H₂O and Ni(NO₃)₂ · 6 H₂O. The reduction kinetics and some physicochemical properties were studied with regard to the dependence on the composition of the system and the effect of pre-irradiation with gamma-rays and fast neutrons. It is known [2] that the conditions of preparation and also the genesis and the "pre-history" of the starting solids influence their reactivity. The aim of the present work was therefore to investigate the reduction of a similar system of oxides, but in this case prepared from a different starting salt of cerium Ce^{III}(NO₃)₃ · 6 H₂O, under otherwise identical conditions. The physicochemical properties of both series of mixed oxides of different "origin", and also the kinetics of their reduction, including reduction after pre-irradiation, were compared.

Experimental

The mixed oxides of various composition were prepared by thermal decomposition of the mixed nitrates. Solutions of Ce(NO₃)₃ · 6 H₂O and Ni(NO₃)₂ · 6 H₂O of reagent grade purity (concentration 1 mol l⁻¹) were filtered, mixed in the required ratios and evaporated to dryness. The crystalline product was decomposed in air, first for 1 h at 200°, and then for 3 h at 400°, and pulverized in an agate mortar.

The content of nickel was determined complexometrically after its separation with diacetyldioxime, and cerium was determined iodometrically after oxidation with ammonium persulphate.

The specific surface area of the samples was measured by means of the low-temperature adsorption of nitrogen from a nitrogen-hydrogen mixture. The morphology of the initial mixed oxides and of the reduced samples was studied using a JSM-50 A (Jeol) scanning electron microscope, and their microstructure was investigated by X-ray diffraction (Cu anode). The average size of the coherent regions of the two oxides was determined from the broadening of the selective reflections.

Part of the prepared mixed oxides was pre-irradiated in air with 10^5 and $5 \cdot 10^5$ Gy doses of ⁶⁰Co gamma-rays. The next fractions were further irradiated with fast neutrons in a commercial source with ²⁵²Cf (Radiochemical Centre, Amersham) so that the total dose was 285 Gy, and with electrons from $\alpha^{90}\text{Sr}$ — ^{90}Y source (IRYS-3, USSR), the total dose applied being $9 \cdot 10^3$ Gy. The content of ionogenic surface oxygen or the oxidation ability of the surface both of the original and of the irradiated samples was determined by iodometric titration. The reduction was followed in the temperature region from 290 to 470° under conditions strictly comparable for all series of mixed oxides under study. The reduction kinetics was studied by means of thermogravimetry. Conditions were established under which the rate and the course of the reaction do not depend on the flow rate of hydrogen for any arbitrary composition of the sample, and standard weight of the sample being 50 mg. In the given arrangement, this region can be guaranteed at a hydrogen flow rate of 56 ml/min, which was employed in all experiments.

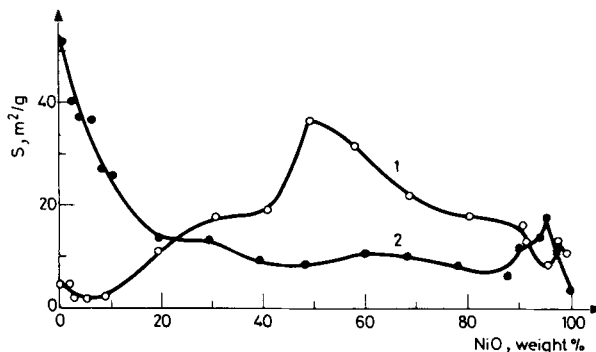
Results and discussion

Physicochemical properties of mixed oxides

It follows from the results of chemical (Table 1) and X-ray analysis that the applied experimental conditions (especially temperature, time and the atmosphere in the decomposition of the starting salts) yield a mixture of mixed oxides NiO—CeO₂ as the major components of the system under study. From the chemical point of view, therefore, it is analogous to the earlier-studied system of different "origin" [1], which will be designated in the following text as system A, in contrast to the present system, designated as system B. In both cases the oxides form separate phases, but the degree and the character of the mutual interaction of the two components are entirely different. This is already evident from the dependence of the specific surface areas on the composition: system A exhibits a pronounced maximum with the mixed oxides containing the components in the ratio 1:1 (Fig. 1, curve 1), whereas the surfaces of system B monotonously decrease with increasing content of NiO, and in the middle of the series are practically independent of the composition (curve 2). It follows from the morphological investigation of the samples that the magnitude of the surface areas are predominantly determined by the size of grains and agglomerates which are formed

Table 1 Compositions of NiO—CeO₂ mixed oxide samples

Sample	NiO, wt. %	CeO ₂ , wt. %	NiO + CeO ₂ wt. %
1	0.00	98.55	98.55
2	2.22	96.96	99.18
3	3.96	94.74	98.70
4	6.18	92.96	99.14
5	8.33	90.63	98.96
6	10.39	88.68	99.07
7	19.48	79.79	99.26
8	29.35	69.30	98.65
9	39.23	59.62	98.82
10	48.25	51.14	99.39
11	59.76	39.66	99.42
12	68.21	31.12	99.33
13	77.95	21.23	99.17
14	87.54	11.48	99.02
15	89.77	9.59	98.96
16	93.69	6.06	99.75
17	94.90	4.74	99.64
18	97.00	2.46	99.46
19	99.70	0.00	99.70

**Fig. 1** Dependence of the specific surface areas S (m²/g) of mixed oxides NiO—CeO₂ of different origin on the composition. 1 — series A (ref. 1), 2 — series B

in the region of CeO₂ excess by partially sintered grains of the majority component in system A (Fig. 2). In contrast, system B is characterized by larger grains, but the degree of sintering is substantially lower (Fig. 3). In both micrographs, samples of the same sintering with surface areas $S_A = 2.15$ m²/g and $S_B = 27.06$ m²/g are compared. The maximum dispersity of the grains of both components in the middle of series A is in accordance with the maximum of the dependence of the



Fig. 2 Electron micrograph of a sample of series A (ref. 1). Composition: 8.99 wt.% NiO and 89.37 wt.% CeO₂. Magnification $3 \cdot 10^3 \times$. The line segment indicated corresponds to $7 \mu\text{m}$

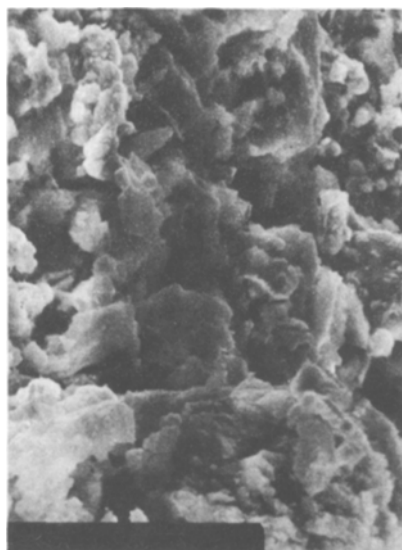


Fig. 3 Electron micrograph of sample no. 5; magnification $3 \cdot 10^3 \times$. The line segment indicated corresponds to $7 \mu\text{m}$

specific surface areas on the composition (Fig. 1). The smaller grain size of CeO₂ in this series, and the higher sensitivity of mixed oxides possessing an excess of CeO₂ to the processes of sintering during the thermal treatment [1], are connected with the high dispersity and the small size of the elementary microcrystallites of CeO₂, which lie in the interval 11.3–16.7 nm for the whole range of composition. The mixed oxides of series B are formed by the microcrystallites of both components, which are about twice as large as compared with system A, i.e. 22–29 nm for CeO₂ and 138–61 nm for NiO. In the latter case the size decreases with decreasing content of NiO. In contrast to series A, the thermal treatment under the same conditions does not lead to a pronounced decrease in the specific surface areas of the samples with an excess of CeO₂. It is very probable that the different dispersity and the epitaxial contact of the two components determine the different character of their mutual interaction in the two compared series.

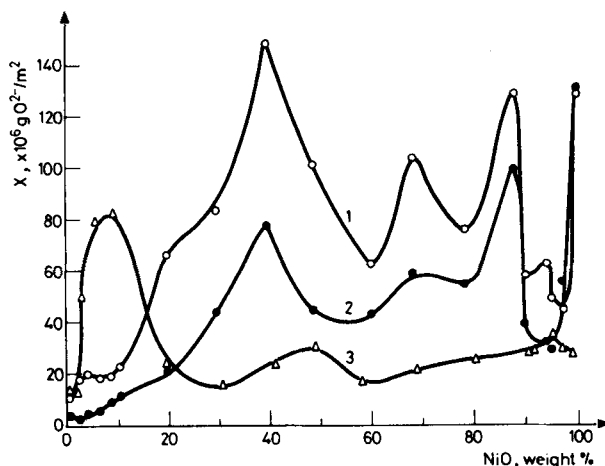


Fig. 4 Oxidation ability of the surface normalized to unit surface area X ($\text{g O}^2/\text{m}^2$) vs composition, 1 – series B after two-year storage in the air, 2 – series B, 3 – series A (ref. 1)

Figure 4 shows the dependence of the iodometrically determined content of superstoichiometric oxygen, or of the surface oxidation ability, normalized to unit surface area of the sample, on the composition. In the case of the *p*-semiconducting NiO, this quantity represents the surface concentration of Ni³⁺ ions which are charge-compensated by the ionogenic oxygen, and for the *n*-semiconducting CeO₂, analogously, the concentration of superstoichiometric interstitial Ce⁴⁺ ions [3]. From the course of the given dependences the different influence of the two components in the compared systems is evident. The high degree of charge interaction in both marginal regions of composition was proved in series A (curve 3), when addition of a small amount of the second component leads to an increase in the content of ionogenic

oxygen or of higher valency ions of both metals (Ni³⁺, Ce⁴⁺) due to the dissociative adsorption of molecular oxygen [1]. With series B (curve 2) the mutual influence in the region of excess CeO₂ is weaker with respect to the insufficient epitaxial contact, which also follows from the morphological investigation, so that the amount of oxygen continuously increases with increasing NiO content, up to about 40%. In the second marginal region the low-percentage addition of CeO₂ leads in contrast to a fall in oxygen content. The degree of interaction is again very high and the observed decrease can be explained on the basis of the general theory of semiconductors. Addition of a small amount of Ce⁴⁺ ions in the form of CeO₂ to NiO must result in a decrease in the nickel(III) ion concentration and therefore in the content of ionogenic oxygen. Curve 1 in Fig. 4 represents the same dependence for series B, which was measured after storage of samples in contact with the atmosphere for two years. The character of the dependence is identical with that for the original system, but the amount of chemisorbed oxygen is higher, except for the samples with the highest content of NiO. Besides the shift in the equilibrium of various forms of sorbed oxygen in favour of the strongly adsorbed ionogenic form, which proceeds with a very low rate, the establishment of a quantitatively new equilibrium due to the oxidation of minority Ce³⁺ ions by aerial oxygen can be assumed. In contrast, the stoichiometry of the oxides containing a high excess of NiO, including pure NiO is practically unchanged with time.

Table 2 Oxidation ability of the surface expressed by the wt.% of O²⁻ in the mixed oxides NiO-CeO₂ (X), and in the oxides pre-irradiated with γ -rays in a dose $D_\gamma = 5 \cdot 10^5$ Gy (Y), and the same quantities per unit surface area, X⁺ and Y⁺ (g O²⁻/m²)

Sample	X · 10 ⁻²	X ⁺ · 10 ⁻⁶	Y · 10 ⁻²	Y ⁺ · 10 ⁻⁶
1	1.7	3.3	7.3	14.2
2	1.1	2.7	7.4	18.4
3	2.0	4.6	4.7	18.1
4	2.0	5.5	9.9	26.9
5	2.2	8.2	9.4	37.7
6	2.9	11.2	7.5	29.8
7	2.8	20.2	10.3	77.9
8	5.8	43.9	10.6	79.7
9	7.2	77.5	11.3	121.2
10	3.8	44.7	10.9	128.1
11	4.6	43.1	9.4	88.2
12	6.0	59.1	9.8	96.2
13	4.4	54.3	8.6	107.3
14	6.1	99.2	10.2	166.9
15	4.4	38.3	9.6	82.8
16	4.3	31.6	9.0	65.5
17	3.7	29.1	8.5	67.8
18	6.1	55.2	9.7	92.4
19	4.1	130.6	5.6	180.5

Similarly as for series A [1], the rise in the content of chemisorbed oxygen in the whole range of composition was also observed for system B after its pre-irradiation with gamma-rays, the applied dose being $5 \cdot 10^5$ Gy (Table 2). With increasing content of NiO, the oxygen increment decreases. With the samples containing an excess of NiO, the concentration increase in the superstoichiometric oxygen is predominantly due to the above-mentioned shift in the equilibrium between various forms of adsorbed oxygen, as was found with pure NiO [4]. Moreover, partial radiation oxidation can proceed, which leads to a pronounced increase in the Ce⁴⁺ ions in the second marginal region of composition. The free charge carriers (electrons) created by irradiation may be stabilized either on the surface oxygen or on the various crystal defects, serving then as new donor centres for chemisorption of oxygen. All these processes result in an enhanced oxidation ability of the surface. In contrast to series A [1], the lower applied dose of gamma-rays (10^5 Gy) has no measurable influence on the amount of superstoichiometric oxygen. With the mixed oxides irradiated with fast neutrons and with electrons, the increase in the chemisorbed oxygen by about 30% was proved only in the samples containing a high excess of NiO. From a comparison of the magnitude of the effect as a function of the applied dose for both series of different "origin", it is evident that in the case of irradiation with fast neutrons or electrons the threshold dose must be exceeded similarly as was found with some pure metal oxides irradiated with gamma-rays [5, 6]. Moreover, both the threshold dose and the magnitude of the discussed effect are influenced by the genesis of the oxides, as well as by the degree of mutual interaction of the two oxides [7]. The specific surface areas crystallographic structures and chemical compositions of the samples were not affected by pre-irradiation, as a consequence of the relatively small doses used.

Kinetics of hydrogen reduction

In accordance with the previously studied series A, NiO is the only reducible component in the given temperature region in system B too. A pronounced influence on the reduction degree of the NiO in the initial stage of the process at lower temperatures by the presence of CeO₂ in the region of its excess was found with system A [1]. A similar effect was not observed with the mixed oxides of series B. This fact, in accordance with the above results, provides evidence for the lower extent of interaction of the two components in this region of composition. This is also borne out by the inexpressive dependence of the rate constants of the reduction on the composition (Fig. 5) in comparison with series A. In both cases, however, the reduction rate rises with increasing content of CeO₂ predominantly at higher temperatures of reduction. The rate constant (k) was calculated from the equation

$$\frac{\alpha + 0.3}{1 - \alpha} = A \exp(kt)$$

which describes the reduction kinetics of both studied systems. In this equation α is the degree of reduction in time t , and A is a constant. Since the reduction proceeds with the maximum rate close to the superficial layers of the grain, which follows from

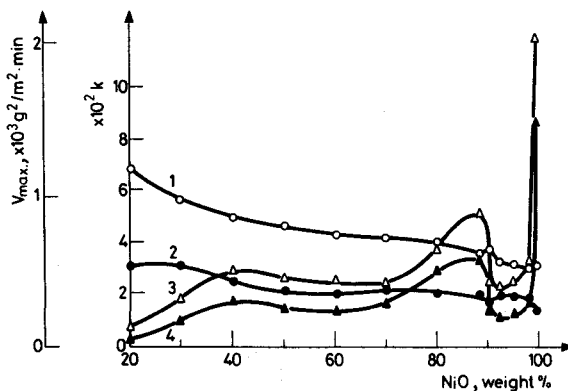


Fig. 5 Dependence of k (in arbitrary units) and of the specific V_{\max} ($\text{g}^2/\text{m}^2 \cdot \text{min}$) on the composition. Reduction temperature 380° : 1 - k , 3 - $V_{\max, s}$; or 290° : 2 - k , 4 - $V_{\max, s}$

the dependence of the instantaneous rate of the reduction on the reduction degree α , the maximum reduction rate (V_{\max}) was normalized to unit surface area of the samples. The dependence of the specific V_{\max} on the composition is also given in Fig. 5. This quantity can be seen to decrease with increasing content of CeO₂. This opposite course of the two quantities (k and V_{\max}), which was found not only for series A (1) but also for some other heterophase mixed oxides [8], is a consequence of several competitive processes which affect the rate of the reduction of NiO [1] and change the rate-determining step in the course of the reaction.

In the initial stage, the adsorption of hydrogen and the nucleation of metallic product on the reactive interface are retarded by the non-reducible CeO₂. In the region of a high excess of NiO and of the close epitaxial contact of the two components a small addition of CeO₂ results in a decrease in the specific V_{\max} . According to the electronic theory of chemisorption on semiconductors, the admixture of the n -type semiconducting CeO₂ should decrease the hydrogen adsorption with respect to its donor character on the surface of NiO. In contrast, in the final period, the CeO₂ facilitates the contact of the reducing gas with the reactive interface, as well as the transfer of the gaseous product (H₂O), because it hinders the formation of a compact layer of metallic product. Moreover, at the higher temperatures the CeO₂ can be partially reduced in the presence of a second component [1, 9]; this leads to the increase of the concentrations of oxygen vacancies in its lattice and of quasi-free electrons. The reduction rate therefore rises with increasing content of CeO₂. The local maxima of the specific V_{\max} , which lie at about 40 and 90 wt.% NiO (Fig. 5), correspond to the maximum values of the dependence of the normalized content of superstoichiometric oxygen on the composition. Since the content of the weakly-bound neutral form of adsorbed oxygen on NiO is several orders of magnitude higher than that of the ionogenic one [10], the higher surface concentration of all oxygen forms, including the easily reducible neutral form (physically adsorbed), can be

assumed in this close composition region. Only with these samples, therefore, is the specific V_{\max} higher. For the same reason, an increase in the reduction rate was observed for the samples measured after a two-year storage (Fig. 6, curve 2). It follows from Fig. 2 that a pronounced increase in the amount of chemisorbed strongly-bound oxygen was found with these mixed oxides, which should cause a decrease in hydrogen adsorption and therefore in the rate of reduction. With respect to the establishment of a new equilibrium, the amount of the iodometrically non-detectable weak form of oxygen must also be higher compared with the initial oxides, and hence the rate of reduction of stored samples should increase. The influence of the ageing of the samples on the reduction kinetics, which is shown in Fig. 6, is expressed by the

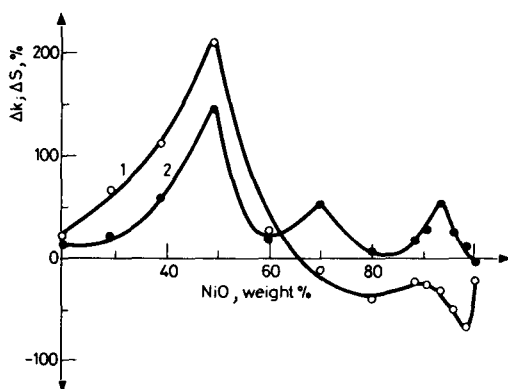


Fig. 6 Plot of Δk for the samples irradiated with γ -rays ($D_\gamma = 5 \cdot 10^5$ Gy) and of $\Delta S(\%)$ vs composition. Reduction temperature 320°: 1 — Δk , 2 — ΔS

quantity $\Delta S(\%) = 100 (k^x - k)/k$, where k^x is the rate constant of reduction of the samples after a two-year storage, and k is the value pertaining to the initial mixed oxides. From the dependence of ΔS on composition it is evident that the rate of reduction of stored samples is higher ($\Delta S > 0$) in the whole range of composition, except for the samples containing high excess of NiO, which do not exhibit changes in the content of superstoichiometric oxygen either. Analogously, an increase in the specific V_{\max} and a decrease in the apparent activation energy of reduction was found for the samples measured after the two-year storage. The effect of pre-irradiation on the reduction kinetics of the mixed oxides is shown in Fig. 6 (curve 1) as the dependence of the quantity Δk on the composition for the samples irradiated with gamma-rays at a dose of $5 \cdot 10^5$ Gy. Δk is defined analogously to the quantity ΔS , while k^x and k are the rate constants of the reduction of irradiated and initial samples, respectively, at the same temperature. From the given dependence, the negative effect of pre-irradiation ($\Delta k < 0$) follows in the region of an excess of NiO. This effect continuously reverts to a positive one with increasing content of CeO₂, and for the samples containing a very high excess of it the magnitude of the positive effect again

decreases. A similar course of this dependence was found for series A [1]. In contrast to the compared series A, the influence of a lower applied dose of gamma-rays (10⁵ Gy) was not observed, and the reduction of samples pre-irradiated with electrons and with fast neutrons proceeded at a lower rate only in the region of an excess of NiO. The decrease in the reduction rate of irradiated samples with a prevailing content of NiO is related with the concentration increase of the ionogenic oxygen or of the Ce⁴⁺ and Ni³⁺ ions after irradiation in the air. The higher-valency ions of the reducible major component (NiO) are compensated by the ionogenic strongly-bound oxygen, which hinders the hydrogen adsorption as well as the rate of reduction. The same effect was found with pure NiO [5]. With increasing content of CeO₂ possessing a defective lattice [3, 11], the concentration of the lattice and biographic perturbations increases, so that the electrons created by ionization can be trapped not only on the adsorbed oxygen but also on these defects. The probability of the latter process increases with rising content of CeO₂. As a result, the concentration of detectable Ni³⁺ and Ce⁴⁺ ions in the irradiated samples will be higher, but in this case these ions are not-compensated by ionogenic oxygen, so that they can serve as the acceptor sites for fast hydrogen adsorption. Consequently, the reduction rate increases and the negative radiation effect reverts to a positive one. The changes in the reduction of irradiated samples are accompanied by corresponding changes in the apparent activation energy, i.e. by its decrease in the region of a positive effect and its increase in the region of a negative radiation effect. The magnitude of the radiation-induced effects strongly depends on the temperature and on the interaction of the two components. With the samples of series B containing a high excess of CeO₂, the positive effect decreases owing to the insufficient influence of the two components. In the same region of system A, the effect reaches a maximum [1] with respect to the close contact of the two constituents. The inexpressive negative effect in the second marginal region (excess of NiO) of the samples pre-irradiated with fast neutrons and electrons, observed at low temperatures, is probably connected with the low applied dose, and it is also in accordance with the changes in the content of ionogenic oxygen. The different degree of interaction in the compared series, following from the non-monotonous dependence of the quantity Δk on the composition and from further results, probably causes the lower sensitivity of system B to γ -irradiation in the vicinity of the threshold dose (10⁵ Gy). In contrast to series A, neither changes in the content of oxygen nor changes in the reduction kinetics were found.

References

- 1 M. Pospíšil and I. Petrecký, Collection Czech. Chem. Commun., in press.
- 2 V. V. Boldyrev, M. Bulens and B. Delmon, The Control of the Reactivity of Solids, Elsevier, Amsterdam, 1979. p. 3.
- 3 R. Blumenthal and M. W. Lee, J. Electrochem. Soc., 118 (1971) 121.
- 4 I. Maxim and T. Braun, J. Phys. Chem. Solids, 24 (1963) 537.
- 5 T. Yamashina and T. Nagamatsuya, Bull. Chem. Soc. Jap., 38 (1965) 507.
- 6 M. S. Ansary, A. H. Tobgy and S. Y. Ezz, Hutnické listy, 9 (1966) 596.
- 7 M. Pospíšil and J. Topinka, Collection Czech. Chem. Commun., 46 (1981) 3198.
- 8 M. Pospíšil and O. Kušnierik, J. Thermal Anal., 25 (1982) 499.
- 9 K. Otsuka, M. Hatano and A. Morikawa, J. Catal., 79 (1983) 493.
- 10 J. Dereň and J. Stock, J. Catal., 18 (1970) 249.
- 11 D. J. Bevan and J. Kordis, J. Inorg. Nucl. Chem., 26 (1964) 1509.

Zusammenfassung — Die Reduktion gemischter NiO—CeO₂-Oxide unterschiedlicher Zusammensetzung mit Wasserstoff wurde thermogravimetrisch im Temperaturbereich von 290—470° untersucht. Einige physikalisch-chemische Eigenschaften des Systems wurden ebenfalls untersucht und mit denen früher untersuchter analoger Proben unterschiedlicher Herkunft verglichen. Der Grad der Wechselwirkung zwischen den zwei Komponenten, die Kinetik der Reduktion und die Empfindlichkeit gegenüber unterschiedlichen Dosen von verschiedenen Arten von Strahlungen (Gammastrahlen, schnelle Neutronen und Elektronen) werden stark durch die "Vorgeschichte" und durch die Zusammensetzung der beiden miteinander verglichenen Serien von gemischten Oxiden beeinflusst.

Резюме — Термогравиметрическим методом в области температур 290—470° изучено восстановление водородом смешанных окислов NiO—CeO₂ с различным составом. Исследованы некоторые физико-химические свойства этой системы окислов и сопоставлены с ранее изученными аналогичными образцами различного происхождения. Степень взаимодействия двух компонентов, кинетика реакции восстановления и чувствительность к различным типам и дозам облучения (гамма-лучи, быстрые нейтроны и электроны) сильно зависят от "предистории" и состава обеих серий смешанных окислов.