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STUDY OF REDUCTION KINETICS OF MIXED OXIDES $NiO-V_2O_5$ WITH HYDROGEN

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The reduction with hydrogen of mixed oxides $NiO-V_2O_5$ of various composition was studied at 350–470° by means of thermogravimetry. With increasing content of V_2O_5 the reduction rate and the oxidation state of vanadium in the reduction product decrease. A correlation has been found between some physico-chemical properties of the system and reduction kinetics which can be quantitatively described by an Erofeev equation. The mutual interaction of the two components is demonstrated by the non-monotonous dependences of the reoxidation, secondary reduction kinetics and rate of reduction of thermally treated samples on the composition.

In addition to pure V_2O_5, multicomponent oxide systems containing V_2O_5 are used as catalysts in oxidation processes. In some cases V_2O_5 is partially reduced to the lower oxides in the course of the catalytic reaction [1]. The presence of the other component markedly affects not only the activity of the catalyst [2], but also the kinetics of reduction of V_2O_5. From this point of view considerable interest has been devoted to the studies of the reduction of V_2O_5 and other oxides of polyvalent metals with a low-percentage admixture of Pt or Pd, which catalytically accelerate the reduction and slow down its initial temperature [3, 4] by the spill-over effect. Besides well-defined stoichiometric lower oxides of vanadium, several new intermediate phases have been found [5] in the composition range $V_2O_3-V_2O_5$. Their compositions and structures are unknown. The formation of these non-stoichiometric oxides as well as the degree of reduction of V_2O_5 can also be modified by the homogeneous or heterogeneous admixture of foreign substances. The present work deals with the study of the reduction kinetics of mixed oxides $NiO-V_2O_5$ with hydrogen as functions of their composition and some physico-chemical properties.

Experimental

In the preparation of the mixed oxides of various compositions, a solution of $Ni(NO_3)_2 \cdot 6\,H_2O$ (2 mol · l^{-1}) was filtered and mixed with a hot solution of NH_4VO_3 (0.25 mol · l^{-1}) in the required ratio. All components used were of reagent grade purity. After evaporation to dryness on a water-bath, the crystalline product was heated in air in an electric resistance furnace, first for 1 h at 200°, then for 4 h at 400°, and pulverized in an agate mortar. After dissolution of samples in concentrated hydrochlorid acid, the nickel content was determined gravimetrically with diacetyldioxime, and vanadium was determined in the filtrate by complexometric titration. The microstructure of the mixed oxides was studied by X-ray powder diffraction techniques (Debye-Scherrer), using a TUR M 62 generator (Zeiss) with a goniometer. Nickel-filtered Cu radiation was used ($\bar{\lambda} = 1.54178$ Å). The size of the coherent regions was quantitatively estimated for the two oxides in the system from the half-widths of the selective reflections. The specific surface areas were obtained from measurements of nitrogen adsorption at low temperature. The morphology of the initial mixed oxides and of the reduced samples were studied using a JSM-50 A (Jeol) scanning electron microscope. The ESR spectra of the whole series of mixed oxides as well as the reduced samples were obtained by means of an ERS 200 spectrometer (Zeiss, Jena). The content of superstoichiometric chemisorbed oxygen in the samples containing a high excess of NiO was determined by iodometric titration. The reduction kinetics was followed over the temperature range 350–470° using an earlier described thermogravimetric apparatus [6]. The limiting conditions were found where the rate and time cours of the reduction, for a standard sample weight of 50 mg, are independent of the flow rate of hydrogen for any arbitrary composition of the sample. Accordingly, the hydrogen flow rate of 56 ml • min^{-1} was employed in our experimental arrangement.

Results and discussion

The notations of the mixed oxides, their compositions and specific surface areas, and the sizes of the coherent regions are given in Table 1.

It follows from the results of the analysis that the used conditions of the decomposition yield a mixture of nickel oxide and vanadium pentoxide which, in the sum of the weight percentages, do not attain 100%. In addition to the separate phases of both these oxides, the presence of vanadium(III) oxide was found by X-ray diffraction in the samples containing a comparable amount of the two major components (samples 7–13). The original oxides up to 10 wt% of V_2O_5 exhibit an ESR signal due to paramagnetic V^{4+} ions. Their concentration decreases monotonously with increasing content of NiO. Since the most intensive signal was found for sample 1 (pure V_2O_5), the presence of V^{4+} ions is probably connected with the formation of solid solutions of vanadium oxides of different stoichiometry, whereas under the given conditions NiO does not form a solid solution with V_2O_5. It is further known [7] that the preparation of the spinel $NiV_2^{(3+)}O_4$ by direct reaction of the two components in the solid phase at high temperatures (~ 900°) is impossible, owing to the reduction of NiO. For this reason the presence of the above spinel phase can also be excluded from the system under study.

Table 1 Sample compositions, specific surface areas (*S*) and the sizes of the coherent regions (*L*) in mixed oxides NiO–V_2O_5

Sample	wt%		mol%		S, m^2/g	L, nm	
	NiO	V_2O_5	NiO	V_2O_5		NiO	V_2O_5
1	0.00	97.64	0.00	100.00	3.8	–	53.7
2	1.14	94.35	2.78	97.22	4.4	–	93.8
3	2.58	91.62	6.42	93.58	5.3	–	222.6
4	3.36	91.20	7.36	92.64	5.1	–	87.0
5	6.00	89.31	13.05	86.95	4.3	–	63.7
6	6.72	88.76	15.49	84.51	5.7	–	87.0
7	12.53	83.27	26.81	73.19	10.1	–	73.0
8	23.51	72.61	44.13	55.87	12.6	–	75.3
9	30.03	67.80	51.76	48.24	15.4	–	87.0
10	41.15	57.46	63.52	36.48	17.1	–	95.1
11	45.58	54.18	72.27	27.73	16.8	–	105.6
12	52.81	43.06	74.98	25.02	18.7	42.4	55.8
13	71.55	26.05	86.93	13.07	19.2	64.3	200.2
14	83.50	12.61	91.87	8.13	23.7	52.0	–
15	85.16	10.23	95.30	4.70	28.1	49.0	–
16	88.19	7.62	96.57	3.43	27.3	49.0	–
17	91.97	4.88	97.86	2.14	25.1	59.2	–
18	95.22	2.86	98.78	1.22	21.6	56.5	–
19	96.26	–	100.00	0.00	13.2	61.0	–

A mutual interaction of the two major constituents is demonstrated by the non-monotonous dependence of the specific surface area on the composition, which has a maximum at about 80–90 wt% of NiO in the sample (Table 1). As follows from the study of the sample morphology and from the dependence of the size of the coherent regions on composition, the higher surface area values for the samples containing an excess of NiO are determined not only by the high dispersity of its crystallites (Table 1), but predominantly by the higher dispersity of its grains and agglomerates (Fig. 1) as compared with those of V_2O_5 (Fig. 2).

Table 2 summarizes the results of the iodometric determination of the chemisorbed oxygen contents of the freshly prepared oxides and the same samples after storage for three months in air at laboratory temperature. The determination was carried out only with the samples containing a pronounced excess of NiO, owing to the solubility of V_2O_5 in the weakly acidic solution used. From this Table it is evident that the amount of chemisorbed oxygen normalized to unit surface area of the sample (Table 2, Y) decreases with increasing content of V_2O_5. From this it can be assumed that the oxygen is predominantly chemisorbed on NiO, which is in accordance with its *p*-type semiconductive character. In the case of V_2O_5, the *n*-type semiconductor connected with the oxygen deficit of the lattice has been proved experimentally, in agreement with the published data [8]. On the other hand, the absolute amount of ionogenic

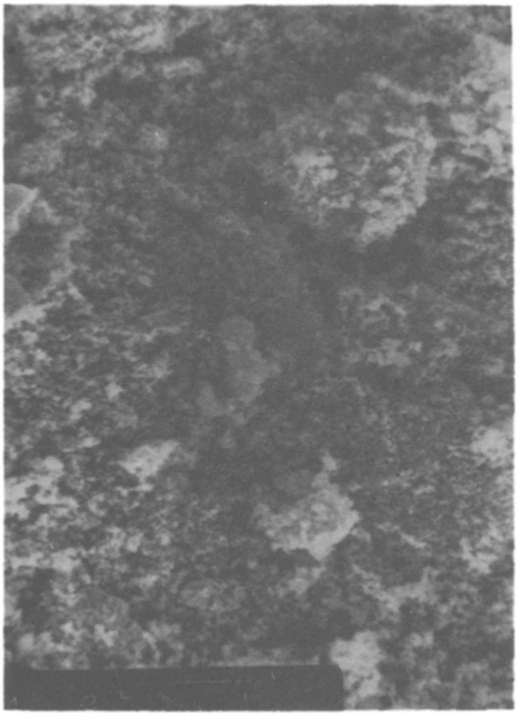

Fig. 1 Electron micrograph of fresh sample 17. Magnification $3 \cdot 10^3$ x; the line segment indicated corresponds to 6 μm

oxygen (Table 2, X), as well as its amount normalized to unit content of nickel in the sample, increases with increasing content of V_2O_5. In the region of low concentrations of V_2O_5 this oxide is highly dispersed, so that it influences the concentration and reactivity of the adsorption centres of the major component, i.e. NiO. In agreement with the concepts of the electron theory of adsorption on semiconductors, the addition of V_2O_5 as an *n*-type semiconductor shifts the Fermi level towards the conductivity band on the surface of NiO, which leads to the increasing of the oxygen adsorption with respect to its acceptor character. Moreover, the oxygen adsorption on V_2O_5 can also be taken into consideration. In addition to the presence of the weakly bonded (iodometrically non-detectable) forms of oxygen [9, 10], the depletive chemisorption of ionogenic forms, which is characterized by a low degree of coverage of the V_2O_5 surface, has also been proved [8, 11]. The increase in the content of chemisorbed oxygen with increasing age of the samples (Table 2, B) is probably connected with the slow rate of establishment of the adsorption–desorption equilibrium on the surface, which has also been observed for several other oxide systems [12]. The direct influencing of both components can be further assumed in the region

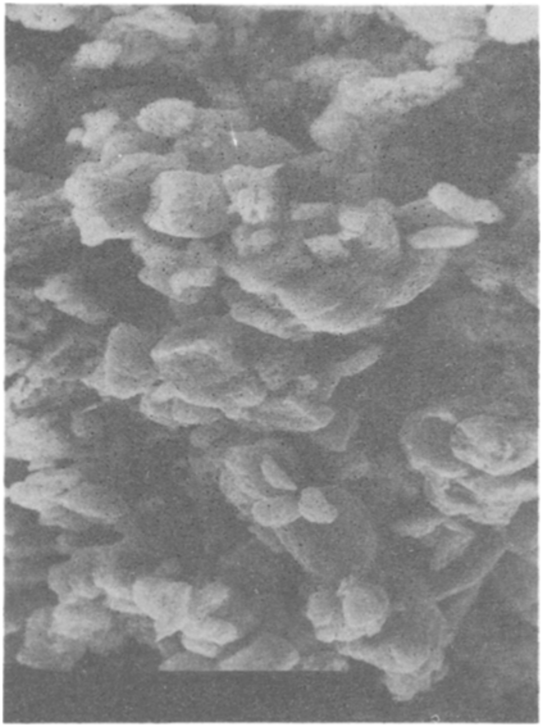

Fig. 2 Electron micrograph of fresh sample 1. Magnification $3 \cdot 10^3$ x; the line segment indicated corresponds to 6 μm

Table 2 Content of chemisorbed ionogenic oxygen, *X* (wt%), and the same quantity per unit surface area, *Y* (g O^{2-}/m^2) in the fresh mixed oxides (*A*) and in the same samples after storage for 3 months in air (*B*)

Sample	*A*		*B*	
	$X \cdot 10^{-2}$	$Y \cdot 10^{-5}$	$X \cdot 10^{-2}$	$Y \cdot 10^{-5}$
19	3.29	2.49	4.31	3.26
18	4.85	2.24	6.56	3.04
17	5.01	1.99	7.58	3.02
16	5.32	1.94	8.20	2.99

of higher concentrations of V_2O_5, which manifests itself by the shift of the equilibrium of their lattice oxygen. This follows from the presence of an independent phase of V_2O_3 only for the mixed oxides containing the two components in the ratio 1 : 1, as well as from the pronounced changes in the rate and degree of oxidation of nickel by atmospheric oxygen as a function of composition after the primary reduction of the system. In the samples from the series centre which, after the total reduction of both oxides at 440° and their removal from the reactor, were cooled down in air, the phases of Ni, V_2O_3 and of the higher oxides of both components (VO_2, V_2O_5, NiO) formed by reoxidation have been proved. In contrast for the samples containing a low concentration of vanadium oxides which after primary reduction were oxidized under the same conditions, no measurable oxidation of metallic nickel was observed.

The mutual interaction of the two components also manifests itself in the starting temperature of the reduction, which changes depending on the composition. At 350° only the samples with an excess of NiO (up to 46 wt%) are reduced at a measurable rate, while the reduction of all samples including pure V_2O_5 proceeds to maximum degree at the highest temperatures of the interval applied (440, 470°). From the weight losses at given temperatures, the oxidation states of vanadium in the reduction product were calculated and compared with the composition of the solid phase according to the literature data [13]. The calculation was carried out with the assumption of the total reduction of NiO to nickel, which was verified experimentally. For thermodynamic reasons, under the given conditions V_2O_5 can be reduced only to oxides of lower valency. The results of this comparison are given in Table 3, which reveals the dependence of the oxidation states of vanadium in the reduction product on the composition of the initial oxides. In contrast to sample 1 (pure V_2O_5), in the mixed samples possessing an excess of NiO the V_2O_5 is not reduced, even at the given highest temperatures where the NiO is totally reduced. On the other hand, in the region of equal concentrations of the two components the presence of metallic nickel determines the partial reduction of V_2O_5 even at 380°, when the reduction of pure V_2O_5 does not proceed at a measurable rate. In this case the metallic nickel probably facilitates the electron transfer and therefore the reduction of the second component. In the former case, however, the reactive centres of V_2O_5 are blocked by a high excess of metallic phase and partially sintered metal hinders the hydrogen transfer. This follows from the pronounced increase in the size of nickel microcrystallites in the course of reduction, proved only for the samples containing an excess of NiO, as well as from the dependence of the surface areas on the reduction degree α, which differs in the samples of various compositions. Figure 3 shows the continuous growth of the surface area of pure V_2O_5 with the increasing degree of its reduction, up to the maximum corresponding to the composition of the reduction product $V_2O_3 + V_3O_5$ (curve 1) and, in contrast, the decrease in surface area for the samples containing the excess of NiO corresponding to the crystallochemical transformation of NiO to nickel (curve 3). For the mixed oxides containing an excess of V_2O_5, the starting growth of the surface area is connected with the formation of the major

Table 3 Values of the experimentally found oxidation states of vanadium (V_2O_x) at reduction temperatures 440 and 470° and the corresponding compositions of the solid phase according to [13]

Sample	440°		470°	
	oxidation state *x*	composition of solid phase	oxidation state *x*	composition of solid phase
1	3.19	$V_2O_3 + V_3O_5$	3.19	$V_2O_3 + V_3O_5$
2	3.11	V_2O_3	3.21	$V_2O_3 + V_3O_5$
3	3.22	$V_2O_3 + V_3O_5$	3.19	$V_2O_3 + V_3O_5$
4	3.21	$V_2O_3 + V_3O_5$	3.26	$V_3O_5 + V_4O_7$
5	3.47	V_4O_7	3.31	V_3O_5
6	3.25	V_3O_5	3.32	V_3O_5
7	3.39	$V_3O_5 + V_4O_7$	3.38	$V_3O_5 + V_4O_7$
8	3.85	$V_7O_{13} + VO_2$	3.48	V_4O_7
9	3.91	$V_7O_{13} + VO_2$	3.71	V_7O_{13}
10	4.36	V_6O_{13}	3.85	$V_7O_{13} + VO_2$
11	4.57	$V_6O_{13} + V_3O_7$	3.99	VO_2
12	3.77	V_7O_{13}	3.61	V_5O_9
13	4.10	$VO_2 + V_6O_{13}$	3.75	V_7O_{13}
14	4.00	VO_2	3.78	V_3O_5
15	3.06	V_2O_3	3.28	V_3O_5
16	4.23	$VO_2 + V_6O_{13}$	3.67	$V_5O_9 + V_6O_{11}$
17	5.00	V_2O_5	5.00	V_2O_5
18	5.00	V_2O_5	5.00	V_2O_5

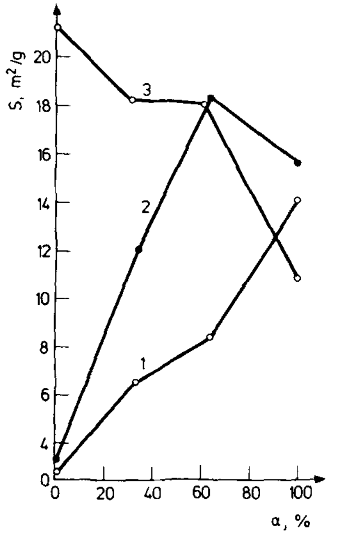

Fig. 3 Dependence of the specific surface area (m^2/g) on the reduction degree α. Reduction temperature 440°. Samples: 1 (1), 5 (2) and 14 (3)

reduction products (lower oxides of vanadium). At a maximum of the function $S = f(\alpha)$, as contrasted with the initial state, all NiO is totally reduced and the subsequent sintering and recrystallization of nickel brings about a drop in surface area (curve 2).

The dissimilar characters of the mutual interaction of the two components in the different regions of composition also follows from the dependence of the reduction rate on the composition (Fig. 4).

In contrast to the reduction degree, the reduction rate of V_2O_5 is practically unaffected by the presence of the NiO up to about 60 wt%. The low-percentage admixture of V_2O_5 however results in a decrease in the reduction rate of NiO. Figure 4 further demonstrates the qualitatively similar dependences of the maximum reduction rate and the rate constant on the composition of the mixed oxides. With respect to the non-monotonous course of both these dependences, the decrease in the reduction rate with increasing content of V_2O_5 is not due to V_2O_5 being thermodynamically a more difficult component to reduce. Provided that the donor-type chemisorption of hydrogen is the rate-determining step of the reduction, it may be expected that the addition of V_2O_5 as an n-type semiconductor leads (in the event of the sufficient contact of the two components) to the lowering of this adsorption and therefore the reduction rate. The second cause of the lowering of reduction rate with increasing content of V_2O_5 can be the blocking of reactive interphase NiO—Ni by the V_2O_5 or its lower oxides which are finely dispersed in the system at low concentrations. The discontinuous change of the interaction degree of the two components in the region of the local minimum in Fig 4 (about 95% of NiO) is also evident from further experimental results. In contrast to other samples, the NiO, which has the highest dis-

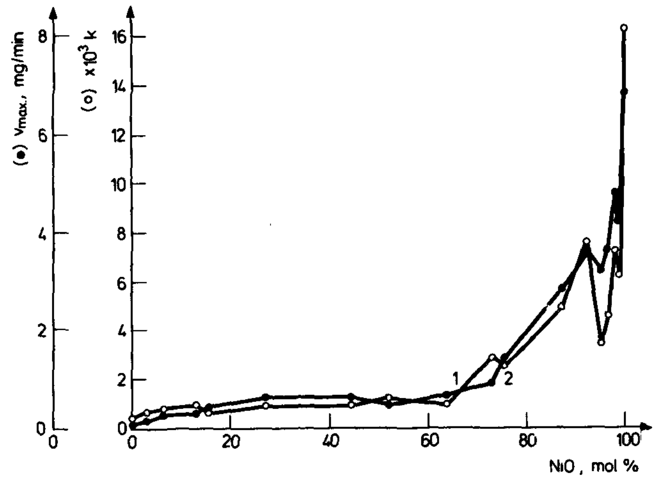

Fig. 4 Dependence of k (in relative units) and of V_{max} (mg · min^{-1}) on the composition. Reduction temperature 440°. (1) k, (2) V_{max}

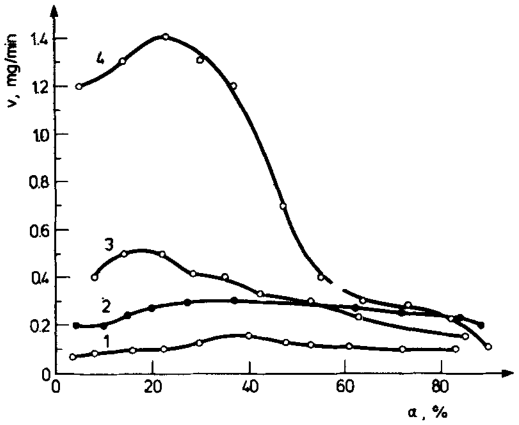

Fig. 5 Plot of reduction rate v (mg • min^{-1}) at 440° *vs* reduction degree α. Samples: 1 (1), 5 (2), 9 (3) and 12 (4)

persity in this region (Table 1), is not totally reduced at lower temperatures. In contrast, in the presence of metallic nickel at higher temperatures, V_2O_5 is reduced to its lowest oxidation state, i.e. V_2O_3 (Table 3). The decrease in the reduction rate for the low-percentage admixture of V_2O_5 is accompanied by an increase in the apparent activation energy (E_a) from 64 kJ/mol (for pure NiO) up to about 117 kJ/mol for the reduction of the samples in the region of the local minimum. With further increase in the content of V_2O_5, E_a increases up to 172 kJ/mol in the region of the highest excess of V_2O_5. From the dependence of the reduction rate on the reduction degree α (Fig. 5) the autocatalytic character of the reduction for all samples of the series is evident. With increasing content of V_2O_5 the rate maximum shifts towards higher values of α. The inflexion in the curve of the reduction of pure V_2O_5 (curve 1) before the maximum corresponds to the solid-phase composition $V_2O_{4.34}$, and the value of the maximum reduction rate accords with the composition VO_2, analogously as in [11].

The reduction kinetics of the mixed oxides (pure NiO inclusive) can be quantitatively expressed by the Erofeev equation [14] $\alpha = 1 - \exp[-kt^n]$, assuming gradual nucleation. In the given relation α is the reduction degree at time t, and k is the total rate constant. In accordance with the morphological examination of the partially reduced samples the exponent $n = 2$ gives evidence for the two-dimensional growth of the nuclei.

The thermal pretreatment of the samples in air for 1 h at 300–450° brings about a pronounced increase in the reduction rate for pure V_2O_5 and mixed oxides containing more than 2.1 wt% of V_2O_5, in spite of the fact that at higher treatment temperature the specific surface areas are lowered by approximately 30–40%, depending on the composition. The thermal activation is probably due to the desorption of trace amounts of water and gaseous impurities from the active surface sites.

Moreover, the new active centres are formed by the partial thermal dissociation of V_2O_5 during the treatment [9]. The mutual interaction of the two componets of the system also manifests itself in the dependence of the secondary reduction and reoxidation kinetics on the composition. These processes have been studied at 440°: the primarily reduced samples were oxidized to a constant degree in the air flow and then secondarily reduced with hydrogen at the same temperature. Owing to the presence of the vanadium oxides, the formation of a relatively compact layer of the oxide on the surface of the nickel grain is hindered, and hence both the rate and degree of the oxidation of nickel in the mixed oxides are markedly enhanced as compared with the pure oxide. The oxidation therefore proceeds, depending on the composition, with a maximum rate in the centre of the series. For the primarily reduced samples containing an excess of V_2O_5, the oxidation proceeds at a high initial rate. As soon as the oxygen content corresponds to the stoichiometry VO_2, the rate of oxidation decreases. The oxidation of these samples is quantitative and its product consists of the nascent oxides NiO and V_2O_5 with a non-stabilized structure. The rate of their secondary reduction is therefore twice as high as for the primary process. With increasing content of NiO, the difference in the primary and secondary reduction rates diminishes. The absolute rate of the secondary reduction increases similarly to the primary one.

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Zusammenfassung — Die Reduktion von NiO—V_2O_5-Gemischen verschiedener Zusammensetzung mit Wasserstoff wurde im Temperaturbereich von 350—470° thermogravimetrisch untersucht. Sowohl die Reduktionsgeschwindigkeit als auch der Oxydationsgrad des Vanadiums im Reaktionsprodukt nehmen mit steigendem V_2O_5-Gehalt ab. Eine mit der Erofeev-Gleichung quantitativ zu beschreibende Korrelation zwischen einigen physikalisch-chemischen Eigenschaften des Systems und der Reduktionskinetik wurde festgestellt. Die gegenseitige Wechselwirkung zwischen beiden Komponenten kommt auch durch die nicht-monotonen Abhängigkeiten der Reoxydation, der sekundären Reduktionskinetik und der Geschwindigkeit der Reduktion thermisch behandelter Proben von der Zusammensetzung zum Ausdruck.

Резюме — С помощью термогравиметрии была изучена при температуре 350—470° реакция восстановления водородом смешанных окислов $NiO-V_2O_5$ различного состава. Найдено, что с увеличением содержания V_2O_5, в продукте восстановления уменьшается как скорость восстановления, так и валентность ванадия. Кинетика реакции восстановления количественно описывается уравнением Ерофеева. Установлена корреляция между некоторыми физико-химическими свойствами системы и кинетикой реакции восстановления. Совместное взаимодействие обоих компонент подтверждается наличием немонотонной зависимости реакции реокисления, вторичной реакций восстановления и скоростью реакции восстановления термически обработанных образцов.