REDUCTION OF $NiO-Mn_2O_3$ MIXED OXIDES WITH HYDROGEN AND ITS AFFECTING BY IONIZING RADIATION

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Reduction of $NiO-Mn_2O_3$ mixed oxides with hydrogen was studied thermogravimetrically at 350–440°C; in the entire composition region, 0–100% of one component, total reduction with the formation of a heterogeneous Ni–MnO system was observed. The character of the kinetic curves of reduction of Mn_2O_3 is affected by the way of preparation and heat treatment of the samples before their reduction in inert atmosphere. In the mixed oxide, nickel accelerates the reduction of manganese sesquioxide, proceeding *via* Mn_3O_4 intermediate product. The mutual interaction of the two components appears in the pronounced dependence of the reaction rate on the composition, correlable with the analogous dependence of the apparent activation energy of reduction. The extent of the interaction, morphological changes, and some physicochemical parameters depend upon the degree of dispersion of the two oxides, which is also a function of the composition. A prior irradiation of the samples by gamma radiation, dose $8 \cdot 10^5$ Gy, or fast neutrons, fluency $6{\cdot}8 \cdot 10^{15}$ n/m^2 ($D_n = 28{\cdot}1$ Gy), brings about a substantial increase in the content of the chemisorbed oxygen, particularly in the range of excess Mn_2O_3. The gamma irradiation results in an acceleration of the reduction of the mixed oxides; the extent of this positive effect is a nonmonotonic function of the composition and depends markedly on the temperature. The complex influence of fast neutrons appears as a negative effect (lowering of the reduction rate) resulting from the destruction of the existing centres (the polishing effect); in dependence on the composition the effect inverts into a positive one on the generated and stabilized new centres, which affect the rate of nucleation of the nickel metal phase.

In the field of study of metal oxides reduction with gases, attention has been recently drawn to polyvalent metal oxides that for thermodynamic reasons are only reduced to lower oxidation degrees[1,2]. In a two-component mixed system the kinetics and degree of reduction can be altered by the presence of the other oxide that in the conditions applied is reduced as far as the metal. Such systems can serve after the reduction as catalysts of various reactions[1,3], the catalytic activity of the metal phase being dependent upon the composition, dispersity, oxidation degree of the other component, as well as other properties of the system[3,4].

In the present work, the reduction of manganese and nickel mixed oxides with hydrogen has been studied and the effect of the composition on the kinetics of the reduction has been investigated. Attention has been also paid to changes in some physicochemical parameters in dependence on the composition. The reactivity of the mixed oxides has been also altered by prior irradiation by gamma radiation of the radionuclide ^{60}Co and by fast neutrons from a ^{252}Cf source, and the effect of the irradiation on the kinetics of the reduction has been examined.

EXPERIMENTAL

The mixed oxides of various composition were prepared by thermal decomposition of the mixed nitrates. 1M solutions of nitrates of the two metals were prepared from the chemicals *p.a.* purity and mixed in the desired ratios. After evaporation to dryness on a water bath, the crystalline product was annealed in an electric resistance furnace. According to[5], dehydrated manganese(II) nitrate decomposes at approximately 200°C to manganese dioxide, which decomposes subsequently to manganese sesquioxide at 530°C. The mixed nitrates were therefore decomposed in air stream first for 30 min using linear rise of temperature (18°C/min) and then for 4 h at 540°C. A fraction, grain size 0·05–0·125 mm, was selected for subsequent experiments by screening the powder preparation. The content of the two metals was determined chelatometrically. The microstructure of the samples was studied by using the Debye–Scherrer and the back-reflection methods. The size of the coherent regions was calculated for the two oxides in the system from the diffraction line half widths. The specific surface areas were obtained from measurements of nitrogen adsorption at low temperatures, the morphology of the initial mixed oxides and of the reduced samples was investigated by means of a scanning electron microscope JSM-50 A (Jeol). The samples were divided into several portions. The first portion was irradiated by gamma radiation from a cobalt source applying the dose of $8 . 10^5$ Gy, the second portion by fast neutrons in a source with ^{252}Cf (Amersham), fluency $6{\cdot}86 . 10^{15}$ n/m^2 (applied dose $D_n = 28{\cdot}1$ Gy). The reduction of the mixed oxides was examined in the temperature region of 350–440°C in the same experimental conditions for the initial oxides and for the prior irradiated samples. The kinetics of reduction was monitored thermogravimetrically using the apparatus[6] in conditions where the time course and reduction rate were independent of the hydrogen flow rate (standard weight of the sample 50 mg irrespective of the composition, hydrogen flow rate 56 ml min^{-1}). The sample numbering, specific surface areas, and size of the coherent regions are summarized in Table I.

RESULTS

The analytical data obtained (Table I) indicate that in the conditions applied, the decomposition of the initial salts results in the formation of two-component mixed oxides NiO–Mn_2O_3; their presence was also confirmed by microstructural analysis. Moreover, additional selective reflections were observed for samples with excess manganese, corresponding to the most intense reflections of manganese dioxide. The presence of an intermediate product with spinel structure in amounts detectable by X-ray analysis is unlikely with regard to the conditions of preparation, because the temperature necessary for a complete decomposition $Mn_2O_3 \rightarrow Mn_3O_4$ is about 940°C (ref.[5]). The occurrence of manganese in a higher oxidation state is indicated also by the content of overstoichiometric oxygen. As follows from Fig. 1, the content of chemisorbed oxygen normalized to the sample surface area increases monotonically with the increasing content of manganese. Analogous is also the dependence of the normalized content of ionogenic oxygen on the composition of samples prior irradiated by gamma radiation or fast neutrons. In both cases the irradiation brings about rise in the oxygen content within the entire composition region, by as much as one order of magnitude in the range of excess manganese sesquioxide (Table II). Chemisorption of oxygen increases also if samples with high proportion of nickel oxide are thermally treated at 500°C in argon atmosphere. A mutual interaction of the two constituents appears in the nonmonotonic dependence of all the examined physicochemical parameters on the composition. The specific surface areas, which cannot be summed up additively from those of the pure components, display a maximum for approximately 20 – 30 mol% Mn_2O_3 (Table I). In the same region lie the maximum absolute

TABLE I

Composition, Specific Surface Area (S), and Size of Coherent Regions (L) of NiO–Mn_2O_3 Mixed Oxides

Sample	Wt. %			Mol. %		S $m^2 g^{-1}$	L, nm	
	NiO	Mn_2O_3	NiO + Mn_2O_3	NiO	Mn_2O_3		NiO	Mn_2O_3
1	—	97·67	97·67	—	100·00	0·71	—	30·86
2	2·33	96·69	99·02	4·85	95·15	1·59	—	43·08
3	7·27	90·76	98·03	14·42	85·58	4·96	—	39·14
4	12·84	82·88	95·72	24·64	75·36	9·75	—	45·24
5	24·22	73·01	97·23	41·22	58·78	10·73	—	41·14
6	33·54	63·14	96·68	52·89	47·11	13·85	—	33·17
7	40·04	53·28	93·32	61·37	38·63	22·63	—	28·84
8	50·29	43·41	93·70	71·00	29·00	32·27	—	28·84
9	59·42	33·54	92·96	78·92	21·08	38·48	—	22·99
10	73·32	23·68	97·00	86·75	13·25	25·32	20·57	—
11	85·30	13·32	98·62	93·13	6·87	24·67	32·78	—
12	95·08	3·16	98·24	98·95	1·55	20·71	39·94	—
13	97·88	—	97·88	100·00	—	8·70	35·04	—

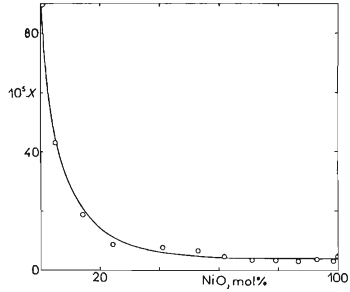

FIG. 1

Dependence of the Content of Ionogenic Overstoichiometric Oxygen per Unit Surface Area X ($g_{O^{2-}}/m^2$) on the Composition content of ionogenic oxygen (Table II), maximum deficit in the chemical analysis, and minimum size of the crystallites of the two components (Table I). As follows from the study of the sample morphology, these dependences, particularly that of the specific area, are correlable with the dependence of the agglomerate size on the composition. In the case of mixed oxides with a pronounced excess of nickel oxide, the reduction is accompanied by destruction of the grains ($d_{eff} \approx 5.10^4$ nm) with large

TABLE II

Content of Ionogenic Overstoichiometric Oxygen in the Initial $NiO-Mn_2O_3$ Mixed Oxides (*A*) and in the Corresponding Samples Irradiated by Gamma Rays (*B*) and by Fast Neutrons (*C*)

Sample	Content, 10^{-2}% (wt.)		
	A	*B*	*C*
1	6·4	79·9	65·2
2	6·9	63·0	44·7
3	9·4	50·0	38·2
4	8·8	55·6	57·6
5	8·5	44·3	61·5
6	11·0	57·9	60·5
7	9·4	76·1	94·7
8	10·2	63·5	69·7
8[a]	90·2	—	—
9	11·1	52·1	99·6
10	6·9	53·9	57·1
11	9·6	71·0	73·2
12	5·6	35·6	36·4
13	4·5	8·1	8·5

[a] Sample thermally treated in argon for 1 h at 500°C.

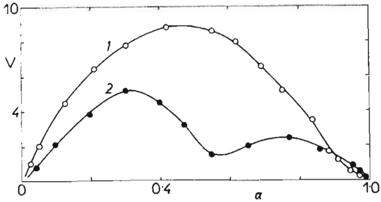

FIG. 2

Dependence of the Reduction Rate *V* (mg/ /min) on the Reduction Degree α

Reduction temperature 440°C; *1* sample 12, 2 sample 3.

surface into ones of average size $d_{\text{eff}} \approx (2-4)\,10^2$ nm. Samples possessing excess manganese sesquioxide form agglomerates with practically nonporous structure ($d_{\text{eff}} \approx 8.10^4$ nm), whose size decreases on the reduction down to $d_{\text{eff}} \approx 1.10^4$ nm. Apparently, in the composition region of 20–30 mol.% Mn_2O_3 the dispersity of the two components is highest. Irradiation of the mixed oxides by the doses applied does not bring about measurable changes in the surface areas or microstructure of the samples. In the temperature region in question, 350–440°C, both constituents of the system are reduced.

The shape of the curves of the reduction course, however, changes appreciably with the composition. As can be seen from Fig. 2, characteristic of mixed oxides with excess manganese sesquioxide is reduction with two expressive rate maxima, lying in the regions of reduction degree $\alpha \approx 0{\cdot}3$ and $0{\cdot}7-0{\cdot}8$. As the content of nickel oxide grows, the second maximum gradually vanishes and the dependence $v = f(\alpha)$ converts to one of an autocatalytic process typical of reduction of nickel oxide, with a single rate maximum at $\alpha \approx 0{\cdot}3-0{\cdot}4$. The reduction of nickel oxide proceeds in these conditions with a higher rate than the reduction of the other component, the length of the induction period being at the given temperature independent of the composition. The maximum experimental weight losses (at the reduction temperature 440°C) correspond to the theoretical values calculated for reduction of nickel oxide to nickel and manganese sesquioxide to manganese monoxide, which indicates that the system is reduced completely; only in the case of sample No 1 (pure Mn_2O_3), the theoretical loss was 27 wt.% surpassed.

The kinetics of reduction of nickel and manganese mixed oxides can be quantitatively described by the equation $1 - \alpha = e^{-kt}$, where α is the reduction degree in the time t and k is the rate constant; only the samples in the comparatively narrow composition range of 50–70 mol.% NiO are exceptional, being in a wide region of $\alpha \approx 0{\cdot}05-0{\cdot}95$ better described by the Prout–Tompkinson equation modified by Bond[7], $(0{\cdot}3 + \alpha)/(1 - \alpha) = e^{kt}$. The apparent activation energy of reduction was calculated from the rate constant dependence in Arrhenius co-ordinates; it was found to decrease monotonically from 125·6 kJ mol^{-1} for reduction of sample No 1 (pure Mn_2O_3) down to 79·5 kJ mol^{-1} for sample No 8 (70 mol.% NiO) and then to increase again with growing content of nickel oxide, up to 100·5 kJ mol^{-1} for reduction of this oxide in the absence of manganese sesquioxide.

The dependence of the maximum rate of reduction on the composition is in a qualitative agreement with the analogous dependence of the rate constant (Fig. 3). In the case of samples with excess manganese sesquioxide, the first rate maximum at $\alpha \approx 0{\cdot}3$ was considered. From the dependences shown it is also apparent that the rate of reduction of nickel oxide at the given temperature is higher than that for the other constituent. A low-percentage addition of manganese sesquioxide brings about a rapid drop of the rate of reduction of nickel oxide, whereas nickel oxide addition rises the rate of reduction of manganese sesquioxide up to a maximum reached for approximately 60–70 mol.% NiO. The character of the dependence is the same in the entire region of reduction temperatures.

The different course of reduction of the mixed oxides in the regions of excess of one or the other component is preserved also if the samples have been thermally treated in inert atmosphere (argon) in various conditions. One hour's treatment at 500°C practically does not affect the kinetics of reduction of samples with excess nickel oxide; treatment at 906°C brings about decreasing rate and maximum reduction degree (Fig. 4, curve *3*), the reduction curve retains its sigmoid character typical for reduction of nickel oxide. Reduction of samples with manganese sesquioxide as the major component, treated at 500°C, remains unaffected only at low α values (Fig. 4, curves *4* and *5*); in the ensuing stage, the reaction proceeds with a lower rate to a lower reduction degree, and the shape of the kinetic curves alters considerably. The reduction of the same sample treated at 960°C in a homogeneous mechanical mixture with pure nickel oxide proceeds practically in two consecutive steps, the two parts of the curve again possessing a sigmoid shape (Fig. 4, curve *2*).

After the primary reduction at 380°C, mixed oxides of different composition were also oxidized in air stream to a constant degree, and at the same temperature secondarily reduced with hydrogen. The primarily reduced samples with excess manganese undergo a rapid process on air, corresponding to oxidation of manganese monoxide to trimanganese tetroxide or even as far as manganese sesquioxide, and successive or parallel slower oxidation of nickel to nickel oxide. The degree of oxidation increases monotonically with growing content of the dispersed nickel metal phase up to 80 mol.% NiO in the initial oxide, then it drops rapidly towards pure nickel oxide. Oxidation of the latter proceeds in the given conditions more slowly than that of manganese monoxide and to a low degree (about 30%), because it is blocked by a rather compact

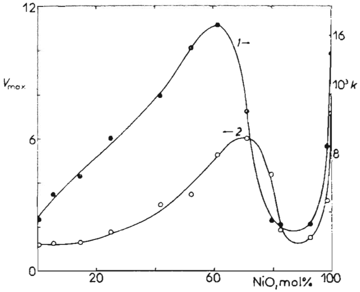

FIG. 3

Dependence of k (in relative units) and of V_{max} (mg/min) on the Composition

Reduction temperature 350°C; *1* k; *2* V_{max}.

oxide layer on the grain surface. The secondary reduction, on the contrary, shows a fast initial rate corresponding to reduction of nascent nickel oxide to nickel and, owing to the higher affinity of manganese oxides to oxygen, a slower reduction of manganese sesquioxide to manganese monoxide or of trimanganese tetroxide to manganese monoxide as the successive reaction. Because of these processes, the degree of secondary reduction (with respect to the content of oxide formed by the oxidation) increases continuously with growing content of nickel oxide in the initial samples. Starting from approximately 50 mol.% NiO, all phases of the oxides formed on the oxidation are completely reduced.

The effect of prior irradiation of the mixed oxides on the kinetics of reduction is shown in Fig. 5 as the dependence of the quantity Δ_k (%) $= 100[(k^* - k)/k]$ on the composition; here k^* is the rate constant of reduction of the irradiated sample at the given temperature and k is the value pertaining to the initial mixed oxide. As can be seen, irradiation by fast neutrons results in a pronounced negative effect (lowering of the reduction rate), which attains maximum at approximately 60 mol.% NiO and continuously converts to a positive effect in the region of low contents of manganese sesquioxide. The effect of gamma irradiation on the kinetics of reduction is opposite: the positive effect grows with increasing content of nickel oxide up to a maximum at approximately 70 mol.% NiO. Another, less pronounced local maximum lies in the region of the positive effect of irradiation by neutrons. Reduction of the pure components practically remains unaffected by irradiation. In contrast to the negative effect resulting from the irradiation by neutrons, the positive effect of the gamma irradiation is considerably temperature dependent: it decreases with rising temperature

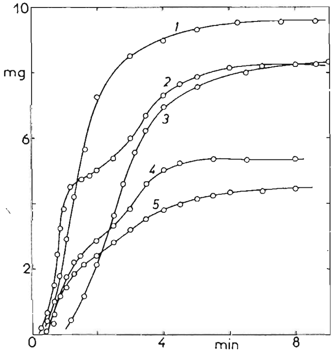

FIG. 4

Time Course of Reduction of Some Mixed Oxides and the Same Samples Treated in Argon for 1 h at Different Temperatures

Reduction temperature 440°C, mechanical mixture 470°C. Initial samples: *1* sample 11; *4* sample 2; heat treated samples: *3* sample 11 (960°C); *5* sample 2 (500°C); *2* mechanical mixture of 50 mg of sample 2 treated at 960°C and 25 mg of NiO.

and virtually vanishes at 440°C. In the region of the positive effect, the activation energy of the reaction practically does not change. The lowering of the reduction rate brought about by the irradiation by neutrons, on the contrary, is accompanied by an increase in the apparent activation energy, approximately by 20%.

DISCUSSION

The experimental results evidence that, in compliance with the thermodynamic properties of the two oxides, manganese sesquioxide or admixtures of manganese dioxide are reduced to manganese monoxide, and nickel oxide is completely reduced to the metal. The time dependences of the course of reduction demonstrate a pronounced mutual influencing of the two constituents over the whole composition region. According to[5], the reduction of the pure oxides of the stoichiometry of manganese dioxide and sesquioxide starts with a maximum rate, which drops rapidly as the content of oxygen in the solid phase decreases. An interval of constant rate follows as a consequence of superposition of two opposite processes – nonautocatalytic reduction of the initial oxides and autocatalytically accelerated reduction of the forming intermediate product, trimanganese tetroxide. Such course of reduction, consisting clearly of two steps – $Mn_2O_3 \rightarrow Mn_3O_4$ and $Mn_3O_4 \rightarrow MnO$ – was observed for sample No 1 (pure manganese sesquioxide), but only at higher temperatures (>410°C). As the experimental results show, the character of the kinetic curve of manganese sesquioxide depends, in addition to temperature, also on the reactivity of the surface of the starting oxide, which can be modified by the preparation procedure of by prior heat treatment. The lowering of the initial rate of reduction at lower temperatures may be due to the relatively high concentration of the ionogenic, strongly adsorbed form of overstoichiometric oxygen (Fig. 1), which hinders adsorption of the reducing

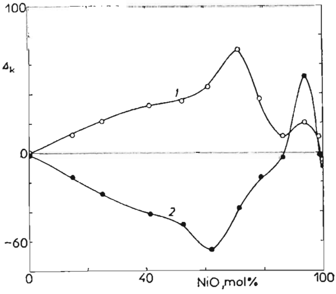

FIG. 5

Dependence of Δ_k (%) on the Composition
Reduction temperature 380°C, irradiation: 1 gamma, 2 neutrons.

hydrogen[8]. The time course of reduction of the sample with high excess of manganese sesquioxide (sample No 2) changes appreciably on 1 hour's treatment in inert atmosphere (Fig. 4, curve 5): an interval of constant reaction rate appears in the central part of the curve. Apart from the effect of the low-percentage admixture of the other component, the heat treatment of this sample brings about partial dissociation of the major component (manganese sesquioxide) associated with oxygen desorption. Thus the retarding effect of oxygen is eliminated and the resulting kinetic curve represents a superposition of the two processes. From a quantitative study of hydrogen adsorption on manganese oxides of different stoichiometry[9] it follows that the sorption of hydrogen on manganese sesquioxide or dioxide increases rapidly on raising the temperature, whereby the rate of reduction increases too. Thus at higher reduction temperatures, retardation of the strating stage of the reaction does not appear either. The rate of reduction decreases from the initial maximum value to the stage where the intermediate product (trimanganese tetroxide) appears in a sufficient concentration for its reduction to proceed autocatalytically as a consecutive process. The autocatalytic course of reduction of this oxide is apparent from Fig. 4 (curve 2). Heat treatment of sample No 2 at 960°C results in a total thermal decomposition of manganese sesquioxide to trimanganese tetroxide. Fig. 4 along with the mass losses also demonstrates that in a homogeneous mechanical mixture of the intermediate product with pure nickel oxide, the two constituents are not reduced simultaneously: nickel oxide is first quantitatively reduced, which is followed continuously by the reduction of the intermediate product. The two segments of the curve display a typical sigmoid shape. Although in the mixed oxides under study the two components constitute separate phases within the entire composition region, they can be assumed to mutually interact to a considerably higher extent than in a mechanical mixture; in the region of excess manganese sesquioxide, its reduction is affected even by low additions of the minor component – nickel oxide. As follows from Fig. 2 and from other data, nickel oxide is reduced first in the mixed system, and the reduced nickel accelerates catalytically the reduction of the other component. The reduction of manganese sesquioxide in the mixed oxide is therefore different from that of the pure oxide: the presence of its admixture in excess nickel oxide shows up in a shift of the maximum reduction rate towards higher α values and a prolongation of the total reduction time. This leads to a stretching of the descending part of the curve $v = f(\alpha)$ in the region of $\alpha \rightarrow 1$ and to a lowering of the rate of reduction of nickel oxide. Increasing degree of reduction of the mixed oxide is accompanied by an increase in the concentration of manganese monoxide, which blocks the active reaction interface. The mutual interaction of the two components alters then the reaction rate specifically in the various composition ranges (Fig. 3).

According to[5], the apparent activation energy of reduction of pure manganese sesquioxide with hydrogen is $E_{a(r)} = 92{\cdot}1 \text{ kJ mol}^{-1}$ and the activation energy of dissociation of this oxide is $E_{a(d)} = 251{\cdot}2 \text{ kJ mol}^{-1}$. We found the E_a value of reduction of sample No 1 higher, $E_{a(r)} = 125 \cdot 6\ \text{kJ mol}^{-1}$; the dependence of this quantity on the composition exhibits a trend correlable with that for the dependence of V_{max} or k (Fig. 3). It can be thus assumed that in addition to the reduction proceeding *via* surface adsorption of hydrogen, the dissociative mechanism plays also a role in the region of excess manganese, owing to the presence of manganese in higher oxidation degrees.

From the point of view of the adsorption mechanism, addition of nickel oxide as a *p*-semiconductor to the amphoteric manganese sesquinoxide (no predominating type of semiconductivity has been found experimentally for this oxide) leads to an increase in the concentration of the major charge carriers – positive holes, and thus to an enhanced donor adsorption of hydrogen. Moreover, growing content of nickel oxide is accompanied by decreasing concentration of the admixture blocking the active interface – the nonreducing manganese monoxide. The reduction rate thus rises with increasing content of nickel oxide (Fig. 3). The maximum is attained approximately in the region of the highest dispersity and thus of the most intimate contact of the two components in the system. The high dispersity is probably also responsible for the maximum adsorption of overstoichiometric oxygen, and as the equilibrium concentration of the neutral, readily reducible form of oxygen appreciably surpasses that of the strongly adsorbed ionogenic form, the system in the region of about 70 mol.% NiO is reduced with the highest rate. With further increasing content of nickel oxide, the dispersity of the major component lowers, the mutual interaction of the two constituents diminishes, the content of the overstoichiometric oxygen reduces, and higher manganese oxides vanish. The rate of reduction decreases and its kinetics obeys an equation different from that valid for the other composition regions. In the case of samples with high excess of nickel oxide (> 90 mol.%), the kinetics is governed by that of reduction of this oxide. The reaction rate increases with further decreasing content of the minor manganese sesquioxide to attain its maximum for pure nickel oxide. The activation energy of reduction, $E_{a(NiO)} = 100 \cdot 5\ \text{kJ mol}^{-1}$, is in a very good agreement with the published data[11].

Heat treatment of samples with high excess of nickel oxide at temperatures above 900°C results in a practically complete desorption of all forms of overstoichiometric oxygen[6,10]. The subsequent reduction of the stoichiometric nickel oxide proceeds with a lower rate and, because of the sintering processes, also to a lower degree as compared with the initial sample (Fig. 4, curves *1* and *3*).

Irradiation of the mixed oxides by gamma radiation or fast neutrons (Table II) brings about a substantial increase of the ionogenic form of overstoichiometric oxygen, the shape of the dependence shown in Fig. 1 being preserved. In view of the fact that all lower manganese oxides accept overstoichiometric oxygen, with which they can form solid solutions of different stoichiometry[12], the observed oxygen rise on the irradiated mixed oxides is first of all a result of radiation oxidation of manganese. In addition, in the entire composition region, particularly in the range of excess nickel oxide, the equilibrium of the various forms of sorbed oxygen can be supposed to be shifted in favour of the strongly adsorbed ionogenic form; this has been proved for pure nickel oxide[13] and some two-component oxides in which nickel oxide is involved[8]. Enhanced degree of reduction as compared with the unirradiated sample was observed neither for irradiated pure manganese sesquioxide nor for irradiated samples with high excess of this oxide. This implies that, owing to the increased concentration of the adsorption centres generated by ionizing radiation, the irradiation on air leads predominantly to increased chemisorption of oxygen, or only to surface oxidation of the initial mixed oxides. In the case of gamma irradiation, the adsorption and reaction centres will be represented mainly by nonequilibrium charge defects or lattice defects. Their concentration increases with increasing interaction of the two components, controlled by the degree of their dispersity, up to a maximum for approximately 70 mol.% NiO. At the same time, the concentration of ionogenic overstoichiometric oxygen lowers with increasing content of this oxide, whereby the rate of the donor process – adsorption of the reducing hydrogen – rises. Thus the gamma irradiation results in a positive kinetic effect (rise of the reduction rate), which grows with increasing content of nickel oxide up to the composition mentioned (Fig. 5, curve *1*). In the region of excess nickel oxide, adsorption of hydrogen is no more accelerated, as the concentration of ionogenic oxygen does not vary any more with the composition (Fig. 1). As a consequence, the Δ_k value lowers, because the magnitude of the positive effect is only given by the actual concentration of the newly formed and stabilized charge centres in the mixed system. The increase in their concentration appears to the highest extent in samples containing about 90 mol.% NiO (the second inexpressive maximum of the positive effect, see Fig. 5), where the unirradiated sample exhibits the minimum reduction rate (Fig. 3). For pure nickel oxide this effect converts continuously to a negative one, in accordance with the previous results[8], because the kinetics of reduction is again controlled by the slow sorption of hydrogen on the oxide with ionogenic overstoichiometric oxygen[8,13].

The assumption that on the gamma irradiation the reactivity of the system is altered particularly owing to an enhanced concentration of defects of charge nature is supported especially by the high sensitivity of the effect to temperature. At approximately 440°C the system recovers quickly and the Δ_k quantity approaches zero. The fact that the activation energy of reduction of the gamma irradiated samples virtually equals that for the initial mixed oxides also indicates that the activity of the reaction centres is not changed appreciably, but their concentration increases on the irradiation.

The negative effect brought about by irradiation of the system by fast neutrons, the inversion of this effect at a sample composition (Fig. 5, curve *2*), as well as the independence of the effect of the temperature over the temperature region examined are obviously associated with the complex effect of neutrons on the solid phase. The irradiation first of all effects formation of point defects in the lattice and to a lesser extent formation of charge defects through secondary ionization. The formation of new centres can spur the process of creation of metal nuclei, which results in an increase in the rate of reduction[14]. As follows from Fig. 5 (curve *2*), the irradiation of the mixed system induces a positive effect in the region where the unirradiated mixed samples are reduced most slowly (Fig. 3). The assumption that the generation of new centres alters the rate of nucleation of the metal phase implies that the reduction should be accelerated in the region of high excess of nickel oxide, which is in accordance with the experiment. On the other hand, in a wide composition region up to approximately 60 – 70 mol.% NiO the irradiation by fast neutrons lowers the rate of reduction, the extent of the negative effect increasing in dependence on the composition, with the maximum value of $\Delta_k \approx 65\%$. The fact that the negative effect is accompanied by a rise of the apparent activation energy of reduction points to lowering of the activity of the reaction centres. The reactivity of the irradiated solid may be reduced either because of capture of the adsorption centres on the point defects formed, or directly because of destruction of the existing centres[15] (the polishing effect of radiation).

Provided that this process is responsible for the lowered rate of reduction of the irradiated samples, the magnitude of the effect will grow with increasing content of nickel oxide up to a maximum at 60 – 70 mol.% NiO. The dependence of the quantity Δ_k on the composition will be symmetrical with respect to the dependence of Δ_k of the positive effect induced by gamma irradiation (Fig. 5) or to the dependences of the reduction rate on the composition (Fig. 3); this is in agreement with the experimental results.

REFERENCES

1. Tsigdinos G. A., Swanson W. W.: Ind. Eng. Chem., Proc. Res. Develop. *17*, 208 (1978).
2. Heynen H. W. G., Camp - van Berkel G. G. M., van der Baan H. S.: J. Catal. *48*, 386 (1977).
3. Parekh B. S., Weller S. W.: J. Catal. *47*, 100 (1977).
4. Taras P., Pospíšil M.: This Journal, in press.
5. Tatevskaya E. P., Chufarov G. I., Antonov V. K.: Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk *3*, 371 (1948).
6. Pospíšil M., Cabicar J., Rejholec V.: This Journal *35*, 1319 (1969).
7. Bond K. D.: J. Phys. Chem. *66*, 1573 (1962).
8. Pospíšil M., Cabicar J.: This Journal *39*, 3056 (1974).
9. Chufarov G. I., Averbuch B. D., Tatevskaya E. P., Antonov V. K.: Zh. Fiz. Khim. *26*, 834 (1952).
10. Dereň J., Stock J.: J. Catal. *18*, 249 (1970).
11. Frety R., Tournayan L., Charcosset H.: Ann. Chim. (Rome) *9*, 341 (1974).
12. Remy H.: *Anorganická chemie*, Vol. II, p. 228. Published by SNTL, Prague 1962.
13. Yamashina T., Nagamatsuya T.: Bull. Chem. Soc. Jap. *38*, 507 (1965).
14. Simnad M., Smoluchowski R., Spilners A.: J. App. Phys. *29*, 1630 (1958).
15. Croham D.: J. Phys. Chem. *66*, 510 (1962).

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