Journal of Thermal Analysis and Calorimetry, Vol. 66 (2001) 449–461

PROPERTIES OF NiO–ThO$_2$ MIXED OXIDES FROM HYDROXIDES AND THEIR HYDROGEN REDUCIBILITY BEHAVIOUR

M. Pospíšil, R. Hošek and R. Silber

Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University,
115 19 Prague 1, Czech Republic

(Received December 10, 2000; in revised form May 2, 2001)

Abstract

Some physico-chemical properties of NiO–ThO$_2$ mixed oxides of various compositions have been investigated. The presence of strongly bound constitutional water in the hydrogel of reactive forms of thorium dioxide, determined by their origin (thermal decomposition of mixed hydroxides) caused the different reduction behaviour as compared with other mixed oxide systems containing the only, thermodynamically less stabile reducible component. The significant effects of the thermal treatment in oxygen atmosphere, pre-irradiation by the gamma rays or accelerated electrons under various conditions (in air or in water suspension) as well as of surface chemical activation with a platinum complex on the reactivity of mixed oxides or reoxidized samples during their hydrogen reduction have been also proved.

Keywords: hydrogen reduction, NiO–ThO$_2$ mixed oxides, physico-chemical properties

Introduction

The hydrogen reduction of metallic oxides and of multicomponent oxide systems represents not only the fundamental process of powder metallurgy but also appears to be one of the most important method for the catalysts preparation or their activation. Depending on the genesis, preparation conditions and composition, the character and degree of mutual interaction of the individual components are significantly varied which affects the reactivity of the mixed oxide systems during their reduction by the gas. Different physico-chemical properties as well as differences in reduction kinetics were observed with various two-component mixed oxides prepared either by thermal decomposition of mixed crystalline salts of both metals or by calcination of co-precipitated insoluble precursors [1]. In the latter case relatively scarce attention until now has been paid to the mixed systems of hydroxide origin, where the presence of constitutionally bound water in various concentrations may significantly affect their reduction behaviour [2]. Therefore, the aim of the present contribution was to study the properties and reducibility, tested by reduction with hydrogen, of the two-compo-

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

nent mixed system, but contrarily to the work [2] containing the only reducible component. Moreover, the influence of various factors modifying the reactivity of mixed oxides in dependence of their composition was also investigated. The NiO–ThO_2 mixed system was chosen for this study.

Experimental

The series of mixed oxides differing in their composition in the range 0–100 mass% of each component were prepared by thermal decomposition of coprecipitated hydroxides for 4 h at 450°C in air (Table 1). Because of the low content of ThO_2 in the pure thorium dioxide (68.8 mass%) obtained under these conditions, the precursor of this sample was repeatedly calcined at 950°C for the same time. The aqueous solutions of thorium sulphate and nickel nitrate were mixed together in required ratios and then coprecipitated during intensive agitation with a 10% stoichiometric excess of a solution of NaOH. The concentration of all solutions was 1 mol L^{-1}. Carefully washed products and dried at 125°C were calcined and pulverized. The solution of thorium sulphate was prepared from the starting thorium dioxide AR grade (Merck) by acid smelting with $KHSO_4$ and leaching from the melt.

Table 1 Notation, composition, specific surface areas (*S*) and size of coherent regions (*L*) of NiO–ThO_2 mixed oxides

Sample	Mass/%			S/m^2 g^{-1}	L/nm	
	NiO	ThO_2	NiO+ThO_2		NiO	ThO_2
1	91.1	0.0	91.1	17.6	47.5	
2	90.0	5.2	95.2	40.0	33.8	
3	84.9	6.8	91.7	61.6	25.3	
4	77.8	14.8	92.6	61.1	26.8	
5	64.4	26.0	90.4	94.8	25.5	
6	57.2	33.7	90.9	36.2	24.9	5.7
7	52.5	38.7	91.2	46.7	24.8	5.8
8	47.5	47.9	95.4	65.2	31.1	6.4
9	46.1	48.1	94.2	26.8	29.5	6.4
10	45.2	49.1	94.3	61.0	25.7	5.9
11	34.7	56.0	90.7	59.0		6.2
12	23.4	70.8	94.2	36.7		6.9
13	12.5	79.9	92.4	33.7		6.3
14	9.1	83.5	92.6	15.1		6.8
15	0.0	68.8	68.8	12.8		6.6
15*	0.0	93.8	93.8	0.2		204

*after recalcination at 950°C

The conditions for thermal decomposition were previously established by thermal analysis of selected samples of precursors, performed on the Netzsch STA 490 – thermoanalyser within the range 20–800°C at a heating rate of 10 deg min^{-1}. The content of both metals in the mixed oxides was determined by atomic absorption spectroscopy and complexometrically with ethylenediaminetetraacetic acid. The microstructure of the samples was investigated by X-ray diffraction using a TUR M62 generator with a goniometer. Nickel-filtered CuK_α radiation was used. Specific surface areas were measured by low temperature selective adsorption of nitrogen from a N_2/H_2 mixture and the morphology of the samples was studied using a JSM-840(A)-Jeol scanning electron microscope. The surface oxidative abilities (content of ionogenic chemisorbed oxygen O^{2-}, normalized to unit surface of area) were determined by iodometric titration.

Part of the samples prepared was, prior to use, irradiated at laboratory temperature with ^{60}Co gamma rays in air or in suspension with distilled water using a dose of 1 MGy. In the latter case the samples were filtered after irradiation, dried in air at 110°C and immediately measured. Next portion of the mixed oxides was analogously (in air at doses of 1 and 3 MGy and in water suspension at 1 MGy) irradiated by accelerated electrons with an average energy of 4 MeV from a high frequency linear accelerator. Selected samples of different composition were further heat treated for two hours at 500 or 600°C in oxygen and argon atmospheres. Finally, some samples were impregnated with 2% aqueous solution of H_2PtCl_6. After three-day storage of suspension the liquid phase was removed by drying at 110°C up to a constant mass. The standard mass of these modified samples was either directly reduced with hydrogen or the kinetics of the thermal decomposition of activator (H_2PtCl_6) in air and following hydrogen reduction at the same temperature were measured. Moreover, the effect of activation of the samples on the reduction kinetics of reoxidized mixed oxides was also studied. In these experiments the activated samples after primary reduction were oxidized in an oxygen flow up to a constant degree and then reduced again at the same temperature. All above mentioned reactions proceeded at 320°C.

The reduction kinetics was partly studied by isothermal thermogravimetry in the temperature range of 290–380°C and partly in the non-isothermal regime (temperature programmed reduction) at a heating rate of 10 deg min^{-1} up to 450°C. All experiments were performed at a hydrogen flow of 60 mL min^{-1}, using a 50 mg mass of the sample. Under these conditions the kinetics of reduction at an arbitrary composition of samples were found to be independent of the flow rate of the reducing gas.

Results and discussion

Physico-chemical properties of NiO–ThO_2 mixed oxides

It follows from the results of chemical (Table 1) and X-ray analysis that the applied conditions in the decomposition of the precursors yield a mixture of mixed oxides NiO–ThO_2 with a cubic structure as the major components of the system under study. A significant deficit in the chemical analysis which was found in the whole range of composition may be due to the presence of non-metallic impurities, excess of oxygen, which seems to be typical of the grey or black non-stoichiometric NiO oxide regardless of its origin [3]. The major part of this deficit appears to be connected with the presence of water determined both by the origin of the samples under study and by the conditions of their preparation. The temperature of decomposition of the starting precursors plays the most important role. Analogously to the earlier studied system based on the nickel oxide of hydroxide origin [2] the DTA curves of the precursors with an excess of nickel show two endothermic effects (Fig. 1, curve 1). The first, broad effect lies in the range 50–200°C and the second sharp one, the magnitude of which decreases with increasing content of thorium, reaches a maximum at about 320°C. Similarly the thermogravimetric curve (Fig. 1, curve TG-1) gives evidence that the decomposition proceeds in two consecutive steps. According to some published data [4] at lower temperatures only the water adsorbed on the surface of particles is released (the first stage). Although the lattice of nickel hydroxide is disturbed already under the temperature of 300°C [4, 5] the hydroxyl groups are fully splitted off at higher temperatures lying in the range of 320–350°C (the second stage of decomposition). This is in conformity with our results. As far as the character of the DTA curves including the position of peaks, it is known that with the salts or complexes of transition metals these parameters changes markedly depending on the pre-history, age and conditions of preparation of the sample [6].

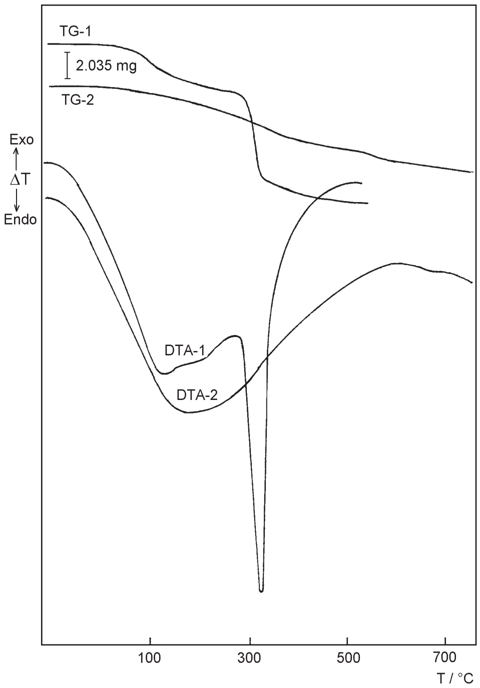

Fig. 1 DTA and TG curves of the precursors (mixed hydroxides) corresponding to samples No. 3 (1) and 15 (2)

As can be seen from the thermogravimetric curve, the temperature used for the preparation of the series (450°C) appears to be insufficient for the complete decomposition of the precursor even though the lattice of nickel hydroxide is fully transformed. The further increasing mass loss of the sample, observed also by other authors [4], can be connected with the releasing of water strongly bound already in the nickel oxide which is formed in situ during the transformation of the original hydroxide lattice. According to some IR spectroscopic investigations it follows that the mentioned mass loss may be caused by the releasing of the solvated water [7] which is bound by hydrogen bonds but the decomposition of various hydrated compounds of nickel oxide [8] cannot be excluded, either. Only at the highest temperatures (about 800–900°C) the stoichiometric green and yellow nickel oxide is formed [3]. As can be seen from Fig. 2 the hydroxide origin of final nickel oxide manifests itself by quite different (needle shaped) morphology as compared with the same oxide prepared from the basic carbonate or nitrate and decomposed at the same temperature. In the latter case the grains are formed by spherical agglomerates being about 200–400 μm in size without distinct porous texture [9, 10].

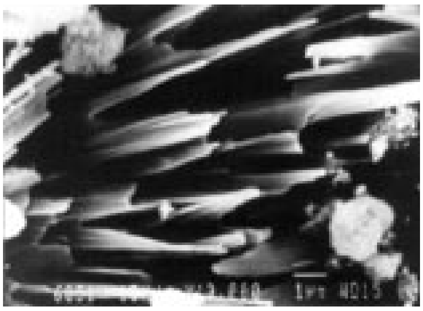

Fig. 2 Electron micrograph showing the needle-shaped morphology of the original sample No. 1, magnification 10 000×

The continuous releasing of water connected with the mass loss during the thermal treatment (Fig. 1, curve 2) gives evidence that the precursor of pure thorium dioxide is rather the hydrogel of reactive form of ThO$_2$ (hydrated oxide $ThO_2 \cdot 2H_2O$) than Th(OH)$_4$. In accordance with a high thermal stability of different hydrated oxides or their hydrogels [11] the standard conditions of decomposition used for the preparation of mixed oxides series appear to be sufficient for transformation of amorphous hydrogel to the cubic structure of ThO$_2$, however with a high content of residual water (Table 1, sample 15). Table 1 also shows that the size of microcrystallites of thorium dioxide (coherent regions) which lie in the interval 5.7–6.9 nm is considerably smaller than that of nickel oxide and is virtually independent of the system composition. The pronounced increase of this parameter for sample 15 (Table 1) recalcinated at 950°C, is due to the sintering processes.

The mutual influence of both components in the system under study results in a non-monotonous dependence of the specific surface areas on the composition (Table 1). Relatively high absolute values of this quantity are in accordance with the genesis of these mixed oxides. In contrast to the mixed systems prepared by the thermal decomposition of various crystalline salts (nitrates, chlorides etc.) where the melt is created during their calcination, the same samples obtained by the decomposition of amorphous precipitates (carbonates, hydroxides) possess, as a rule, higher surface area values [12]. No significant difference in this parameter was found between the original samples and those pre-irradiated under the above-mentioned conditions. This is in accordance with published data [13]. In contrast with radioactive substances the measurable changes of parameters such as microstructure, morphology and surface areas of mixed oxides, can be induced as a result of pre-irradiation only by high energy corpuscular radiation at the higher doses then those applied in this work. Heat treatment at 500 or 600°C in various atmospheres used led to the decrease in the specific surface areas by about 30%. In the region of the maximum value of surface area and with the samples containing pronounced excess of ThO$_2$ the system appears to be the most sensitive to the treatment. It results in the decrease of this quantity up to 50% of its original value for sample 5 and 70% for sample 13 (Table 1). In addition to the grain sintering which was proved by microscopic investigation, releasing additional portions of water bound in the system at temperatures lying over the standard decomposition temperature may also affect the magnitude of specific surface area values.

As can be seen from Fig. 3 the small admixture of ThO$_2$ leads to the decrease of surface oxidative ability which gives evidence for the decrease of concentration of Ni^{3+} ions in the nickel oxide. The non-monotonous dependence of this parameter on the composition shows two sharp reproducible maxima, the first one in the region of the middle of series and the second one with the sample of thorium dioxide containing a small admixture of the second component. Excluding the samples with the highest excess of nickel oxide (samples 1 and 2) the absolute values of this quantity as well as the character of mentioned dependence were found to be preserved in the samples after their long (two years) storage in air at room temperature. In contrast to

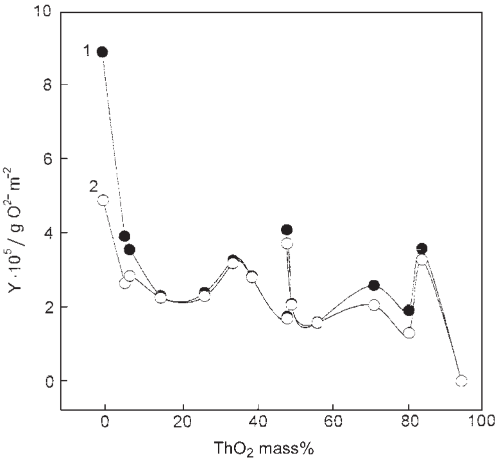

Fig. 3 Content of the ionogenic oxygen normalized to unit surface area *Y vs.* composition. 1 – freshly prepared samples; 2 – samples after two years storage

the stable mixed oxides the decrease of the oxidative ability of NiO oxide during its storage (by about 45 and 33% with sample 2) may be connected with recrystallization processes and establishment of a new equilibrium between surface and atmospheric oxygen. This is supported by the fact that the heat treatment only in the oxygen atmosphere caused the increase of the oxidative ability of pure NiO oxide by 50%. On the contrary, no changes of this quantity were found with all samples including pure NiO oxide treated in Ar atmosphere and with mixed oxides treated in oxygen.

Table 2 Changes in the surface oxidative ability (ΔY) of mixed oxides due to gamma irradiation (dose 1 MGy) and accelerated electrons (doses 1 and 3 MGy) under different conditions

Sample	ΔY/%				
	e^-, 1 MGy, a	e^-, 3 MGy, a	e^-, 1 MGy, ws	γ, a	γ, ws
1	14.9	3.7	38.7	61.9	146.0
2	43.6	87.5	20.5	123.5	100.0
3	9.0	15.0	17.8	15.8	25.9
4	6.9	39.1	–16.9	51.6	–47.5
5	–2.4	–34.8	–11.2	–3.8	–55.6
6	–15.1	–26.1	–32.6	–10.5	–52.6
7	–27.6	–20.5	–42.4	–10.8	–55.2
8	–23.0	–20.1	–31.6	15.3	–14.1
9	–33.4	–33.7	–13.7	20.4	–19.9
10	–20.9	–15.6	–37.1	2.8	–41.6
11	–5.6	–12.7	–22.3	–15.6	–36.3
12	–7.8	–45.1	–40.2	–18.5	–35.8
13	–7.1	–7.1	–15.8	–9.8	–37.8
14	–13.1	–46.8	–46.4	8.6	–46.2
15	0.0	0.0	0.0	0.0	0.0

[a] irradiated in air

[ws] irradiated in water suspension

The influence of pre-irradiation on the surface oxidative abilities of all samples, expressed by the quantity ΔY is summarized in Table 2. This quantity is defined by the relation ΔY (%)=100 (Y^*–Y/Y), where Y^* and Y represent the normalized content of ionogenic oxygen of the irradiated and original samples, respectively. From the given data the highest sensitivity towards irradiation only with the samples containing an extremely high amount of NiO oxide is evident, too. In this region of the composition the positive effect dominates, whereas for the mixed oxides containing a sufficient amount of thorium dioxide the negative effect is typical. The increase of surface oxidative ability is due to the radiation-induced oxidation of Ni^{2+} ions (more precisely Ni^{2+}–Ni^{2+} centres) which was observed already in the earlier studied systems containing nickel oxide [1, 14]. From this point of view no differences among the various morphological forms of nickel oxide were found. In water suspension probably the radiolytic oxidation by strongly oxidizing OH radiacals takes place. Depending on the composition the positive effect of radiation can be counteracted by the competing negative influence i. e. by reduction action of solvated electrons in the mixed samples containing sufficient content of thorium dioxide. The cause of this may be low concentration of centres which can be oxidized and the increase of the centres (ions in higher valency states) which may be reduced. With regard to the experimental errors (±15%) the resulting zero effect or inexpressive decrease of the surface oxidative abilities are characteristic for these samples. The different values observed with the samples irradiated by gamma rays as compared with those irradiated by accelerated electrons at the same dose of radiation can be connected with the different manner of energy deposition in the surface layers and in the bulk of the solid. Moreover the migration of activated oxygen from bulk to the surface may proceed in the case of gamma irradiation.

Reactivity of NiO–ThO_2 mixed oxides tested by hydrogen reduction

From the thermodynamic stability of both oxides it follows that under given conditions the nickel oxide is the only reducible component in the studied system. However the experimental degrees of reduction achieved at 380°C exceeded the theoretical values calculated assuming the total reduction of nickel oxide in the region of its prevailing content (Fig. 4). From the given dependences can be deduced that during the reduction of NiO oxide and crystallochemical transformation of its lattice the releasing of residual water present in the samples takes place, which increases overall mass losses. At lower temperatures of reduction or with the samples containing an excess of second component its strong influence appears to be evident. The reactive interface is blocked by non-reducible finely dispersed thorium dioxide so that the re-

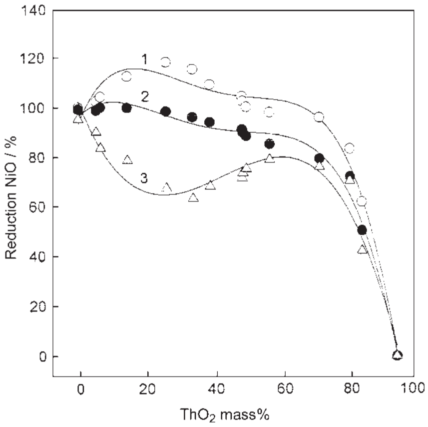

Fig. 4 Dependence of the percentage reduction at different temperatures over the theoretical value corresponding to the total reduction of NiO oxide on the composition. 1 – 380°C; 2 – 320°C; 3 – 290°C

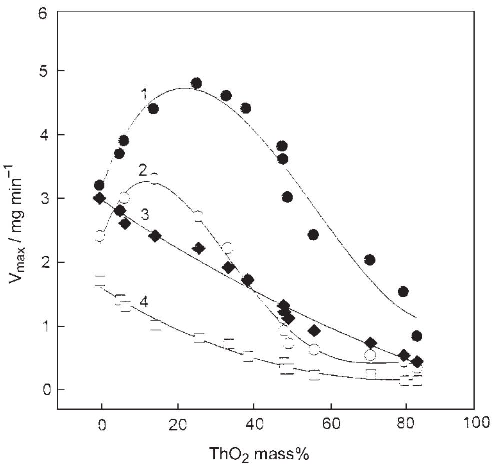

Fig. 5 Plot of maximum reduction rate $V_{max.}$ *vs.* composition at different temperatures and reduction in non-isothermal regime. 1 – 380°C; 2 – 320°C; 3 – non-isothermal reduction; 4 – 290°C

duction of NiO oxide proceeds only to lower degrees. As can be seen from Fig. 5 the thorium dioxide significantly affects not only the degree but also the kinetics of reduction of nickel oxide. This influence appears to be different in dependence on the composition and temperature. Only at lower temperatures of reduction (curve 4) or during the reduction proceeding in non-isothermal regime (curve 3) the maximum reduction rate monotonously decreases with increasing content of thorium dioxide. This course is typical of homogeneous two-component systems containing a single reducible component and has been observed with other various mixed oxides [15]. On the contrary, with heterophase-type mixed oxides the mutual interaction of the two components may be still affected by steric and other factors. These determine not only the retarding influence of the unreducible component but also positive (accelerating) effects in dependence on temperature, actual degree of reduction and composition [9, 14]. With the samples containing an excess of NiO oxide its reduction was found to be accelerated by the admixture of thorium dioxide at higher temperatures of reduction (curves 1 and 2). As it was mentioned above, only under those conditions the reduction of majority nickel oxide evokes the releasing of water strongly bound in the stabile thorium dioxide hydrates. It may be the cause of the accelerating effect observed. This is supported by the fact that the apparent activation energies of reduction in this region of composition reached values around 55 kJ mol^{-1}. This value lies below that given in the literature for reduction of nickel oxide [10] (and generally majority of chemical reactions) and gives evidence for the participation of transport processes. Moreover during the rapid reduction of nickel oxide which takes place at higher temperatures the minority thorium dioxide probably hinders the formation of a coherent metallic layer on the reduction interface. This effect leads also to the acceleration of reaction.

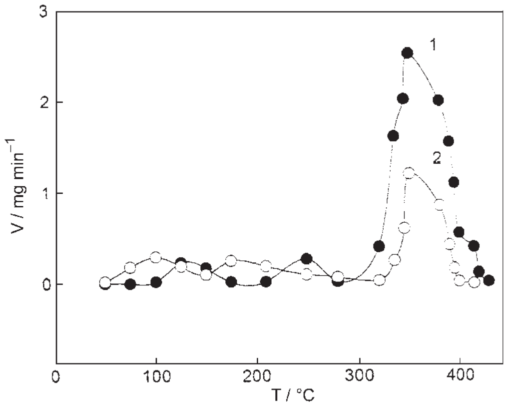

Fig. 6 Temperature-programmed reduction profiles of samples No. 2 (1) and 8 (2)

As can be seen from the temperature-programmed reduction profiles, i.e. from the dependence of instantaneous reduction rate on the temperature (Fig. 6), various portions of weakly bound (adsorbed) water appear to be released already at lower temperatures in the whole range of composition. The proper reduction follows as a consecutive process, which is connected with releasing both the reduction product-water vapour and the water strongly bound in stabile hydrates of thorium dioxide. The desorption of gaseous impurities and water adsorbed on the surface proceed also during the thermal pre-treatment of the samples under above given conditions. The activation of present or the creation of new reduction centres result in the acceleration of the reduction, predominantly with the treated samples containing an excess of tho-

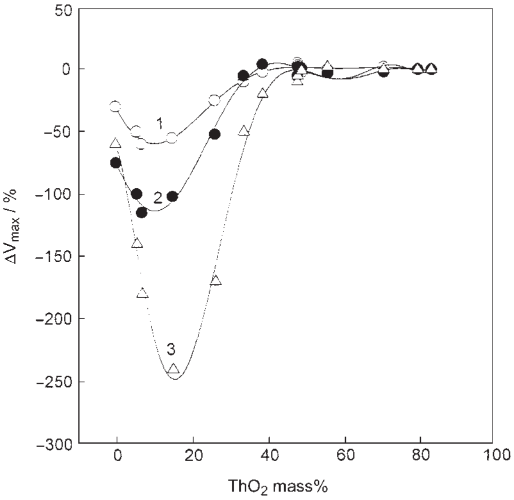

Fig. 7 Dependence of the quantity $\Delta V_{\mathrm{max.}}$ on composition of the samples irradiated by gamma rays, 1 MGy in water suspension (1), accelerated electrons, 3 MGy in air (2) and accelerated electrons, 1 MGy in water suspension (3)

rium dioxide. This effect can be expressed by the quantity ΔV_{max} (%) defined analogously to the quantity ΔY, where Y and Y^* are replaced by the maximum reduction rate of the original sample (V_{max}) and the same sample after treatment (V^*_{max}). This quantity being in all cases higher for oxygen treatment changes in dependence on composition from 30 to 95%.

Figure 7 shows the effect of pre-irradiation under various conditions on the reduction kinetics expressed by means of the quantity ΔV_{max}. It follows from this figure that the system under study appears to be the most sensitive to irradiation only in the region of an excess of nickel oxide where the reduction of non-irradiated samples proceeds with the maximum rate. The decrease in reduction rate of pure irradiated nickel oxide, which was repeatedly observed earlier [16, 17], may be connected with increasing over-stoichiometry of this oxide formed predominantly by strongly bound ionogenic oxygen retarding the donor chemisorption of reducing gas. The presence of water introduced to the system by the small admixtures of thorium dioxide results in further drop of reduction rate in the irradiated samples. The fact that the negative radiation effect appears to be in all cases markedly higher with the samples irradiated in water suspension gives evidence for the retarding influence of the oxidizing products created by the radiolysis of water. Similar behaviour was also observed with other two-component mixed systems containing nickel oxide irradiated either in water or in air [17]. Only small dependence on the dose applied was found with the samples irradiated by accelerated electrons in air and generally a lowering of radiation effects with increasing temperature was observed. This indicates that with higher doses of

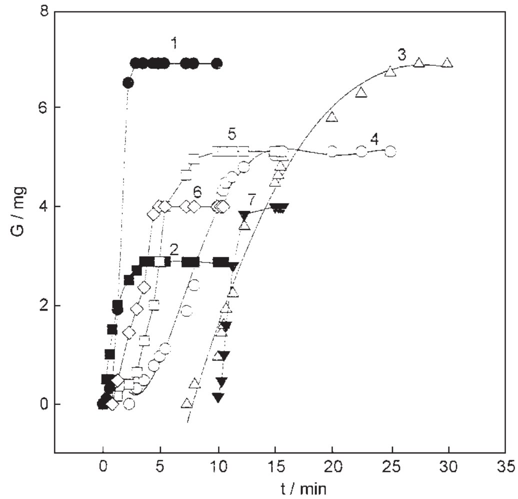

Fig. 8 Reduction with hydrogen of the original samples 6 (3) and 8 (4) followed by isothermal thermogravimetry at 320°C. Reduction of sample 8 after impregnation with H_2PtCl_6 and drying (5), its oxidation in the flow of oxygen (6) followed by the secondary reduction with hydrogen (7). Thermal pre-decomposition of the activator in air (sample 6, curve 2) and subsequent reduction of the activated sample 6 with hydrogen (1)

radiation and at higher temperatures of reduction the recombination and recovering processes play increasingly their part.

Figure 8 demonstrates the influence of platinum on the reactivity of two samples of different composition during their primary or secondary reduction by hydrogen. Curves 3 and 4 represent the time course of reduction of the original samples 6 and 8, curve 5 belongs to the reductive decomposition of the activator (H_2PtCl_6) and reduction of the activated sample 8. Both processes occurred in dry hydrogen with a high rate. However the integral kinetic curve did not make possible to distinguish their consecutivity. Curves 2 and 1 represent the preliminary thermal decomposition of the activator in air (2) and the subsequent hydrogen reduction of the activated sample 6 (1). Both these reactions proceeded with an extremely high rate without measurable induction period. Curve 6 belongs to the oxidation of activated and primarily reduced sample 8 in the flow of oxygen. The course of subsequent secondary reduction of this sample by hydrogen is demonstrated by curve 7. All above described processes took place at 320°C. It is evident from these dependences that the activation leads to a pronounced increase in the rate of reduction even in the case of reoxidized samples (secondary reduction) or the samples possessing a high content of non-reducible component. From this it may be deduced that the non-reducible oxide can probably act as a transmitter of active species (atomic hydrogen). Similar effects were observed with other two component mixed systems activated by platinum, containing only one reducible oxide [15].

Conclusions

The thermal decomposition of mixed nickel and thorium hydroxides leads to the formation of nickel oxide with a needle-shaped morphology in close epitaxial contact with thorium dioxide containing a relatively high amount of residual strongly bound water. The presence of thorium dioxide as well as the pre-irradiation of the samples by gamma rays or accelerated electrons in air or in a water suspension significantly affects the surface oxidative ability of nickel oxide. The sign of the resultant effect depends on the composition and appears to be a superposition of two competing processes.

Thermodynamically less stable nickel oxide is the only reducible component in the system under study. The degree and the rate of its hydrogen reduction are markedly influenced by the second component depending on the composition and temperature of reduction. Only at lower temperatures the dependences of the reduction rate on composition are similar those for the two-component mixed oxide systems containing one stable non-reducible component. These differences are caused by the presence of water released during the reduction at higher temperatures.

The action of the products of water radiolysis is probably the major cause for the significant negative effect of pre-irradiation on the reduction kinetics for samples with an excess of nickel oxide. The reduction kinetics may be positively influenced (accelerated) by the admixture of platinum activator regardless of the composition. Therefore the non-reducible component acts as a transmitter of active species (atomic hydrogen). The positive effect remains unchanged also for the secondary reduction of reoxidized samples.

References

1 M. Pospíšil and M. Martykán, Thermochim. Acta, 184 (1991) 159.
2 M. Pospíšil, J. Thermal Anal., 36 (1990) 489.
3 J. Dereň and J. Stock, J. Catal., 18 (1970) 249.
4 I. F. Hezell and R. J. Irving, J. Chem. Soc. A, (1966) 669.
5 N. G. Klyukina and G. M. Kudryashova, Zh. prikl. Khim. Leningrad, 36 (1963) 495.
6 N. Deb, P. K. Gogei and N. N. Dass, J. Thermal Anal., 35 (1989) 27.
7 D. I. Lafer, V. I. Yakerson, M. I. Romanova, V. Ya. Danyuschevski and A. A. Rubinstein, Izv. Akad. Nauk SSSR, 7 (1971) 1448.
8 E. Ya. Rode, Zh. neorg. Khim., 1 (1956) 1430.
9 M. Pospíšil and I. Petrecký, Collect. Czech. Chem. Commun., 49 (1984) 2241.
10 W. Verhoeven and B. Delmon, Bull. Soc. Chim. France, 10 (1966) 3065.
11 M. Pospíšil, Thermochim. Acta, 119 (1987) 261.
12 V. Múčka, Radiat. Phys. Chem. 41 (1993) 843.
13 V. I. Spitzyn and V. V. Gromov, In: Physicochemical Properties of Radioactive Solids (in Russian), Atomizdat, Moscow 1973, p. 103.
14 M. Pospíšil, J. Thermal Anal., 29 (1984) 49.
15 M. Pospíšil and P. Kaňoková, J. Therm. Anal. Cal., 58 (1999) 77.
16 T. Yamashina and T. Nagamatsuya, Bull. Chem. Soc. Japan, 38 (1965) 5077.
17 M. Pospíšil and R. Klik, Radiat. Phys. Chem., 47 (1996) 131.