HYDROGEN PEROXIDE DECOMPOSITION ON A NON-IRRADIATED AND GAMMA PRE-IRRADIATED NiO-U_3O_8 CATALYST

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This paper deals with some physico-chemical properties of a two component catalyst NiO–U_3O_8, prepared with varying ratio of both components. Special interest was given to the catalytic properties — tested by decomposition of aqueous solution of hydrogen peroxide. The study presented evidence of mutual charge interaction between both components of the catalyst. This enables one to explain the observed behaviour of the studied system on the basis of the principle of bivalent sites. A pre-irradiation of a catalyst by gamma rays leads to significant increase of the oxidation states of both catalyst components.

Uranium containing catalysts were investigated in a series of heterogeneous catalytic reactions. The obtained results indicate that uranium, present in the catalyst as the basic or added component, exhibits catalytic properties given primarily by its chemical character of a transition polyvalent element. In this respect, radioactivity of uranium seems to be of little significance. It was proven that *e.g.*[1] bismuth uranate Bi_2UO_6 catalyzes the dealkylation of toluene. However, if reduced, uranate loses its catalytic activity. It is known from a series of papers concerned with hydrogen peroxide decomposition that the valency of the catalytically active metal can play a decisive role in this reaction — which is the basis of the principle of bivalent catalytic sites[2].

In the present paper, a catalyst composed of nickel oxide and triuranium octaoxide NiO–U_3O_8 (with relative abundance of both components varying from 0 – 100%) was chosen in order to investigate the catalytic role of uranium oxide in the hydrogen peroxide decomposition, as well as to verify the validity of the principle of bivalent catalytic sites. The prepared catalysts were examined with the aim to find out whether mutual interaction of both components would result in a change of the overall catalyst activity. It was further the purpose of this work to examine the influence of gamma irradiation, especially in connection with the radiation energy transfer described with uranium oxide in its radiolytic applications[3].

EXPERIMENTAL

The NiO–U_3O_8 catalysts of different composition were prepared from nickel(II) nitrate and uranyl(VI) nitrate solutions (of reagent grade purity and 1 mol/l concentrations). After the solutions had been mixed at the given ratios, the samples were crystallized by water evaporation and calcinated in an electric furnace in the air atmosphere at 1 073 K for four hours. After grinding, the thus prepared samples were analyzed and tested. The nickel content was measured after preliminary uranium precipitation by complexometric titration. The uranium content was determined according to Sakharov[4] by titration of iron(II) ions (added in the form of ammonium iron(II) sulfate) with a solution of ammonium vanadate(V). The crystallographic structure of the catalysts was examined by X-ray diffraction of the K_α copper line and from the broadening of selective reflections the size of coherent regions of both components was calculated. The specific surface areas were measured by means of low temperature adsorption and subsequent desorption of nitrogen, carried out from a 3 : 1 nitrogen–hydrogen mixture. The oxidative ability of the catalyst surface with respect to the iodide in solution was determined by iodometric titration. The catalysts were pre-treated thermally for one hour in an electric resistance furnace in air at temperatures 673, 873 and 1 073 K. Before testing, part of the prepared catalysts was pre-irradiated in air by a 10^5 Gy dose of ^{60}Co gamma rays. Immediately after irradiation the catalysts were tested by hydrogen peroxide decomposition under conditions strictly comparable with the non-irradiated samples. Determination of the catalytic activity was based on the rate of oxygen evolution in the hydrogen peroxide decomposition at constant temperature. Four different temperatures — 293, 298, 303, 308 K — kept with accuracy of $\pm 0{\cdot}1$ K were used in these measurements (carried out with 1·2 mol/l initial concentrations of the aqueous solution of hydrogen peroxide). The volume of released oxygen was measured in a gas byrette, with the pressure kept constant within ± 10 Pa. The total measurement error varied, depending on the measured oxygen volume, between 0·5—2%. The test reactions proceeded up to about 5% decomposition, with several samples the reaction kinetics was followed up to 50%. It was proved experimentally that under the above conditions the reaction proceeded in the kinetic region.

RESULTS AND DISCUSSION

Physical Properties

From the chemical analysis it follows (Table I) that the prepared catalysts consist of nickel oxide and triuranium octaoxide U_3O_8, with individual samples spreading rather homogeneously throughout the 0 – 100% composition range. The amount of other impurities present in the samples averages around 1 weight %, but this value may be influenced by the possible non-stoichiometry of the fundamental oxides. The fact that the studied system is formed from NiO and U_3O_8 oxides was verified by X ray diffraction. In structural analysis the mutual interaction of both oxides results – with the increasing content of uranium oxide in the sample – in a size decrease of NiO coherent regions, as apparent especially on samples with low uranium oxide content (Fig. 1, curve *1*). The size of the U_3O_8 coherent regions is significantly modified by the presence of even a small amount of nickel oxide (2·5 weight %): this value drops from 265 nm to 75 nm. No further change of this values is observed with additional increase of NiO content within the experimental error of measurement. Another evidence of the mutual interaction between both catalyst components is obtained from a non-monotonic feature of the specific surface *vs* the catalyst composition plot (Fig. 1, curve 2): With increasing relative abundance of uranium oxide in the sample, the specific surface area first becomes larger, reaches its maximum between 10 – 30 weight % of U_3O_8 and descends gradually to the value corresponding to pure triuranium octaoxide. The growth of the specific surface values, found with the increasing content of uranium oxide – in the NiO excess region, can be correlated with the size decrease of the nickel oxide crystallites. Accepting for the purpose

TABLE I

Composition of the catalysts and apparent activation energy values of the reaction obtained with some of the samples: after their preparation (E_A) and with samples 4 months old (E_B)

Sample	NiO weight %	U_3O_8 weight %	$E_A \cdot 10^{-4}$ J mol^{-1}	$E_B \cdot 10^{-4}$ J mol^{-1}
1	99·69	0·00		
2	97·25	2·11		
3	86·64	10·77	6·0	4·6
4	84·01	15·60		
5	78·27	20·96		
6	68·35	30·95	5·9	5·8
7	56·17	41·79		
8	49·60	50·34		
9	37·94	60·55	4·6	5·2
10	28·81	71·17		
11	19·58	80·39	2·0	4·7
12	13·30	85·98		
13	8·48	90·74		
14	1·63	97·46		
15	0·00	98·99		

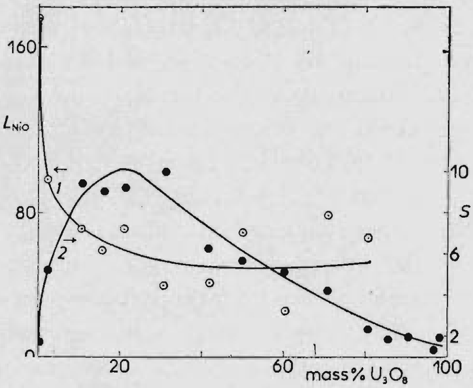

FIG. 1

Dependence of the NiO coherent region size L_{NiO} (nm) 1 and of the specific surface area of the catalyst S (m^2 g^{-1}) 2 on the catalyst composition of comparison a model in which the catalyst grains assume the shape of spheres – with the sphere radius being directly related to radius r of the crystallites (in this approximation the crystallites are supposed to be sphere-shaped as well), then an n-fold increase of the crystallite radius should results in an n^2-fold drop of the surface area of the model grains. Comparing the experimental values of the crystallite size for samples 1–3 (Table I) with their specific surface, the following relations are obtained within the frame of this model:

$$n_{1,2} = r_1/r_2 = 174/2/96/2 = 1{\cdot}8\,; \quad n_{1,2}^2 = 3{\cdot}3 \tag{1}$$

$$S_2/S_1 = 5{\cdot}15/1{\cdot}65 = 3{\cdot}1 \tag{2}$$

$$n_{1,3} = r_1/r_3 = 174/2/72/2 = 2{\cdot}4\,; \quad n_{1,3}^2 = 5{\cdot}8 \tag{3}$$

$$S_3/S_1 = 9{\cdot}4/1{\cdot}65 = 5{\cdot}7\,, \tag{4}$$

where r denotes the measured "radius" of the crystallites and S the experimental value of the specific surface. The subscripts correspond to sample numbers in (Table I). From comparison (*1*), (*2*) and (*3*). (*4*) it follows that $n_{1,2}^2$ roughly equals S_2/S_1 and $n_{1,3}^2$ roughly equals S_3/S_1. Such results support the assumption of the existing correlation between the crystallite size and the measured specific surface area in the samples. Samples with higher content of uranium oxide (above 10 weight %) do not show any further change in the NiO crystallite size with the increased participation of U_3O_8 (Fig. 1, curve *1*); as mentioned above, the size of uranium oxide crystallites also remains constant in this region. Therefore, additional increase of uranium oxide content leads to a maximum in the specific surface value between 10–30 weight % of U_3O_8, with a consequent decrease of the surface value – caused by the growing amount of the low surface U_3O_8 in the sample. The fact that the presence of a small amount of nickel oxide does lead to significantly smaller uranium oxide crystallites, but does not result in any change of the specific surface of the catalyst (sample 15: pure U_3O_8 and sample 14: 2·5 weight % of NiO), leads to the conclusion that with triuranium octaoxide there is no direct relation between the size of crystallites and the specific surface area (unless such relation is hidden by other factors). Specific surface measurements of thermally treated samples have shown that a treatment at temperatures 673 and 873 K does not lead to any measurable change of the specific surface value. Only after a treatment at 1 073 K lower values of the specific surface were found, evidently as a consequence of sintrating processes on the catalyst surface at this temperature. The chemical composition of the catalysts, their crystallographic structure and the measured specific surface values were not influenced by irradiation of the samples, as a consequence of the relatively small doses used[5]. The oxidative ability of the catalyst surface/per unit surface area, (which in fact represents the surface concentration of the metal ions in higher oxidation states in the oxide capable to oxidize the iodide ions in weak acid solutions⁶), depends on a composition of the catalyst in the extreme regions of the composition diagram (Fig. 2, curve *1*). An addition of small amount of uranium oxide to nickel oxide (within units of weight %) leads to a lower specific surface value, probably as the consequence of charge interaction between both catalyst components. An addition of comparatively small amounts of uranium(IV) or uranium(VI) ions in the form of uranium oxide to nickel oxide (which is superstoichiometric with respect to oxygen and contains nickel(III) ions) must – on the basis of general theory of semiconductors – result in a decrease of the nickel(III) ions concentration. This explains the observed decrease of the discussed dependence in the extreme concentration region of nickel oxide excess (Fig. 2, curve *1*). In the other extreme region (of uranium oxide excess) one would analogically expect to find, as the result of a low NiO content, a lesser concentration of uranium ions in the lower oxidation state (U^{4+}). Nevertheless, this decrease can not explain the decrease of the dependence (Fig. 2, curve *1*), observed with the increasing concentration of NiO. Taking in account that in the samples with uranium excess most probably the surface concentration of uranium(VI) ions is detected by the iodometric titration, we can assume that in the region of large uranium oxide excess, an increase of NiO concentration leads to the lower uranium(VI) ion concentration. Such process is evidently caused by the partial reduction of uranium(VI) by nickel oxide. The basic assumption of such conclusion (the surface concentration of uranium(VI) ions being measured by the iodometric titration) is verified by experiments with gamma pre-irradiated samples, where irradiation of the pure uranium oxide leads to a several times higher oxidative ability of the catalyst surface/per unit surface area (Fig. 2, curve *2*). Such behaviour can be at least partially attributed

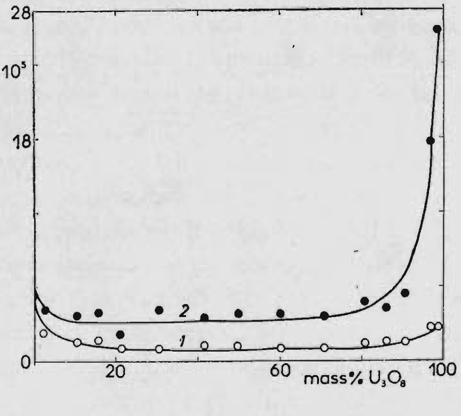

FIG. 2

Dependence of the oxidative ability of the catalyst surface per unit surface α ($g_{O^{2-}} . m^{-2}$) on the composition of non-irradiated *1* and irradiated *2* samples to the radiochemical oxidation of uranium(IV) to uranium(VI), since such solid state reaction was proven by Gromov[7] in the uranium oxide irradiation in air by gamma rays. Besides to that, the radiation induced charge defects – positive holes – stabilized on the catalyst surface, can act as additional oxidative centres. A pre-irradiation leads with all samples (with the exception of NiO) to an increased oxidative ability of the catalyst surface/per unit surface – with features of the dependence of the oxidative ability on the catalyst composition being closely similar to the non-irradiated system (Fig. 2). From that one can conclude that a partial radiative oxidation, respectively a formation of charge defects occurs in all studied samples, with the mutual interaction between the two basic oxides being the same both in the non-irradiated and irradiated system.

Catalytic Activity

In the kinetic study of the higher degree hydrogen peroxide decomposition (up to 50%) it was found that under the given conditions the reaction proceeds as a first-order process. One can therefore assume that during the reaction no qualitative nor quantitative changes of the active centres occur on the catalyst surface, in agreement with the results found for the majority of the so far studied two component catalysts. An exception was found with the systems containing dichromium trioxide (Cr_2O_3–ZnO) (ref.[8]), (NiO–Cr_2O_3) (ref.[6]), dimanganese trioxide (NiO–Mn_2O_3) (ref.[9]) and molybdenum trioxide (NiO–MoO_3) (ref.[10]). This is in agreement with the previously mentioned fact that the deviation from the number one reaction order is substantially smaller with the two component catalysts than with the single component ones[11]. The measured reaction order made it possible to characterize the catalytic activity of all samples by a first order reaction constant k (related to a unit catalyst weight) or by a specific catalytic activity constant k_s (related to a unit catalyst surface).The dependence of catalytic activity k on the catalyst composition shows non-monotonic features. This could result, at least to some extent, from the non-monotonic relation between the size of the specific surface and the composition of the measured system (Fig. 1, curve 2). Similar features are qualitatively found also in the dependence of the specific catalytic activity on the sample composition (Fig. 3), which enables one to assume that the observed relation between the specific catalytic activity and the catalyst composition results from the mutual interaction between both components of the catalyst, similarly to what was found with all the so far studied two component catalysts. Following explanation for the non-monotonic features of the discussed dependence – based on the principle of bivalent catalytic sites[2] – can be given: In the extreme concentration region of NiO excess, a presence of a small amount of uranium oxide leads to the lower concentration of Ni^{3+} ions in the catalyst, as was verified by the surface concentration measurements of superstoichiometric oxygen. Because in this region the catalytic activity is primarily given by the catalytic activity of NiO (as the result of large NiO surplus) and since the catalytic activity of NiO is given by the surface concentration of Ni^{3+} ions (minor sites)[12], a lesser surface concentration of these ions must lead to a lower activity of the catalyst. The large drop of catalytic activity, observed with the increasing relative abundance of NiO in the region of uranium oxide excess can be explained in a similar way. In agreement with the results in other papers[13,14], verifying the conclusions following from the general theory of semiconductors, one can assume that the addition of NiO to uranium oxide leads to a formation of positive holes of the U^{5+} and U^{6+} type, in order to preserve the neutral charge of sample. As a result, the U^{4+} concentration goes down, which can explain the observed lower catalytic activity (under assumption that the uranium(IV) ions represent the minor donor catalytic sites in the reaction). Taking into account the previous conclusion, based on the measurement of the oxidative ability of the catalyst surface, one can conclude that the nickel oxide, present in U_3O_8 in a small amount (up to 10 weight %) on one side reduces uranium(VI) to its lower oxidation state (determined by the redox potential of both substances), on the other hand due to the semiconductor character of both components- the U^{4+} ions are oxidized to U^{5+} and U^{6+} ions (the formation of positive holes). There is a question under which conditions can both these opposite-heading processes (the simultaneous decrease of the U^{6+} and U^{4+} concentrations) appear at the same time. In order to clear this question, let us carry out a following consideration: We assume at first that uranium can exist in the oxide only in two oxidation states, *e.g.* U^{4+} and U^{6+}. The reduction of uranium(VI)

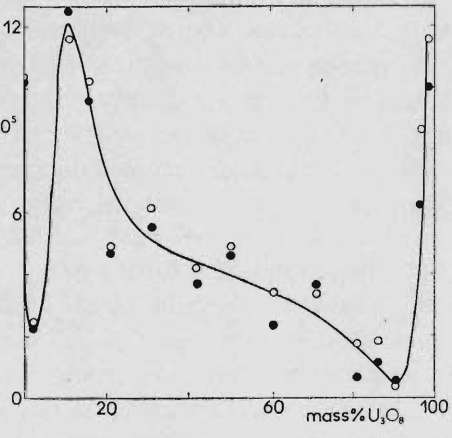

FIG. 3

Dependence of the specific catalytic activity k_s (l m^{-2} min^{-1}) (at 308 K) on the composition of non-irradiated (○) and irradiated (●) catalyst can be described by equation (*5*), the process of the positive holes formation in the oxide by equation (*6*):

$$d'\mathrm{U}^{6+} = d'\mathrm{U}^{4+} \tag{5}$$

$$d\mathrm{U}^{4+} = d\mathrm{U}^{6+}\,, \tag{6}$$

where symbol d signifies the concentration change of the given ion. Conditions describing the observed concentration decrease of U^{6+} resp. U^{4+} are given by relations (*7*) and (*8*):

$$d\mathrm{U}^{6+} < d'\mathrm{U}^{6+} \tag{7}$$

$$d'\mathrm{U}^{4+} < d\mathrm{U}^{4+}\,. \tag{8}$$

From equations (*5*) and (*6*) it is clear that unequalities (*7*) and (*8*) can not be valid both at the same time. This means that, if uranium would exist only in the two oxidation states, one could not simultaneously observe a decrease of oxidative ability of the catalyst surface as well as a decrease of catalytic activity – both with an increasing content of NiO in the sample (all that under the assumption that a surface concentration of U^{6+} ions is measured by the iodometric titration and that the catalytic activity is given by the U^{4+} concentration). If we now expect that in uranium oxide uranium can exist also in a third oxidation state, *e.g.* U^{5+} (in addition to U^{4+} and U^{6+}) – in agreement with a study of magnetic properties of $\mathrm{U_3O_8}$ (ref.[15]) – then the reduction of uranium(VI) can be written as (*9*) and the formation of positive holes in the oxide as (*10*):

$$d'\mathrm{U}^{6+} = d'\mathrm{U}^{5+} + d'\mathrm{U}^{4+} \tag{9}$$

$$d\mathrm{U}^{4+} = d\mathrm{U}^{5+} + d\mathrm{U}^{6+}\,. \tag{10}$$

Applying relations (*9*) and (*10*) to conditions describing the decrease of U^{6+} and U^{4+} concentrations (*7*) and (*8*) we have:

$$d\mathrm{U}^{4+} - d'\mathrm{U}^{4+} < d'\mathrm{U}^{5+} + d\mathrm{U}^{5+} \tag{11}$$

$$d'\mathrm{U}^{6+} - d\mathrm{U}^{6+} < d\mathrm{U}^{5+} + d'\mathrm{U}^{5+}\,. \tag{12}$$

This means that the overall decrease both of the uranium(IV) and uranium(VI) ion concentrations must be smaller than the total increase of the uranium(V) ion concentration. Under such conditions it is possible that, as the result of both discussed processes (the reduction of U^{6+} ions and the formation of U^{5+} and U^{6+} positive holes), the U^{6+} and U^{4+} concentrations can decrease simultaneously.

From a quantitative comparison of the discussed correlations (Fig. 2, curve *1* and Fig. 3) one is justified to assume that in the extreme concentration region of uranium oxide excess, the processes leading to the formation of positive holes in the oxide prevail over the reduction of uranium(VI). On the basis of the above mentioned facts one can suggest (in agreement with the principle of bivalent sites[2]) a model of elementary catalytic reactions leading to the hydrogen peroxide decomposition on the studied two component catalyst – valid for both limiting composition regions. For the region of NiO excess we can write:

$$Ni^{2+} \rightarrow Ni^{3+} + e^- \qquad (A)$$

$$H^+ + e^- \rightarrow H \qquad (B)$$

$$HO_2^- \rightarrow HO_2 + e^- \qquad (C)$$

$$Ni^{3+} + e^- \rightarrow Ni^{2+}. \qquad (D)$$

Decisive for the catalytic activity of the catalyst is the donor process (*C*) and (*D*), proceeding on the minor acceptor sites formed by Ni^{3+} ions. For the region of U_3O_8 excess we have:

$$U^{4+} \rightarrow U^{6+} + 2\,e^- \qquad (E)$$

$$2\,H^+ + 2\,e^- \rightarrow 2\,H \qquad (F)$$

$$2\,HO_2^- \rightarrow 2\,HO_2 + 2\,e^- \qquad (G)$$

$$U^{6+} + 2\,e^- \rightarrow U^{4+} \qquad (H)$$

In this case the catalytic activity of the catalyst is determined by the acceptor process (*E*) and (*F*), proceeding on the minor sites formed by U^{4+} ions. Besides the mentioned (U^{4+}–U^{6+}) pair of sites, also the pairs (U^{4+}–U^{5+}) and (U^{5+}–U^{6+}) can participate in the reaction.

The dependence of the specific activity on the catalyst composition observed in both limiting composition regions (Fig. 3) can be, on the basis of the discussed model, explained – for increasing content of that component which is less abundant – by the decreasing surface concentration of catalytic minor sites.

In the composition range 20–80 of weight % of U_3O_8 is the change of catalytic activity with the catalyst composition probably caused only by the changing relative abundance of two components of different catalytic activity (the monotonic part of the plot in Fig. 3). A maximum observed on the discussed dependence with the sample of about 10 weight % of U_3O_8 can be on basis of the principle of bivalent catalytic sites – explained similarly to many other two component catalysts[2]. In this case the reaction can proceed, due to proper dispersity of both components, not only on the NiO and uranium oxide sites (as it was the case in the 20–80% U_3O_8 range), but probably also on the mixed pair sites (U^{4+}–Ni^{3+}) and (Ni^{2+}–U^{6+}). With the first pair according to relations (*E*), (*F*), (*C*), (*D*) and (*I*):

$$2\,Ni^{3+} + U^{4+} \rightleftharpoons 2\,Ni^{2+} + U^{6+}\,. \qquad (I)$$

With the second pair according to relations (*A*), (*B*), (*G*), (*H*) and (*K*):

$$2\,Ni^{2+} + U^{6+} \rightleftharpoons 2\,Ni^{3+} + U^{4+}\,. \qquad (K)$$

A dissociation of the H_2O_2 molecule to H^+ and HO_2^- ions is assumed in all the above schemes. Relations (*I*), and (*K*) in the last two schemes express the equilibration process between the donor and acceptor catalyst sites. In both extreme composition regions is the equilibrium given by equations (*A*), (*D*), (*E*), (*H*). From (Fig. 3) one can see that the applied irradiation does not influence the reaction mechanism. The fact that an irradiation of the high content uranium samples does several times increase the number of oxidative surface species (probably uranium(VI)), while at the same time the catalytic activity of theses samples remains unchanged (Fig. 2, Fig. 3) – supports the basic assumption of the suggested model, according to which the catalytic activity of uranium oxide does not depend on the surface concentration of uranium(VI) ions, which are according to the model the major catalytic reaction sites. The fact that in both, close to the borderline composition regions decreases the value of the apparent reaction activation energy with the increasing amount of the minor catalyst component (Fig. 4) suggests a participation of a growing

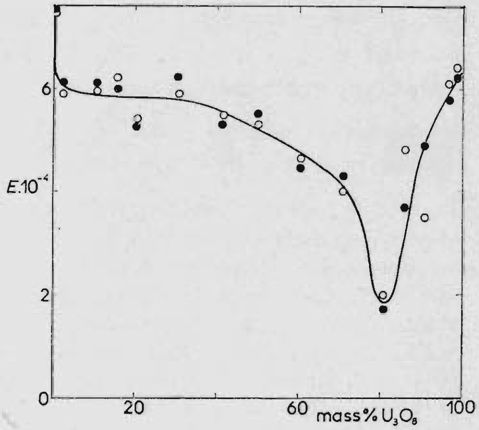

FIG. 4

Dependence of the apparent activation energy *E* (J mol^{-1}) on the composition of non-irradiated (○) and irradiated (●) catalyst number of more active catalyst sites in the reaction. Such effect is especially significant in the region of uranium oxide excess and it can not be influenced by an irradiation of the catalyst. It is possible that this is connected with a participation of the (U^{4+}–U^{5+}) and (U^{5+}–U^{6+}) sites in the reaction (in addition to the (U^{4+}–U^{6+}) sites). Besides to that, vacancies in the anion sublattice of uranium oxide can also act as catalytic acceptor sites. Such vacancies can be formed as the result of NiO presence (as the second way of a neutral charge balance – in addition to the already mentioned positive holes formation[13,14]). From the fact that the decrease of the apparent activation energy – observed with a growing content of NiO in U_3O_8 (Fig. 4) – is connected with lesser catalytic activity (Fig. 3), one can conclude that the process of positive holes formation prevails over the formation of oxygen vacancies (especially in the NiO low content region), in agreement with the results[13,14].

A thermal treatment of sample 3 (Table I), containing 11 weight % of U_3O_8 (the sample with the highest specific catalytic activity – Fig. 3), results in an increase of the specific activity in the case when the sample was treated at a temperature not below the calcination temperature (1 073 K); the following values of specific catalytic activity were measured (at 308 K) for samples treated at 673, 873 and 1 073 K: 11·2, 12·0 and 21·04 ($\text{l m}^{-2} \text{min}^{-1}$). A significant increase of activity is observed in the last case, in spite of sintering processes in the sample (at 1073 K), leading to lower specific surface values. An explanation can be found in possible formation of a new equilibrium among all types of catalytic centres, which can occur as a result of redox processes or as a consequence of the increased mutual charge interaction between both catalyst components; the later stipulates the participation of catalytic mixed-pair sites in the reaction. Confirmation of the fact that different catalytic sites take part in the catalytic process can be seen also on the time dependence of the measured apparent activation energy values of the studied reaction (Table I). The obtained values depended on time at which the samples were left in air at the laboratory temperature. The observed changes are probably connected with equilibration among various types of catalytic centres on the catalyst surface, in a similar way as it was observed with the system nickel(II) oxide–copper(II) oxide[16]. Comparable changes were found with catalysts irradiated with gamma rays.

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