

## DECOMPOSITION OF HYDROGEN PEROXIDE ON A MIXED $\text{Cr}_2\text{O}_3$ -ZnO CATALYST

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The paper deals with the behaviour of a two-component catalyst based on chromium(III) and zinc oxides in the decomposition of hydrogen peroxide. Explanation for the mechanism of elementary processes of the test reaction is based on the principle of bivalent sites. The experiments made on samples irradiated with fast neutrons and gamma radiation proved "sensitivity" of this catalyst to the applied radiation only at a quite definite composition of the catalyst.

Decomposition of hydrogen peroxide on chromium(III) oxide has been many times studied. It was found that chromium(III) oxide or the same oxide deposited on aluminium oxide exhibits a several times higher catalytic activity than the same sample tested after reduction<sup>1</sup>. In the study of the effect of alkaline admixtures on the catalytic activity of oxide it has been established<sup>2</sup> that the catalytic activity rises with amount of the admixture ( $\text{K}_2\text{O}$ ), this fact being according to the authors in connection with stabilization of chromates in the oxide. An opposite effect—decrease in catalytic activity of oxide with an alkaline admixture added—was observed by other authors<sup>3</sup> who interpret this effect likewise by the stabilizing effect of the alkaline admixture upon chromate present in chromium(III) oxide which is catalytically inactive. The fact that the ratio of trivalent and hexavalent chromium plays here probably an essential role is confirmed by constant catalytic activity of chromium(III) oxide samples prepared in various ways, if activity is related to the unit amount of superstoichiometric oxygen<sup>4</sup>. Analogously, further authors<sup>5,6</sup> anticipate the  $\text{Cr}^{3+}$  ions and  $\text{Cr}^{6+}$  ions to function in chromium(III) oxide as catalytic donor or acceptor sites, respectively. A distinct role of chromium occurring in two different valency states has been pointed out also by Mochida and Takeshita<sup>7</sup> who, of course, assume catalytic sites formed by  $\text{Cr}^{2+}$  and  $\text{Cr}^{3+}$  ions.

In the present paper, catalytic properties of a two-component catalyst of chromium-(III) oxide-zinc oxide with various quantities of both components within the whole concentration range of 0–100% of the pure component have been studied. As a test reaction, decomposition of aqueous solution of hydrogen peroxide (1.2 M/L) was employed. The obtained results may be compared with some results of papers referred above as well as with those presented in papers dealing with catalytic properties of two-component oxide catalysts of the NiO-ZnO (ref.<sup>8,9</sup>), NiO-CuO (ref.<sup>9,10</sup>), and CuO-ZnO (ref.<sup>11</sup>) types. The present paper aims at checking, whether the principle of bivalent catalytic sites can be applied to this system in an analogous way as in the

systems mentioned above. In addition, the paper deals with the effect of ionizing radiation on the catalyst examined.

### EXPERIMENTAL

The samples of the mixed catalyst were prepared by a stepwise precipitation of a mixture of chromium(III) and zinc nitrates (1 M/L, A.R.), having various concentrations of both metals, with saturated sodium carbonate solution (A.R.) at 40°C. The precipitate was, after filtering and thorough washing, dried for 12 hours at room temperature and for 24 hours at 110°C. The subsequent calcination was carried out in the air in an electric furnace at 380°C for a period of 6 hours. After the calcination, chromates were washed out from the sample with distilled water. Chemical analysis of the samples was accomplished iodometrically (determination of chromium) and complexometrically (determination of zinc)<sup>1,2</sup>. Chemisorbed oxygen was determined iodometrically. The structure of the catalysts was studied by X-ray diffraction (Cu-anode). Specific surface area of the samples was measured by a low-temperature adsorption of nitrogen from a nitrogen-hydrogen mixture. The catalytic activity of individual samples was established by measuring quantity of oxygen evolved at constant temperature and pressure<sup>8</sup>. The measurement was made at four different reaction temperatures within 30–45°C. It was found by preliminary experiments that under given conditions (200 mg of catalyst, 25 ml of hydrogen peroxide solution of the 1.2 M/L starting concentration, reaction temperature of 30–45°C) the reaction takes place in a kinetic region and is not influenced by external transport processes. The test reaction was accomplished maximally up to the 5% degree of hydrogen peroxide decomposition and the catalytic activity of individual samples was characterized by the rate constant of the first order reaction. The catalytic activity of samples treated by ionizing radiation in advance was determined in the same way. The samples were irradiated by gamma radiation of <sup>60</sup>Co so that the absorbed dose amounted to  $7 \cdot 10^6$  J/kg, and by fast neutrons from the Am-Be source (the portion of thermal neutrons was smaller than 5%), the dose being 37 J/kg.

### RESULTS

It follows from the results of chemical analysis (Table I) that the system prepared under given conditions is obviously not composed from chromium(III) oxide and zinc oxide only (sum of weight % does not reach 100%). The deficiency is a nonmonotonic function of the catalysts composition (Fig. 1). In spite of the fact that this deficiency is for some samples relatively great (almost 20%), further crystalline structure could be detected by X-ray diffraction for none of them. As follows from Table I, the method made it possible to determine the amount of superstoichiometric chemisorbed oxygen merely in samples containing excess of chromium oxide. As follows from the comparison of values belonging to samples 7, 7a, and 7b, higher temperature of calcination leads to a decrease in the amount of chemisorbed oxygen.

The fact that the studied catalytic system has a more complicated surface structure is proved by the dependence of specific surface areas of samples upon their composition (Table I), where three distinct maxima at 52.4, 66.7, and 77.4 molar % of zinc oxide can be observed. By comparing appropriate values of the specific surface in samples 7, 7a, and 7b, calcinated at various temperatures, it follows that higher

temperature of calcination results in a decrease in specific surface area of the mixed oxide. With the rising temperature of an additional thermal treatment of the catalyst in a nitrogen atmosphere for 2 hours, magnitude of the specific surface decreases, provided this temperature is higher than that of the calcination. The effect of the ap-

TABLE I

Composition, Amount of Chemisorbed Oxygen  $O^{2-}$  (weight %) and Specific Surface  $S$  ( $m^2 g^{-1}$ ) of Catalysts

7a; 7b: temperature of calcination 280°C and 900°C, resp.

Sample	ZnO weight %	Cr <sub>2</sub> O <sub>3</sub> weight %	ZnO mol %	Cr <sub>2</sub> O <sub>3</sub> mol %	O <sup>2-</sup>	S
1	0.0	88.0	0.0	100.0	0.049	11.3
2	0.4	94.1	0.7	99.3	0.023	8.5
3	13.5	76.1	25.0	75.0	0.026	24.2
4	18.3	76.6	32.4	67.6	0.021	27.4
5	30.2	51.4	52.4	47.6	0.026	45.3
6	38.6	50.0	59.1	40.9	0.000	15.0
7	47.4	40.4	66.7	33.3	0.034	46.8
7a	47.4	40.4	66.7	33.3	0.043	53.5
7b	47.4	40.4	66.7	33.3	0.000	1.7
8	52.3	31.6	74.8	25.2	0.000	24.9
9	53.5	29.2	77.4	22.6	0.000	55.0
10	66.2	19.8	86.3	13.7	0.000	37.0
11	79.2	6.7	95.7	4.3	0.000	25.6
12	91.2	0.7	99.6	0.4	0.000	17.4

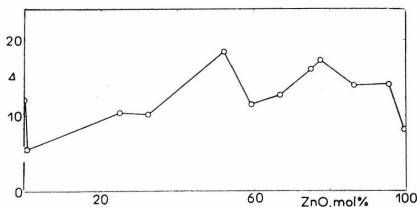


FIG. 1

Plot of Deficiency of Chemical Analysis ( $\Delta/[\%]$ ) against Composition of Samples

plied radiation is at the same time of no substantial influence on this quantity (Table II).

The catalytic activity of the prepared catalysts is a nonmonotonic function of their composition (Fig. 2, curve 1) with three distinct maxima at the composition equal to that for maxima of the specific surface (Table I). The qualitatively consistent course of this dependence was also found for irradiated samples (Fig. 2, curves 2, 3). Calculation of the specific catalytic activity (the rate constant standardized for unit of the catalyst surface area) (Fig. 3) shows this value, independent of magnitude of the spe-

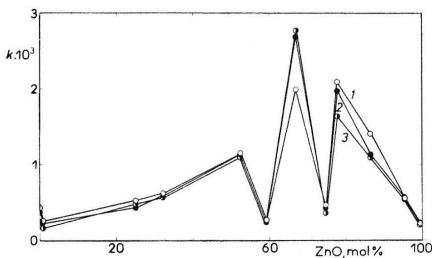


FIG. 2

Plot of Rate Constant  $k$  ( $\text{Lg}^{-1} \text{min}^{-1}$ ) at  $45^\circ\text{C}$  against Composition on Nonirradiated (1), gamma-Irradiated (2), and Neutron Irradiated (3) Catalysts

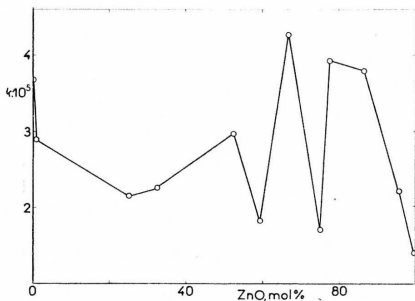


FIG. 3

Plot of Specific Catalytic Activity  $k_s$  ( $\text{Lm}^{-2} \text{min}^{-1}$ ) at  $45^\circ\text{C}$  against Composition of the Catalysts

cific surface, to exhibit three maxima at the catalyst composition already mentioned. The measurement of the catalytic activity of the samples at various temperatures led to the establishment of apparent activation energy of the reaction, which does not exhibit any marked dependence on the catalyst composition and its average value for nonirradiated and irradiated samples is  $8.4 \cdot 10^4 \pm 1 \cdot 10^4$  J/mol.

Effect of various treatment of some samples on their catalytic activity is summarized in Table III, which shows that with the increasing temperature of calcination specific catalytic activity of the catalyst decreases along with the apparent activation energy of the reaction (7a, 7, 7b). Unsuccessful washing out of chromates from the sample (7c) results in a significant decrease in the specific surface area and in an increase of specific catalytic activity by one order of magnitude. A significant increase in the catalytic activity of the sample can be achieved also by treating the catalyst — sample 9a

TABLE II

Effect of Thermal Treatment and of Irradiation of Catalyst No 9 by gama-Radiation and Neutrons upon Specific Surface Area  $S$

Irradiation	—	gama	—	—	—	n	n	n	n
$t, ^\circ\text{C}$	—	—	300	500	800	—	300	500	800
$S, \text{m}^2 \text{g}^{-1}$	55.0	59.2	72.1	45.0	17.4	54.5	70.0	51.8	11.6

TABLE III

Effect of Different Treatment of Samples on their Specific Surface  $S$ , Catalytic Activity  $k$ , Specific Catalytic Activity  $k_s$ , and Apparent Activation Energy  $E$

7c sample with nonwashed chromates; 9a sample treated with conc. hydrogen peroxide; 9b sample 9a washed with water; 9c filtrate of the washed sample.

Sample	$S$ $\text{m}^2 \text{g}^{-1}$	$k \cdot 10^5$ $\text{L g}^{-1}$ $\text{min}^{-1}$	$k_s \cdot 10^5$ $\text{L m}^{-2}$ $\text{min}^{-1}$	$E \cdot 10^{-4}$ $\text{J mol}^{-1}$
7	46.8	200	4.27	7.6
7a	53.5	384	7.25	10.2
7b	1.7	2.75	1.62	4.9
7c	17.4	1 420	81.50	7.3
9	55.0	216	3.92	9.8
9a	68.4	595	8.70	7.9
9b	63.4	311	4.90	7.6
9c	—	4.86	—	4.7

(the sample was stirred for several minutes in the 30% hydrogen peroxide solution, filtered, and dried at 120°C) with a 30% hydrogen peroxide solution.

Washing of the sample treated in such a way leads to a decrease in enhanced catalytic activity (9b). It was proved at the same time that chromates which can be washed out with water exhibit a very low catalytic activity (9c). Measuring of the catalytic activity in the first stage of the hydrogen peroxide decomposition showed (Fig. 4, curve 1) that there exists a very well reproducible mild deviation of the first reaction order in accordance with the autocatalytic process. This effect disappears with the increasing temperatures of thermal treatment of the catalyst and changes into an opposite one-deviation from the first reaction order in the retarding sense (Fig. 4, curves 2, 3).

## DISCUSSION

It follows from the results of analysis of the samples that catalysts prepared under given conditions are not composed merely from stoichiometric oxides. The deficiency found may be due to water present in the samples, which is relatively difficult to be completely removed from chromium(III) oxide<sup>13</sup>. In addition to this, the fact that in the prepared samples, chromates were qualitatively proved, and on the basis of literature data<sup>2-5,13</sup>, it can be justifiably anticipated that in the system prepared under given conditions chromium arises in various states of valency, which can be reason for the deficiency found. It has been proved<sup>5</sup> by a detailed study of conditions of the preparation of chromium(III) oxide that at the calcination temperature of 350°C

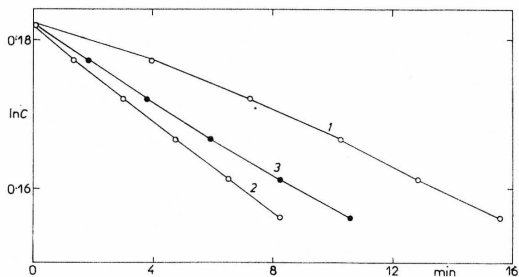


FIG. 4

Time Dependence of Natural Logarithm of Immediate Hydrogen Peroxide Concentration for Sample 9 at the Reaction Temperature of 30°C

Treatment: 1 untreated; 2 300°C; 3 500°C.

as many as 95% of the high-valent form of chromium is in the  $\text{Cr}^{6+}$  state. Hence, chromates can be assumed to be present also in our case, even when the valency state of chromium can be here affected by presence of zinc oxide in the sample.

Results of the above-mentioned papers obviously show that presence of the high-valent chromium in oxide is connected with the quantity of oxygen chemisorbed on its surface. On the other hand, zinc oxide is well-known to be substoichiometric in respect to oxygen<sup>14</sup>. Thus the fact can be explained that in the prepared series of catalysts, chemisorbed oxygen was found only in samples having excess of chromium(III) oxide in an amount approximately the same for all these samples. This can be reason for the fact that in our case no correlation between the amount of chromates anticipated in the sample and that of chemisorbed oxygen in the sample (Fig. 1, Table I) can be found, since reaction  $\text{Cr}^{3+} \rightarrow \text{Cr}^{6+} + 3 e^-$  can be here accompanied, beside reaction  $\text{O}^0 + e^- \rightarrow \text{O}^-$ , also by reaction  $\text{Zn}^{2+} + e^- \rightarrow \text{Zn}^+$  to follow electroneutrality of the sample. This has been also proved by the fact that for pure chromium(III) oxide an amount of chemisorbed oxygen<sup>5</sup> approximately of one order of magnitude higher than in our case was found.

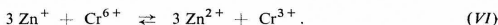
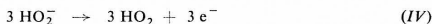
Nonmonotonic dependence of the specific surface area upon composition (Table I) expresses possible influence of both oxides between one another, analogously to other two-component systems<sup>8-11</sup>. The fact that the edge maxima are being found for the same composition of samples as maxima of the analysis deficiency, gives possibility to anticipate in this case that they have the same cause in both cases. If the deficiency mentioned is due to the chromate present, also a larger specific surface area may be caused by chromate. Owing to the fact, however, that chromates capable of being washed out decrease the specific surface area (Table III, 7c), it can be assumed that chromates sufficiently firmly built in the oxide catalyst are here probably concerned. Different character of chromates in chromium(III) oxides is confirmed also by other results<sup>5</sup>. This question, however, still remains open and for its elucidation, further detailed research of the chromium catalyst will be needed. Observed decrease in the specific surface with the increasing temperature of calcination is likely due to the sintering process occurring in the catalyst surface. In connection to this, also amount of chemisorbed oxygen (expressed in weight %) in the sample surface obviously decreases, since the factor characterizing decrease in the specific surface area amounts to 1.1, and that of the decrease in the amount of chemisorbed oxygen 1.2 (Table I). The same can be said of the effect of thermal treatment of the samples (Table II). Higher value of the specific surface of samples thermally treated at a temperature of 300°C is obviously connected with the fact that at this temperature, formation of partially amorphous chromium(III) oxide may be expected<sup>5</sup>. Practically no effect of applicable radiation on value of the specific surface of samples can be connected with relatively low fluency of radiation, which is insufficient to evocate a measurable change in the magnitude of specific surface area<sup>15</sup>.

If nonmonotonic dependence of specific surface area on the composition of samples is due to presence of chromates, it can be anticipated that likewise nonmonotonic dependence of specific catalytic activity on the composition (Fig. 3) is incidental to the chromate present, since maxima of both dependences take place for the same composition of the catalyst. A qualitatively equal course of the last-mentioned dependence was observed likewise in a series of other two-component catalysts<sup>9-11</sup>. An explanation for this course was based on an assumption that both components are influenced between one another, provided that principle of bivalent catalytic sites<sup>16</sup> was valid. It is possible to assume that also in our case, influence of both oxides between one another may be concerned; this influence can be on the basis of the above-mentioned principle reason for the effect observed.

From the study of the catalytic activity of pure zinc oxide<sup>17</sup> the  $Zn^+$  ions, which are represented in a minority and are in equilibrium with acceptor majority sites  $Zn^{2+}$ , can be assumed to act here in terms of donor sites. For chromium(III) oxide, the  $Cr^{3+}$  donor sites probably seem to act here as the majority sites and chromium ions of higher valency to be minority sites of the acceptor nature. This assumption is confirmed in papers showing that catalytic activity of oxide is proportional to the amount of chemisorbed oxygen<sup>2,4,6</sup>. According to the result given in<sup>5</sup> the acceptor sites are very probably ions of hexavalent chromium. This assumption is supported also by our finding that unsufficiently washed sample (containing a considerable amount of chromates) shows by one order of magnitude higher activity than the washed samples (Table III, 7c).

On the basis of these facts the catalytic system under study can be described by characteristic constants<sup>16</sup> in the following way:  $D = Zn$ ;  $A = Cr$ ;  $d = 1$ ;  $a = 3$ ;  $\delta = 1$ ;  $\alpha = 3$ , where  $D, A$  are elements with a function of a donor and acceptor catalytic site resp.,  $d, a$  is number of electrons transferred in one elementary step by the donor and acceptor site resp.,  $\delta, \alpha$  is the lowest valency state of the element which has a function of the donor and acceptor catalytic site resp.

The decomposition of hydrogen peroxide can be for the studied system described by a general diagram<sup>16</sup> which for the chromium(III) oxide-zinc oxide system has the following form:



Reactions (II) and (III) express the acceptor process, reactions (IV) and (V) the donor process, and reaction (VI) secures equilibrium of both kinds of catalytic sites. Explanation for the nonmonotonic dependence of the catalytic activity on the catalysts composition is the same as for other two-component systems<sup>8-11</sup>. Maxima at the



composition of 52.4 mol % and 77.4 mol % of zinc oxide can be accounted for the fact that for this composition, maximum concentration of pairs of acceptor and donor reactions sites lies in the surface of the sample. This opinion is also confirmed by maxima of the chemical analysis deficiency (Fig. 1) found in the experiment. The fact that both maxima under discussion are in the region of the excess of zinc oxide (unlike to other two-component systems) is likely connected with the presence of chromates in individual samples and with dispersity of individual components of the catalyst. The maximum of catalytic activity at 66.7 mol % of zinc oxide is probably of a differing nature and may be explained in the same way as for other systems by a large area of a highly defected interphase of the system at this composition. This assumption is also confirmed by the maximum of magnitude of the specific surface for the given composition of the catalyst (Table I). Also result of the measurement of the catalytic activity of irradiated catalysts confirms the assumption presented. The reaction mechanism is here obviously identical (qualitatively consistent course of dependence of the catalytic activity on the composition of irradiated as well as nonirradiated samples, Fig. 2) with that of nonirradiated samples. Evaluation of the relative effect of radiation shows (Fig. 5), however, that a significant influence of samples by radiation can be observed just at the composition of 66.7 mol % of zinc oxide (in addition to a negative effect of practically pure chromium(III) oxide irradiated by neutrons; this fact, of course, can be influenced by a relatively large error owing to a relatively low catalytic activity of this sample). This can be explained, analogously to the nickel oxide-zinc oxide system simultaneously irradiated by gamma rays and neutrons<sup>18</sup>, by the fact that the nonequilibrium charge defects produced in the sample after its irradiation are stabilized on crystallographic defects of interphases and can thus serve as catalytic sites of the test reaction.

From the viewpoint of the mechanism suggested, also increased catalytic activity of the sample pretreated with concentrated hydrogen peroxide (Table III, 9a) can be

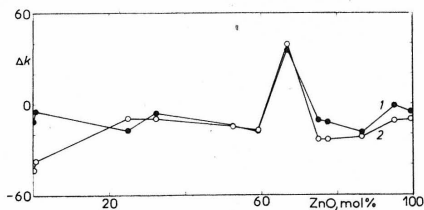


FIG. 5

Plot of the Effect of gamma-Radiation (1) and Neutrons (2) on Catalytic Activity ( $\Delta k$ /[%]) Against Composition of Samples

explained. This treatment probably leads to a partial oxidation of trivalent chromium, thus the surface concentration of the minority acceptor sites of the catalyst being increased. After washing out produced chromates from the sample (Table III, 9b), partial decrease in catalytic activity takes place. This fact, however, suggests a problem, whether the reaction proceeds or not as a homogeneous catalytic process after the partial dissolution of chromates in the solution of hydrogen peroxide. However, catalytic activity of the filtrate is after washing the sample (Table III, 9c) negligible to the catalytic activity of studied catalysts, which, similarly as in<sup>5</sup>, gives evidence of the heterogeneous nature of the test reaction. These findings allow then to assume that chromate raises catalytic activity of chromium(III) oxide or that of the chromium(III) oxide-zinc oxide system, provided that suitable dispersity and sufficiently firm contact with oxide are achieved, although chromate itself is catalytically inactive. This is quite in accordance with the principle of bivalent catalytic sites<sup>16</sup>, since in the chromate itself chromium of lower valency obviously cannot be assumed. This is likely an explanation for contradictory observations concerning the effect of chromate or alkali metal oxides on the catalytic activity of chromium(III) oxide<sup>2,3,5</sup>.

It follows from the presented model of hydrogen peroxide decomposition (reactions I-VI) that in one elementary step taking place on the acceptor site, 3 electrons ( $a = 3$ ) are being exchanged. From the systems studied hitherto, when during one elementary step more than 1 electron is exchanged, nickel oxide prepared from oxalate<sup>19</sup> ( $d = 2$ ) and copper(II) oxide produced from hydroxide<sup>20</sup> ( $d = 2$ ) were involved. The catalysts exhibited in both cases lower value of apparent activation energy of the test reaction. However, for the two-component catalyst followed in this paper, no distinct dependence of this quantity on the catalyst composition has been observed. This is obviously due to the presence of zinc oxide in the system, on the sites of which transfer of only one electron takes place, and furthermore to the fact that this oxide can affect the oxidation state of chromium in the catalyst. As a result of this, ions of lower valency  $\text{Cr}^{5+}$ ,  $\text{Cr}^{4+}$ , which were proved in chromium(III) oxide calcinated at lower temperature<sup>5</sup>, can here appear, in addition to the  $\text{Cr}^{6+}$  ions, as the minority acceptor sites. This has been also proved by a feeble dependence of the amount of chemisorbed oxygen on composition (Table I). Likewise, the "compensating" effect observed in samples calcinated at various temperatures (Table III, 7a, 7, 7b) supports the given assumption in a similar way as was observed in pure chromium(III) oxide<sup>5</sup>. The major part of chromium is assumed to turn into a higher oxidation state with growing temperature of calcination; as a result of this number of sites characterized by constants  $a = 3$  increases, whereby the apparent activation energy of the reaction decreases. Simultaneously, however, higher temperature of calcination evidently destroys catalytic sites and the catalytic activity of the catalyst decreases.

Following the suggested model of hydrogen peroxide decomposition the observed deviation of the reaction order from 1 in the first stages of the reaction (Fig. 4) may be

discussed. Analogously to other systems under investigation<sup>8-11,19,20</sup> it may be even here assumed that on dipping the catalyst into the hydrogen peroxide solution new equilibrium of the reduction-oxidation states of catalytic active sites is established, this equilibrium being obviously in this case, due to oxidation of chromium, shifted according to reaction(VI) towards the left side. The experiments made cannot give an unambiguous decision, whether hydrogen peroxide or atomic oxygen evolving during the reaction here appears as an oxidizing agent. Thermal treatment of the sample, as has been presented, provides in advance partial oxidation of chromium to higher valency states, whereby effect of the autocatalytic process is then for these samples smaller or turns at last into the retarding process caused by reduction of higher oxidation states of chromium (minority acceptor sites), similarly as has been observed with pure zinc oxide<sup>17</sup>. This phenomenon likewise supports validity of the principle of bivalent catalytic sites.

## REFERENCES

1. Voltz S. E., Weller S. W.: *J. Amer. Chem. Soc.* **76**, 1586 (1954).
2. Voltz S. E., Weller S. W.: *J. Phys. Chem.* **59**, 569 (1955).
3. Kraus M., Andreev A., Mihailova D., Nondek L.: *This Journal* **40**, 3856 (1975).
4. Matsunaga Y.: *Bull. Chem. Soc. Jap.* **30**, 984 (1957).
5. Deren J., Haber J., Podgorecka A., Burzyk J.: *J. Catal.* **2**, 161 (1963).
6. Deren J., Haber J.: *J. Catal.* **4**, 22 (1965).
7. Mochida I., Takeshita K.: *J. Phys. Chem.* **78**, 1653 (1974).
8. Múčka V., Cabicar J.: *This Journal* **40**, 236 (1975).
9. Múčka V., Cabicar J., Motl A.: *This Journal* **40**, 340 (1975).
10. Múčka V.: *This Journal* **42**, 391 (1977).
11. Múčka V., Malý P.: *This Journal* **41**, 3679 (1976).
12. Klumpar J.: *Thesis*. Czech Technical University, Prague 1976.
13. Weller S. W., Voltz S. E.: *J. Amer. Chem. Soc.* **76**, 4695 (1954).
14. Mach G. W., Schwab G. M., Sizmann R.: *J. Catal.* **14**, 261 (1969).
15. Taylor E. H.: *Advan. Catal. Relat. Subj.* **18**, 111 (1969).
16. Múčka V.: *This Journal* **42**, 2074 (1977).
17. Múčka V.: *This Journal* **41**, 3504 (1976).
18. Múčka V., Cabicar J.: *This Journal* **40**, 947 (1975).
19. Schwab G. M., Múčka V.: *Z. Phys. Chem. (Frankfurt am Main)* **93**, 77 (1974).
20. Múčka V.: *This Journal* **41**, 1717 (1976).

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