HYDROGEN PEROXIDE DECOMPOSITION ON A TWO-COMPONENT CuO–Cr$_2$O$_3$ CATALYST

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Some physical and catalytic properties of the two-component copper(II)oxide–chromium(III) oxide catalysts with different content of both components were studied using the decomposition of the aqueous solution of hydrogen peroxide as a testing reaction. It has been found that along to both basic components, the system under study contains also the spinel structure CuCr$_2$O$_4$, chromate washable by water and hexavalent ions of chromium unwashable by water. The soluble chromate is catalytically active. During the first period of the reaction the equilibrium is being established in both homogeneous and heterogeneous catalytic systems. The catalytic activity as well as the specific surface area of the washed solid is a non-monotonous function of its composition. It seems highly probable that the extreme values of both these quantities are not connected with the detected admixtures in the catalytic system. The system under study is very insensitive with regard to the applied doses of gamma radiation. Its catalytic properties are changed rather significantly after the thermal treatment and particularly after the partial reduction to low degree by hydrogen. The observed changes of the catalytic activity of the system under study are very probably in connection with the changes of the valence state of the catalytically active components of the catalyst.

The specific catalytic activity of two-component oxide catalysts tested by the decomposition of hydrogen peroxide has typically[1] a non-monotonous or at least non-linear dependence on their composition. This is evidently given by the mutual interaction of both components of the catalyst. From this point of view it seemed interesting to investigate the system CuO–Cr$_2$O$_3$ as the interaction of these oxides can result in the formation of a compound (spinel CuCr$_2$O$_4$). Moreover, both copper and chromium can exist in the form of stable ions of different valence states what can exhibit a profound effect on the catalytic activity of this catalyst. In the case of cupric oxide[2] the ions Cu$^+$ and in the case of chromium sesquioxide the ions Cr^{6+} (connected with chemisorbed oxygen[3-6]) have to be taken into consideration. The valence state of both these metal ions in these oxides can be changed by irradiation and this fact should be reflected in the changes of the catalytic activity as it was observed in the case of chromium sesquioxide catalyzing the decomposition of hydrogen peroxide[7] or cracking of 1-hexane[8] or in the case of both these oxides with respect to the decomposition of propanol[9]. The change of the valence state of the irradiated oxide active component causes evidently the modification of the irradiated

two-component oxide catalyst activity[10]. This was the reason of the investigation of the sensitivity of the system under study, i.e., $CuO-Cr_2O_3$,with respect to the ionizing radiation.

EXPERIMENTAL

Two-component oxide catalysts of copper and chromium were prepared from the solutions of the respective nitrates (analytical grade) mixed in such ratios that the resulting catalysts covered the whole region of composition, i.e., from 0 to 100% of either component. The metal nitrates in these solutions were precipitated by the solution of sodium carbonate (analytical grade) at 40°C. After a multiple decantation of the precipitate (up to the negative reaction for nitrate ions) the precipitate was filtered, dried at the room temperature, crushed in agate mortar and calcinated for 4 hours on air at the temperature of $(400 \pm 20)°C$.

Chemical analysis of the samples was made after alkaline fusion using electrolysis (for the determination of copper) and iodometry (for the determination of chromium). The specific surface areas of samples were measured using the low-temperature adsorption of nitrogen from the mixture $N_2 : H_2 = 1 : 3$. The crystalline structures were determined by X-ray diffraction using the K_α emission line of chromium.

The photoelectron spectra (ESCA) were measured with selected samples using the spectrometer VG ESCA 3 Mk and the spectrometer Perkin–Elmer 684 was used for the measurement of infrared spectra. The morphology of samples was followed by the scanning electron microscope JSM 50 (Jeol).

Before testing their properties the soluble chromates were washed out from the aliquots of samples by distilled water up to the negative reaction with silver nitrate. The washed samples were dried at the room temperature for 7—10 days. The washed-out chromates were determined by iodometry.

Catalytic activity of all samples was tested by the decomposition of the aqueous solution of hydrogen peroxide (analytical grade) of the concentration of $1\cdot2$ mol l^{-1} at the temperatures of 30, 35, 40, and 45°C, under constant pressure. The rate of oxygen formation was taken as the measure of the catalytic effect. The overall error of the measurements did not exceed $\pm 10\%$. The catalytic actiity of samples was characterized by the first-order rate constant normalized to the weight (k_m) or to specific surface area (specific catalytic activity k_s) of the catalysts. The apparent activation energy of the testing reaction was calculated from the Arrhenius law. The same tests were used also for catalysts pre-irradiated by ^{60}Co gamma radiation with doses $5 \cdot 10^5$, $1\cdot7 \cdot 10^6$, and $2\cdot6 \cdot 10^6$ Gy, respectively.

RESULTS AND DISCUSSION

Physico-chemical Properties

The prepared series of catalysts is composed mainly of cupric oxide CuO and chromium sesquioxide Cr_2O_3 and it covers the whole range from 0 to 100% of either component (Table I). From the chemical analysis deficit δ, the dependence of which on the system composition is illustrated by Fig. 1, curve *1*, it is evident that the system contains also other components. Their concentration is a non-monotonous

function of the system composition. However, an analogous dependence of this quantity on the system composition for samples prepared by calcination of nitrates of both metals is linear[11]. This fact indicates a significant effect of the catalytic system preparation method on its properties. X-ray diffraction analysis of the system under study confirmed that along with the basic oxides both the cubic and tetragonal spinel structures of $CuCr_2O_4$ (Table I) are present in samples of certain composition. This structure is formed during the calcination of precursors (basic carbonates). The presence of spinel structure in some samples was also confirmed by the infrared spectroscopy. However, the presence of the spinel structure cannot be directly responsible for the magnitude of the chemical analysis deficit δ (and also the data given in Table I are not in correlation with the shape of the curve *1* in Fig. 1). This

TABLE I

Composition of catalysts, the apparent activation energies E of the testing reaction as measured on the unwashed (a), washed (b) samples and after 13-month storage of washed (c) catalysts and the crystalline phases present

Sample	CuO wt. %	Cr_2O_3 wt. %	E, kJ/mol			Phase[a]
			a	b	c	
1	0·0	87·8	53	52	66	Cr_2O_3
2	1·8	88·5	54	54	57	Cr_2O_3
3	4·0	88·4	48	50	48	Cr_2O_3
4	5·7	90·2	70	58	73	Cr_2O_3
5	7·9	90·7	76	72	96	Cr_2O_3
6	9·9	83·8	85	75	79	Cr_2O_3
7	18·8	74·6	78	75	43	Cr_2O_3, $CuCr_2O_4$(T)
8	28·7	62·9	78	70	65	Cr_2O_3, $CuCr_2O_4$(T), partly $CuCr_2O_4$(C)
9	40·3	55·6	71	81	69	defective $CuCr_2O_4$(C), traces of $CuCr_2O_4$(T)
10	48·7	47·2	87	89	76	$CuCr_2O_4$(C), CuO
11	59·0	40·8	93	94	78	decreasing increasing
12	67·6	32·8	98	97	85	conc. conc.
13	77·3	19·9	106	106	93	
14	88·8	10·2	90	98	91	CuO, traces of $CuCr_2O_4$(C)
15	90·2	8·2	96	100	92	CuO, tracew of $CuCr_2O_4$(C)
16	91·1	6·5	100	109	95	CuO
17	95·3	3·9	93	103	119	CuO
18	97·1	2·0	99	100	110	CuO
19	99·0	0·0	109	109	125	CuO

[a] (T) — tetragonal, (C) — cubic.

fact indicates that another phase, amorphous or finely dispersed, is present in the system. It is probable, as confirmed by some previously published results[6,12], that sodium ions introduced into the system in course of the carbonate precipitation are relatively strongly adsorbed on the precipitate formed and then a finely dispersed sodium chromate is formed in the system during calcination. This chromate can be washed out from the calcinated catalysts by water. The amount of chromate washed out by water from 1 g of a given sample is shown in Fig. 1, curve 2. The qualitatively identical shape of both curves in this figure demonstrates that the chemical analysis deficit of catalysts is given predominantly by the chromates washed out by water (however, other chromates, water, or further impurities present in the sample contribute also to this deficit). The micrographs of washed and unwashed samples taken with the 10,000-fold magnification show that the washable chromates form an independent agglomeration on the surface of the catalysts that fills the space between the grains of basic oxides, in full agreement with the previously published results[12]. Thus the presence of these chromates on the surface of samples decreases their specific surface area, especially in samples with a high content of chromium. In samples with the cupric oxide content > 30 wt. % the washable chromates have no significant effect on this quantity, the value of which is practically the same in samples prior or after washing (Fig. 2). From this figure it is also evident that in the region of approximately equal contents of both basic components of the catalyst the value of the specific surface area of samples reaches its maximum value. From the comparison of this dependences with the dependences shown in Fig. 1 in this
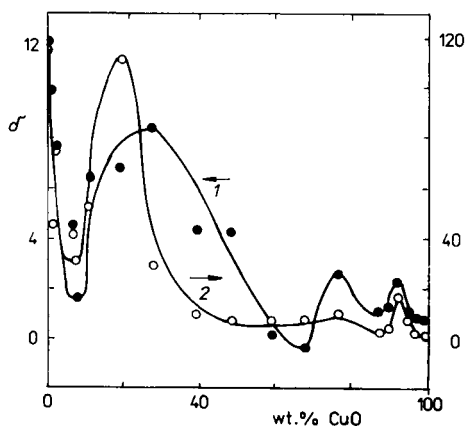

FIG. 1

Chemical analysis deficit δ(%) (*1*) and the amount of washable chromates m (mg/g) (2) vs the catalyst composition
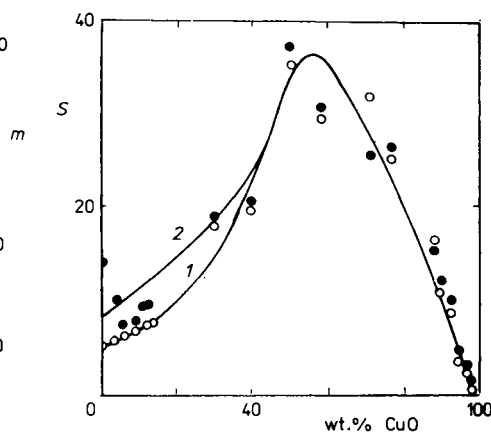
FIG. 2

Specific surface area S (m^2/g) of catalysts vs their composition, before (*1*) and after (2) washing with water

composition region it can be concluded that the above-mentioned maximum specific surface area of samples of this composition is connected neither with the washable chromates nor with other admixtures detected as the chemical analysis deficit δ. It seems probable that this maximum is due to the interaction of both basic oxides of the system the interphase contact area of which has a maximum in this region. This interaction is relatively stable with time as the character and even the absolute values of the function given in Fig. 2 exhibited no changes after the storage of samples at the room temperature for 13 months.

The interaction of both basic oxides in this system (given in this case by the interaction of electrical charges) has an effect also on the presence of univalent copper ions and hexavalent chromium ions on the surface of catalysts with different composition. The ions Cu^+ were found by ESCA only in the samples No. 4, 8, and 10. A relatively high abundance of Cr^{6+} ions (of the order of tens per cent with respect to the total number of chromium atoms) was found in samples with a low content of chromium. This abundance decreases with the increasing content of Cr and it reaches an approximately constant value in samples with approximately equal contents of both components and this value remains unchanged even in samples with a high content of Cr — cf. Table II. The presence of these ions is probably not directly connected with the washable chromate phase in the catalysts. It seems probable[13] that the presence of non-washable chromates is related to the interaction of the system with the air oxygen.

No changes of the physico-chemical parameters of the system under study have been observed in catalysts irradiated with the doses of γ rays mentioned above.

Catalytic Activity

The kinetic curves of the hydrogen peroxide decomposition on the catalysts with a high and low contents of washable chromates (samples No. 7 and 10, Fig. 3, curves 1(7), 1(10)), the curves for the decomposition proceeding in the homogeneous liquid phase in the filtrate after a long-term decomposition using the original (unwashed) sample (Fig. 3, curves 2(7), 2(10)), the kinetic curves for the decomposition proceeding on washed samples No. 7 and 10 (Fig. 3, curves 3(7), 3(10)), and finally the

TABLE II
Abundances (in %) of Cu^+ and Cr^{6+} ions on the surface of selected samples of catalysts

Sample	1	4	6	8	10	13	15	17	19
Cu^+, %	0	6	0	17	9	0	0	0	0
Cr^{6+}, %	25	31	20	20	22	37	71	80	0

curves for the decomposition proceeding in the filtrate after the decomposition using a washed sample (Fig. 3, curves 4(7) and 4(10)), all these results show that 1. the catalytic activity of the unwashed sample with a high content of washable chromate is comparable with the activity of the dissolved chromate (Fig. 3, curves 1(7), 2(7)); 2. the catalytic activity of the unwashed sample with a low content of washable chromate is significantly higher than the activity of the respective filtrate (Fig. 3, curves 1(10), 2(10)); 3. the catalytic activity of the washed sample with a high content of washable chromates (curve 3(7)) is significantly lower than the activity of the original sample (curve 1(7)) or of the corresponding filtrate (curve 2(7)) but it is higher than the practically negligible activity of the filtrate after the decomposition using washed samples (curve 4(7)); 4. the catalytic activity of the washed sample with a low content of washable chromates (curve 3(10)) is comparable with the activity of the original sample (curve 1(10)) and it is significantly higher than the practically negligible activity of filtrates after the decomposition using either washed (curve 4(10)) or unwashed samples (curve 2(10)).

With regard to the fact that the character of kinetic curves for other samples is similar (in dependence on the content of washable chromates) it can be concluded
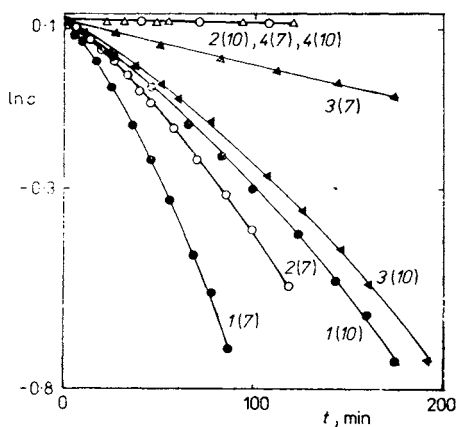
FIG. 3

Kinetic curves of the hydrogen peroxide decomposition at 25°C measured with the original (unwashed) samples No. 7 and 10 (1(7), 1(10)), with the filtrate after the H$_2$O$_2$ decomposition using the original sample (2(7), 2(10)), with washed samples (3(7), 3(10)), and with the filtrate after the decomposition with washed samples (4(7), 4(10)). On y-axis for 0·1 read 0·2
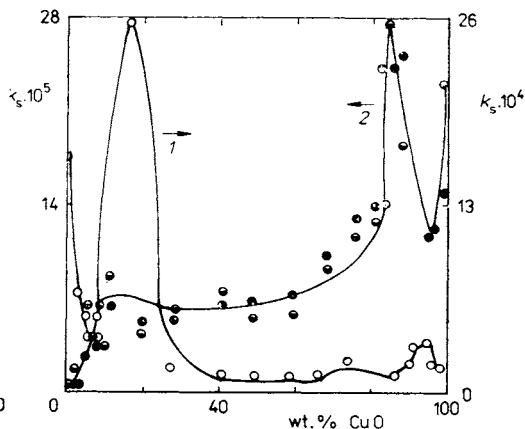
FIG. 4

Specific catalytic activity k_s(s^{-1} m^{-2}) vs the composition of samples. 1 unwashed samples, 2 washed samples (●) and after 13-month storage of washed samples (◒)

from the facts enumerated above that *1.* the catalytic activity of unwashed samples with a high content of washable chromates is given predominantly by the activity of the dissolved chromate, *2.* the catalytic activity of the unwashed samples with a low content of washable chromates is given by the catalytic activity of the solid phase itself, and *3.* the catalytic activity of washed samples with both high and low contents of washable chromates is also given by the solid phase itself and the reaction proceeds via a heterogeneous mechanism.

Moreover, from Fig. 3 it is also evident (and this fact has been confirmed for all other samples) that all kinetic curves have a concave shape in their initial stages and this means that the testing reaction is accelerated in this region. This is probably in connection with the reduction-oxidation equilibrium establishment on the catalyst surface that is in contact with the hydrogen peroxide molecules or with the oxygen molecules produced in the reaction. In later stages of the decomposition these dependences are linear with sufficient accuracy. This means that after the equilibrium establishment the testing reaction proceeds as a first-order process. It is evident that the equilibrium is established also during the reaction in the homogeneous liquid phase (Fig. 3, curve 2(7)).

The dependence of the specific catalytic activity of unwashed catalysts on their composition is evidently non-monotonous (Fig. 4, curve (1)). In the region of chromium excess the character of this dependence is significantly affected by the chromate dissolution in the liquid phase. In spite of this fact the position and nature of extremes of this dependence correspond to the dependences given in Fig. 1. From these results it follows that the non-monotonous character of the dependence of the specific catalytic activity of samples on their composition is first of all given by the amount of soluble chromates transferred into the liquid phase during the reaction. However, the fact that the activity of soluble chromates in samples with a low content of washable chromates (samples with an excess of cupric oxide) is negligible in comparison with the solid phase activity (Fig. 3) indicates that the validity of the statement mentioned above is limited only to samples with an excess of chromium sesquioxide. This is also confirmed by the dependence of the specific catalytic activity of washed catalysts on their composition (Fig. 4, curve (2)). This dependence shows neither a deep minimum nor a conspicuous maximum as it was observed in unwashed samples with about 10 and 20 wt. % of CuO. These extremes (identical with extremes in Fig. 1) are therefore unequivocally caused by the different amounts of the catalytically active dissolved chromate. However, on the dependence under discussion (Fig. 4, curve 2) there is still a marked extreme in the region of high excess of cupric oxide (about 85 wt. % of CuO) that is not related to the dissolution of chromates.

The dependence of the specific catalytic activity of washed samples on their composition (Fig. 4, curve (2)) has typically two maxima in the flank regions of composition (at 10 and at about 85 wt. % of CuO) that is evidently given by the charge interaction of both oxides as it was observed[1] in many other two-component oxide

catalysts. The existence of these maxima can be qualitatively explained in terms of the principle of bivalent catalytic centers[14] as in this region there is the highest concentration of mixed catalytic centers of the type Cu^+-Cr^{6+} and $Cu^{2+}-Cr^{3+}$, on which the reaction proceeds according to the general mechanism discussed in literature[14]. The fact that the position of the maximum on the dependence under discussion in the region of CuO excess (85 wt. %) is not in agreement with the region of the enhanced surface concentration of Cu^+ ions as detected by ESCA (Table II) may be ascribed to the fact that the charge state of the catalyst surface ions is changed in the hydrogen peroxide medium (as witnessed by the character of the decomposition kinetic curves (Fig. 3)). Moreover, the catalytic centers $Cu^{2+}-Cr^{3+}$ that are not connected with the surface concentration of Cu^+ ions can play an important role in this respect.

In samples No. 7 – 13 (about 20 – 80 wt. % of CuO), in which the existence of the spinel structure $CuCr_2O_4$ has been proved, no extreme has been found on the specific catalytic activity dependence so that it can be concluded that this structure has no significant effect on the catalytic properties of the system under study.

The existence of the equilibrium catalytic centers on the surface of samples under study is corroborated by the fact that neither the catalytic activity nor the value of the apparent activation energy of the testing reaction is changed during the 13-month storage of samples at the room temperature (Fig. 4, curve 2, Table I). The pure cupric oxide is the only exception as its catalytic activity increased by 67% after the storage (Fig. 4).

The fact that the apparent activation energies of the reaction proceeding on both washed and unwashed samples do not differ significantly indicates that from the point of view of the reaction energy relations the homogeneous catalytic process (proceeding in the unwashed samples with a high content of chromium after the dissolution of chromates in the reaction system) is equivalent to the heterogeneous process.

The thermal treatment of catalysts in nitrogen atmosphere at the temperatures of 475 and 850°C for one hour results in both positive and negative changes of the specific catalytic activities (by about tens of per cent) for catalysts with different composition (Table III). It is probable that the surface concentrations of chromium and copper ions in a given valence state are changed in course of the thermal treatment of samples, leading thus to changes of the catalytic activity of the treated catalysts.

The irradiation of catalysts by gamma doses ranging from $5 . 10^5$ to $2·6 . 10^6$ Gy is reflected in the changes of the specific catalytic activity in lesser extent than the thermal treatment. The observed changes of the specific catalytic activity and of the apparent activation energy of the reaction achieve only the values of units or tens of per cent (Table III) and they are usually lower than the respective measurement errors. Changes of the catalytic activity of pure cupric oxide can be observed[15] only after gamma doses of $1·38 . 10^7$ Gy and chromium sesquioxide is insensitive[16] to

TABLE III

Changes of the specific catalytic activity of selected samples of washed catalysts due to (a) the thermal treatment in air at 475°C (Δ_{475}) and 850°C (Δ_{850}), (b) gamma irradiation with doses of $5 . 10^5$ Gy (Δ_I), $1·7 . 10^6$ Gy (Δ_{II}), and $2·6 . 10^6$ Gy (Δ_{III}), and the changes of the apparent activation energy (kJ/mol) of the testing reaction after irradiation with the doses mentioned above ($\Delta_{E,I}$, $\Delta_{E,II}$, $\Delta_{E,III}$)

Parameter	Sample						
	1	3	8	10	13	17	19
Δ_{475}	50·0	−35·5	−44·7	43·3	−38·5	−60·2	−7·9
Δ_{850}	200·0	0·0	−75·0	—	—	53·8	—
Δ_I	0·0	—	5·3	−13·4	14·8	14·7	−1·3
Δ_{II}	12·5	−6·5	−6·6	−4·5	−19·3	−13·2	6·6
Δ_{III}	12·5	−3·2	−26·3	−14·9	−17·0	−12·8	2·6
$\Delta_{E,I}$	19·2	—	0·0	−3·4	−3·8	−2·9	—
$\Delta_{E,II}$	24·5	22·0	7·1	−4·5	−3·8	−2·9	−0·9
$\Delta_{E,III}$	22·6	22·0	11·4	1·1	−1·9	−2·9	—

TABLE IV

Character of the kinetic curves for the hydrogen peroxide decomposition at 25°C for the Sample No. 13 reduced in various degrees $\alpha(\%)$; + convex shape, − concave shape

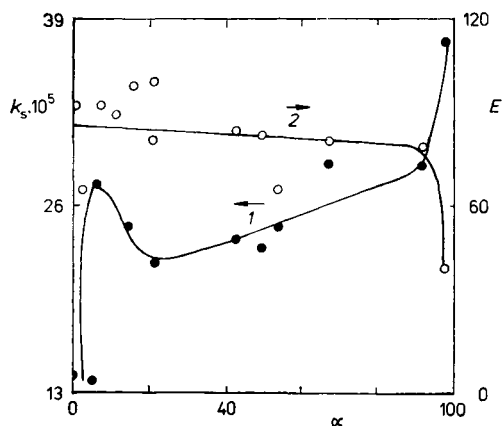| α	0·0	4·2	7·1	14·1	21·3	43·7	49·9	54·1	73·4	92·8	97·7
Character	−	−	−	−	−·−	+	+	+	+	+	+

FIG. 5

Specific catalytic activity $k_s(s^{-1} m^{-2})$ (1) and the apparent activation energy E (kJ/mol) (2) vs the reduction degree $\alpha(\%)$ of the sample No. 13

a dose of $7 . 10^6$ Gy, therefore it can be concluded that the mixed oxide catalysts are certainly not more sensitive to the applied radiation than the pure components.

Changes of the charge state of the catalytically active metals of the catalyst are probably also responsible for the observed changes of the catalytic properties of the washed system under study after its partial reduction by hydrogen, up to a certain degree given by the mass loss of the reduced sample at the given temperature. The reduction degree has an effect on the character of the decomposition kinetics curves of hydrogen peroxide. As it has been found, e.g., for the sample No. 13 (77.3 wt. % of CuO), the kinetic curves exhibit a concave shape in the initial stage of decomposition, if the reduction degree $\alpha \leq 14.1\%$, otherwise these curves have a convex shape (Table IV). The specific catalytic activity of this sample sharply increases with the increasing reduction degree (up to about 10%), then it increases only moderately and a significant increase is observed again only at high reduction degrees (97.7%). At the same time the value of the apparent activation energy remains unchanged, except for a substantial drop for the highest degree of reduction (Fig. 5). The initial increase of the catalytic activity without any change of the apparent activation energy of the reaction can be connected with a higher surface concentration of Cu^+ ions (and therefore also of the number of the catalytic centers Cu^+-Cu^{2+}) in samples reduced to a low degree, the activity increase accompanied by a decrease of the apparent activation energy value in the practically totally reduced sample may indicate the formation of new-type catalytic centers, e.g., $Cu^\circ-Cu^{2+}$. The discussed changes of the kinetic curves character with the reduction degree of the sample indicate the establishment of a reduction-oxidation equilibrium on the oxide surface during the initial stages of the catalytic process that is determined by the physical parameters of the given catalytic system.

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