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Exoemission accompanying electron interactions in complex copper-cerium oxide catalysts and synergism phenomena

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The formation of the electronic structure of the surface of complex copper-cerium oxide catalysts with different copper concentrations was studied using the exoemission methods at different stages of preparation. The introduction of copper enhances the emissivity of CeO_2, and the number of charges emitted from the catalyst surface exceeds the emission activity of the starting CeO_2 and CuO components. The synergism phenomenon in exoemission is compared with synergism in the catalysis of CO oxidation by these systems. The problem of electron interactions between the components of the complex oxides is discussed. The electron interactions are caused by the electron transitions at the interface and result in an increase in both the emission of weakly bound electrons and catalytic activity in the oxidation of CO.

Key words: exoemission of catalysts, complex oxides, synergism, catalytic oxidation, carbon monoxide.

A great attention has recently been given to the synergism and promotion phenomena in catalysis.[1—5] The influence of the electron transfer between the active phase and the support on the catalytic activity has been discussed long ago.[6] The works using the modern methods of analysis of the surface, *viz.*, IR spectroscopy, ESR spectroscopy, XPS, and temperature-programmed desorption (TPD), made it possible to conclude with a more certainty about the metal—oxide electron interaction. Cerium dioxide is used as a reservoir for oxygen storage in the three-way catalysts for purification of automobile exhausts. The interaction of CeO_2 with noble metals (Pt, Pd, Rh) and its effect on the catalytic activity in oxidation have been studied in detail.[7,8] The recent studies have shown that the catalytic activity of the cerium-containing catalysts in oxidation is substantially enhanced when transition metals, including copper, are introduced.[1,3,4] The effect of CeO_2 promotion with copper in the catalytic oxidation processes is in accordance with synergism in the redox properties of this system.[9] This is a consequence of the interaction between the components. Due to the reactions in the $CuO—CeO_2$ system, the processes of oxidation with oxygen and reduction with carbon monoxide occur with a higher efficiency than those in the case of the starting components. The results obtained in ESR and TPD studies indicate the simultaneous involvement of CuO and CeO_2 in the redox processes. Carbon monoxide is assumed to be oxidized on the sites localized at the interface of the oxides.[1,9] It has been established[10] that the strong interaction between transition metals and CeO_2 enhances the ability of CeO_2 to absorb oxygen. However, the nature of this interaction remains unclear. As mentioned,[1] electron interactions can occur in the complex copper-cerium oxide catalysts involving the finest Schottky transitions at the interface of the oxides.[11] The electron interactions in the metal—oxide system, resulting in the promotion effect of the CeO_2-supported metals, have been considered.[5] However, the electronic properties of the catalyst surface were not directly studied in the published works.[5,11] It is very difficult to find a direct relationship between the electronic properties of the catalysts and their catalytic activity.[1] In present work we used electron and ion exoemission to study the formation of the electronic structure of the surface and electron interactions in the copper-cerium oxide catalysts for oxidation.

Exoemission (EE) is the low-temperature emission of low-energy electrons and ions. It occurs from the surface of solids (metals, semiconductors, dielectrics) after they were affected by different ways ("excitation") and possesses a significant sluggishness (after-emission, AE). The excitation of solids occurs due to the radiation or mechanical (thermomechanical) action, phase transformations, or physicochemical processes that occur on the surface (adsorption, desorption, oxidation, corrosion, heterogeneous catalytic reactions[12,13]). The majority of metals, semiconductors and their oxides, and hydrophilic materials of different nature are characterized by the "spontaneous" emission of negative ions (O_2^-, OH^-, CO_2^-) and electrons from the surface, which is due to the technological treatment and storage in air or in aggressive

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media. The subsequent heating in the linear regime results in the thermostimulated emission (TSE) of electrons and ions or "thermal desorption" of charged particles. Irradiation in the region of wavelengths exceeding the photoeffect boundary leads to photostimulated emission (PSE). Exoelectrons (ions) are emitted from external (≤10 nm) surface layers and provide an information on the energy spectrum of the localization levels (or the activation energy of charge desorption) on the surface. The exoemission currents are small (10^{-17}—10^{-19} A), so that exoemission is detected in the pulse regime using a gas-flow Geiger counter or *in vacuo* with a secondary electron multiplier (SEM). Such a detection ensures a high sensitivity of the EE methods (~10^{-9} of the total number of surface atoms), which exceeds by several orders of magnitude the sensitivity of the traditional methods for studying the surface (Auger spectroscopy, XPS, XRD, and others).

The purpose of this work is to study the electron interactions in the Cu—Ce—O system as the most probable reason for synergism using the EE methods. Exoemission was measured for the samples prepared according to the procedure described elsewhere,[1] taking into account the results of this comprehensive study.

Experimental

Catalysts were prepared using the coprecipitation method,[14] which coincided completely with a commonly accepted procedure described in our previous work[15] in detail, and contained 5, 10, and 25 wt.% copper. Starting 10% solutions of nitrates were precipitated with sodium hydrocarbonate at 80 °C. After the precipitate aged, it was washed with distilled water to remove Na^+ and CO_3^- ions and dried at 50 °C. In subsequent experiments, the samples were calcined in air at 650 °C. The starting CeO_2 and CuO oxides were prepared using the same procedure. The sample loading for EE measurements was 30 mg. The DTA and DTG methods have previously[14] been used for analysis of structural phase transitions during the formation of the complex copper-cerium oxides studied in this work.

Exoemission was detected with the gas-flow Geiger counter of a Protoka industrial instrument (Russia) modified[16] by us for measurements of TSE and PSE of negative charges. Methane was the working gas of the counter. Series of narrow-band filters in the 578—257 nm wavelength interval were used to detect PSE under irradiation with a DRT-230 quartz mercury lamp. The TSE intensity was measured on heating the samples with a rate of 5 deg min^{-1} in the 20—360 °C temperature interval. After the sample was placed in the working chamber of the counter and purged with the working gas (methane), the emission of negative charges (AE) was detected, which descended in time to the background level of 1—3 pulse min^{-1}. After AE due to the presence of "biographical" charges on the surface decayed, the spectrum of PSE excitation was obtained, which represented the plot of the EE intensity *vs.* wavelength of the incident light. Then the sample was heated to 360 °C with the simultaneous detection of TSE. After the sample was cooled, the spectral plot of PSE was measured again. In order to determine the stage of formation of the electronic structure of the catalyst surface, TSE was measured for the samples heated to 50 °C and calcined in air for 3 h at 650 °C (the last stage of preparation of the copper-cerium oxide catalysts for CO oxidation carried out according to the previously described procedure[1]).

The catalytic activity of the CeO_2, CuO, and Cu—Ce—O (25% Cu) samples in CO oxidation was determined using a microcatalytic setup in the pulse regime. X-ray patterns were obtained with a DRON-2 diffractometer for the CuO and CeO_2 samples and Cu—Ce—O (25% Cu) catalyst. The main reflections in the X-ray diffraction patterns of the catalyst and starting oxides coincided, although some lines of CuO were absent in the pattern of the coprecipitated sample. The half-width of the peaks corresponding to CuO in the catalyst is ~2-fold larger than that in the patterns of the starting oxides, indicating an increase in its deficiency in the presence of CeO_2. However, the degree of dispersion cannot be estimated unambiguously using these data.

Results and Discussion

After-emission and photostimulated emission. After the starting samples were placed in the working chamber of the counter and a positive potential was applied to the anode, an enhanced "background" was observed, that is, the emission of negative charges descending in time (AE), whose intensity depends on the copper concentration in the samples. After AE decayed to the level of the natural background, the spectra of PSE excitation were detected: the plots of the EE intensity *vs.* wavelength of the incident light. The excitation spectra of PSE for the CeO_2 and CuO samples and two copper-containing catalysts in the long-wave spectral region are presented in Fig. 1. Analysis of the data shows that PSE for the samples under study is the selective photoeffect with $\lambda_{max} = 550$ nm.

The PSE intensity (I) for the copper-cerium oxide catalysts is higher than I_{PSE} for CeO_2 and CuO, indicating a synergism in the electronic properties of the surface characterized by PSE.

The results of detection of the starting AE values (the first reading of I) and the starting I_{PSE} values at different compositions of the samples at each wavelength of the incident light used are presented in Table 1. It can be seen that the I values of both AE and PSE depend on the copper content in the samples. The synergism phenomenon is observed: the AE and PSE intensities from the catalysts exceed I of the emission from the starting samples. This regularity is violated on going to PSE in the region of the UV action: under UV irradiation with $\lambda = 257$ nm, where the surface layer can be decomposed photochemically (reduced), the PSE intensity increases dramatically (by one—two orders of magnitude). After the samples were heated to 360 °C (during the detection of TSE), the PSE intensity decreased sharply.

Thermostimulated emission from the samples. The results of detection of TSE from the samples with different copper concentrations heated after coprecipitation to

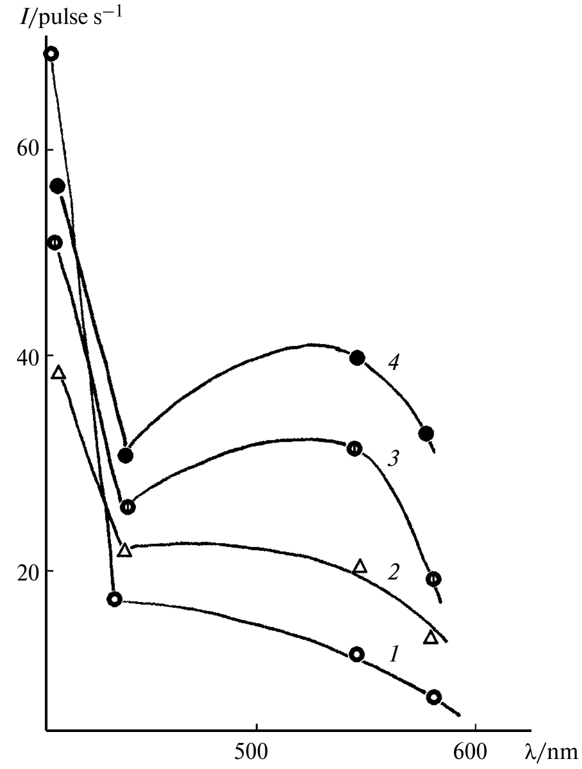

Fig. 1. Excitation spectra of PSE in the long-wave region for the samples of CeO_2 (*1*), CuO (*2*), and Cu—Ce—O with the copper content 5 (*3*) and 10 wt.% (*4*).

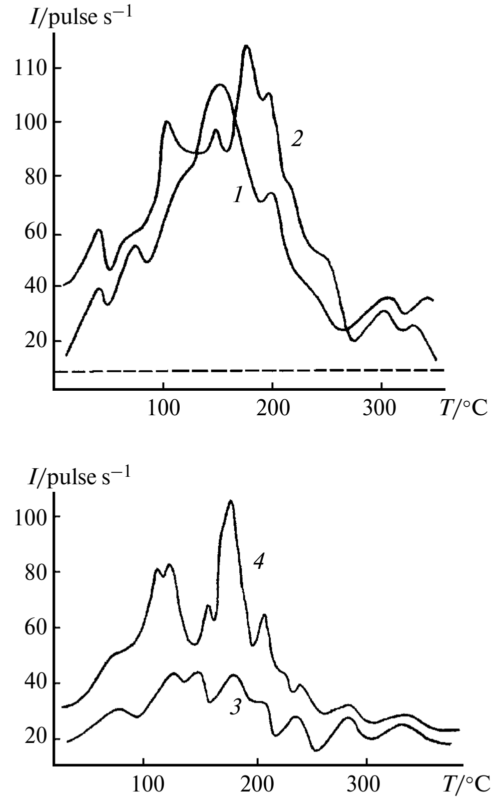

Fig. 2. Thermostimulated emission from the starting oxides and Cu—Ce—O samples heated at 50 °C: 10 wt.% Cu (*1*), 25 wt.% Cu (*2*), CeO_2 (*3*), and CuO (*4*). Dotted line corresponds to background.

50 °C are presented in Fig. 2. For the samples containing copper in CeO_2 (curves *1* and *2*), the main most intense TSE peak is localized in the 120—180 °C temperature interval. Many jumps and special points in the TSE curves are due to the diversity of charged forms of oxygen and OH^- groups, which are coordinated in different manners on the surface and are retained with different bonding energies.[12,13] Then the Cu—Ce—O samples were calcined for 3 h at 650 °C in air, which corresponds to the last stage of catalyst preparation. The results of TSE detection are

Table 1. After-emission and photostimulated emission (*I*/pulse s^{-1}) from the starting Cu—Ce—O samples heated at 50 °C (*1*) and below *T* = 360 °C during TSE (*2*)*

Sample**	AE	PSE at different λ***/nm													
		257		313		365		405		436		546		578	
		1	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*
CeO_2	5	500	5	40	Background	5	Background	70	Background	18	10	13	Background	8	10
Cu—Ce—O (5)	20	9	1	60	Background	20	9	50	5	25	10	36	Background	22	6
Cu—Ce—O (10)	60	6	2	60	Background	20	7	55	Background	30	20	42	5	35	6
Cu—Ce—O (25)	45	11	5	25	Background	20	5	40	Background	20	10	20	5	15	7
CuO	20	16	338	25	Background	30	Background	40	Background	20	Background	20	8	15	4

* Taking into account transmission of the filters.

** The content of Cu (wt.%) is indicated in parentheses.

*** Wavelength of the stimulating light.

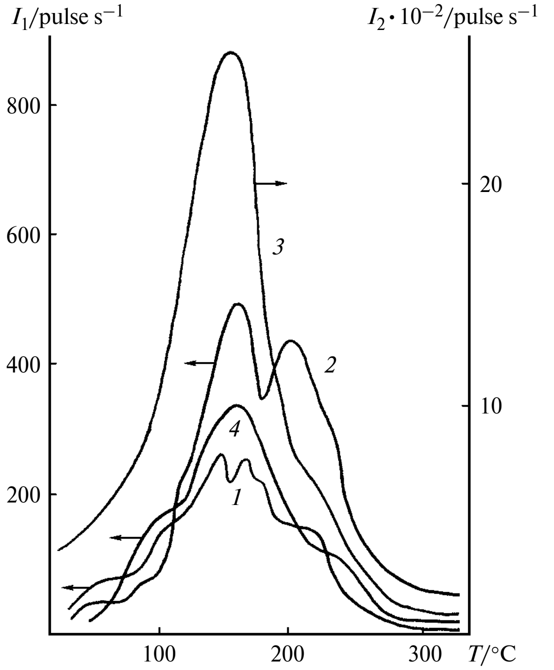

Fig. 3. Thermostimulated emission from the Cu—Ce—O samples and starting oxides calcined in air at 650 °C: CeO_2 (*1*), 10 (*2*) and 25 wt.% Cu (*3*), CuO (*4*).

presented in Fig. 3. For all samples, the most intense TSE peak is localized at $T \approx 150$ °C corresponding to the decomposition of the adsorbed radical ion $(O_2{}^{\bullet -})_{ads}$ accompanied by the emission of negative charges and TSD.

A comparison of Figs. 2 and 3 shows that the main TSE peak ($T_{max} = 150$ °C) for the catalysts under study is manifested already at the first stage of their formation after the coprecipitation of the precursors and heating to 50 °C. However, the intensity of this peak increases ~5 times for the catalysts calcined in air at 650 °C and ~25 times for the sample with the highest copper content (25 wt.%).

Analysis of numerous published[17,18] and our[12,13] data shows that the TSE maximum at $T \approx 150$ °C corresponds to the following transformations in the adsorbed (weakly bound) oxygen layer:

$$(O_2{}^{-})_{ads} \rightarrow O^{-}\uparrow + O_{ads}, \qquad (1)$$

$$2\,O_{ads} \rightarrow O_2 + Q_{rec}, \qquad (2)$$

$$(O^{-})_{ads} + O_{ads} + Q_{rec} \rightarrow O_2 + e\uparrow. \qquad (3)$$

According to Eqs. (1)—(3), TSE of electrons and ions is a consequence of transformations in the layer of weakly bound (adsorbed) oxygen, surface diffusion, and recombination of adsorbed species (including ions), whose energy (Q_{rec}) is consumed to yield electrons and ions.[12,13] As a rule, the temperatures of the TSE peaks and desorption rate coincide.[19]

The activation energy of the charge emission, which was calculated using the TSE curves (see Fig. 3), is ~0.8 eV, while the activation energy of $O_2{}^{-}$ desorption or decomposition $O_2{}^{-} \rightarrow O^{-} + O$ is equal[20] to 0.8—1.1 eV, which agrees satisfactorily with the data on TSE. The energy of atomic recombination O + O + M (M is the third species, in our case, it is the recombination site) is[21] 5.17 eV, whereas the energy of interaction $O^{-} + O$ is equal[22] to 4.1 eV. Therefore, the energy of recombination of active species is sufficient for the emission (desorption) of charged species. Equations (1)—(3) presented above are only some of possible surface reactions resulting in exoemission. The presently accepted scheme of formation of the sorption layer of oxygen and its desorption (on heating or under irradiation) has the following form[23]:

$$(O_2)_{ads} \rightleftharpoons (O_2{}^{-})_{ads} \rightleftharpoons (O^{-})_{ads} \rightleftharpoons (O^{2-})_{ads} \rightleftharpoons (O^{2-})_{lat}, \qquad (4)$$

where O_{lat} is lattice oxygen.

Catalytic activity of the samples. The results of measuring the catalytic activity in CO oxidation for the Cu—Ce—O catalysts and starting oxides (CuO, CeO_2) studied in this work (curves *1*—*3*) and in the previous paper[1] are presented in Fig. 4. In both cases, the 100% conversion $CO \rightarrow CO_2$ for the copper-containing catalysts is achieved at $T < 100$ °C (curves *3*—*6*), while for the copper oxide it is achieved at $T = 170$—180 °C (curves *2* and *5*), and for CeO_2 this temperature is much higher (curves *1* and *4*).

The most interesting is the synergism phenomenon in EE of the complex copper-cerium oxide catalysts, where the intensity (I) or the total number (ΣI) of emitted charges of AE, PSE (see Table 1), and TSE (see Figs. 2 and 3) exceeds EE from the starting samples. The syner-

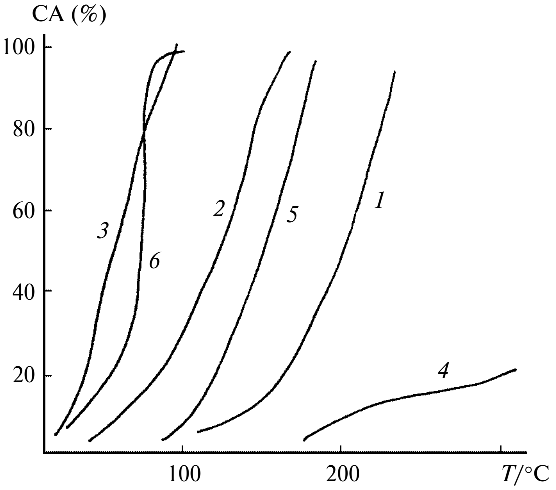

Fig. 4. Catalytic activity in the oxidation of CO on the CeO_2 (*1*), CuO (*2*), and Cu—Ce—O (25 wt.% Cu) samples (*3*) studied in this work and the CeO_2 (*4*), CuO (*5*), and Cu—Ce—O (25 wt.% Cu) (*6*) samples according to the published data.[1]

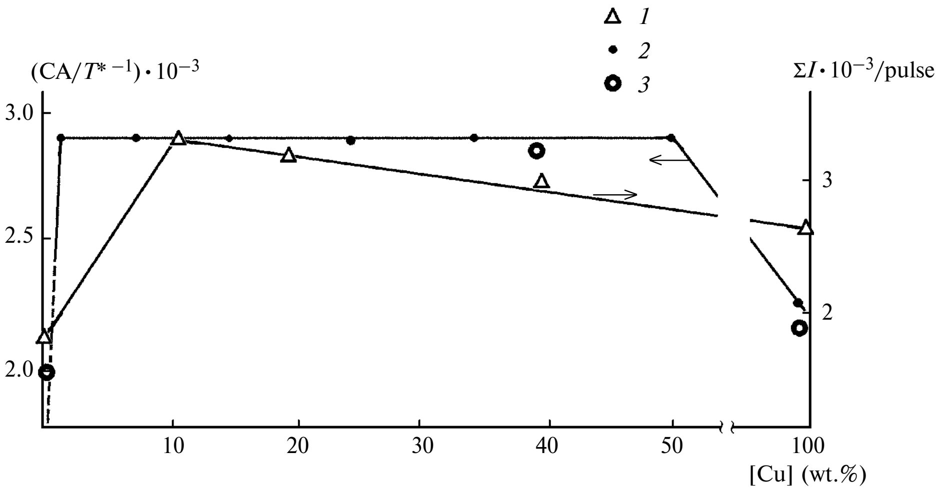

Fig. 5. Sum of the emitted charges (Σ*I*) in the interval T = 20—350 °C (*1*) and the catalytic activity (CA) (*2*, *3*) as functions of the Cu content: published data[1] (*2*) and results of this work (*3*); T^* is the temperature of 100% CO oxidation.

gism phenomenon in TSE is manifested at both the first (see Fig. 2) and last (see Fig. 3) stages of preparation of the catalysts. The plots of the catalytic acitivity (CA) and the sum of emitted charges (Σ*I*) *vs.* copper content are presented in Fig. 5.

Thus, according to the results obtained for both the heterogeneous catalytic oxidation of CO and the study of EE, synergism phenomena are observed. They are especially pronounced in Fig. 5, indicating that weakly bound oxygen is involved in these processes and the nature of the sites of EE and oxidative catalysis is the same: these are the active surface sites for which electron exchange is facilitated.

Nature of synergism phenomena. Based on the analysis of the presented published and our experimental data, including XRD, we propose the following scheme of electron interactions, which induce the synergism phenomena in the catalysis of CO oxidation and in EE, for the Cu—Ce—O catalysts studied. When the coordinatively unsaturated cerium ions (in the reduced state) are present on the surface, CeO_2 is an n-type semiconductor,[5] while the copper oxide is a semiconductor with the hole-type conductivity. It is known[24] that the contact of two semiconductors with the n- and p-types of conductivity results in the charge separation at the boundary (Fig. 6). The "depleted" layer with the enhanced concentration of electrons in the p-semiconductor and holes in the n-semiconductor appears near the boundary. The thickness of the boundary layer can reach 10^2—10^4 Å.

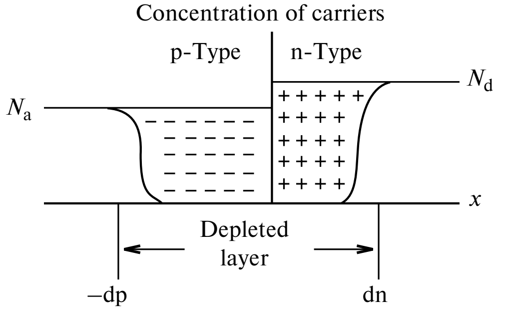

Fig. 6. Scheme of the depleted layer near the contact of the p- and n-semiconductors. Concentration of the charge carriers in the depleted layer at different positions of the point of the relatively sharp p—n-transition. Axis *x* is the distance from the boundary deep into the semiconductor: N_a and N_d are the concentrations of acceptors and donors with the constant value everywhere, except for the dp and dn points, where they change jumpwise.[24]

Localization of holes in the near-boundary layer of CeO_2 designates the formation of weakly bound oxygen (O^-, O) according to the scheme

$$(O^{2-})_{lat} + p \rightarrow (O^-)_{ads} + V^*, \quad (5)$$

$$(O^-)_{ads} + p \rightarrow O_{ads}, \quad (6)$$

where V* is the oxygen vacancy.

The subsequent recombination of these species can result in the desorption (emission) of the charged and neutral forms of oxygen, for example, according to Eq. (3). Emission occurs due to the energy of the electron-hole or other types of recombination of oxygen species accompanied by energy evolution.

In the region of the depleted (negatively charged) CuO layer at the boundary of the p—n transition, the Cu^{2+} ions, which prevail[4] in the Cu—Ce—O catalysts, are reduced, adding electrons to form Cu^+ (or Cu^0). The Cu^+ ions were found[1] in the Cu—Ce—O catalysts using XPS. Thus, the weakly bound oxygen species (O^-, O) (see Eqs. (5) and (6)), oxygen vacancies V*, which are sites of oxygen adsorption, and Cu^+ ions (active sites of CO adsorption) are simultaneously present at the CuO/CeO_2

interface. The charge equilibrium in the boundary layer is violated during CO or O_2 adsorption, and the processes of O_2 and CO adsorption should occur simultaneously to retain the equilibrium, which is consistent with the previously published data.[4]

Both the CeO_2 and Cu_2O clusters, on which the active copper sites are localized, have been shown[9] to be simultaneously reduced (in CO) or oxidized (in O_2). The high activity and synergism in CO oxidation are attributed[4] to the high redox ability of the sites at the interface of the oxides, and this agrees with the mechanism of electron interactions (see reactions (5) and (6)) proposed by us for the adsorption and catalysis at the interface of the oxides of electron and hole semiconductors. The model presented allows one to understand the reason for the easier reduction of CeO_2 in the presence of copper.[10]

Measurements of TSE in a high vacuum. In order to check experimentally the applicability of the scheme of electron transitions on contact of the oxides with different types of conductivity (see Fig. 6), we carried out experiments on the detection of TSE *in vacuo* (10^{-6} Torr) using a VEU-6 secondary electron multiplier using the previously described[13] setup. Figure 7 presents the TSE from the starting CeO_2 sample and Cu—Ce—O (25 wt.% Cu) catalyst heated in air at 650 °C. Curve *1* corresponds to the TSE intensity from CeO_2. The maxima of TSE for measurements *in vacuo* are localized at $T = 90—160$ °C, and the more intense peak is localized at $T = 250—300$ °C; TSE is accompanied by jumps of gas evolution marked in Fig. 7. On the repeated heating, the TSE peaks at $T < 200$ °C are not manifested due to the removal of weakly bound adsorbates, whereas the TSE peak at 275 °C is reproduced due to the diffusion of charged oxygen (in the form of O^-) from the bulk. Curve *2* in Fig. 7 presents the results of measuring TSE from CeO_2 containing 25 wt.% Cu. Here the sharp jump of the emission current is observed near $T = 200$ °C and has, most likely, the electric breakdown character. The further heating to 275 °C, which coincides with T_{max} of TSE from CeO_2, results in a sharp increase in the emission current and gas evolution followed by the electric breakdown in the sample—EE detector gap in the chamber for emission measurements. Strong electric fields appeared at the interface of the p—n oxides can achieve[24] 10^6 V cm^{-1}. The application of a positive potential to the detector under the conditions of gas evolution results in the breakdown of the vacuum gap between the catalyst surface and detector. It is characteristic that the repeated heating of this sample results in a low level of the emission current, which is almost independent of the temperature below $T = 275$ °C, after which it decreases sharply to the level of the background: the neutralization of charges upon the breakdown at the interface of the oxides resulted in the disappearance of TSE at the temperature exceeding the breakdown temperature.

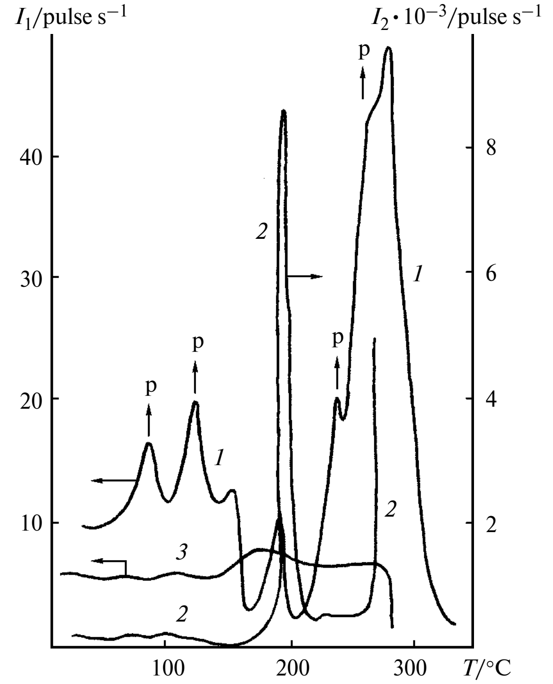

Fig. 7. Thermostimulated emission from the CeO_2 (*1*) and Cu—Ce—O (25 wt.% Cu) (*2*, *3*) samples calcined at 650 °C and stored in air, for the first (*2*) and second measurements of TSE (*3*). Measurements were carried out in a deep vacuum: p↑ are jumps of gas evolution during the detection of TSE from CeO_2.

The synergism phenomena observed in EE and catalytic CO oxidation on the complex copper-cerium oxide catalysts are explained from the viewpoint of electron transitions appeared on contact of semiconductors with different types of conductivity: n-type CeO_2 and p-type Cu_2O. The direct study of the electronic properties of the catalyst surface, which is inaccessible for the transitional methods of studying the surface, using the exoemission (AE, PSE, and TSE) methods confirmed the assumption on possible electron interactions in the complex oxide catalysts resulting in the synergism phenomena in catalysis.

It should be noted in conclusion that, despite the intense development of studies of catalysts using the modern (traditional) methods for analysis of the surface,[25] no data on electronic (ionic) processes in catalysts were obtained. According to the published data,[25,26] the methods of studying catalytic processes, which can fix the stages of catalyst preparation or reactions with electron or ion transfer, are presently not available. Exoemission is the only efficient method for studying electronic and ionic processes on the surface accompanied by the formation of active sites,[27] heterogeneous catalytic processes *in situ*,[28,29,30] and electron interactions in metallic supported and complex oxide catalysts.

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