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Exoemission and catalytic activity of oxides with perovskite and spinel structures in the oxidation of CO and hydrocarbons

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Low-temperature (20—400 °C) exoemission of negative charges from mixed oxides having the perovskite structure $M^1M^2O_3$ (M^1 = La; M^2 = Co, Mn, Ni) or the spinel structure $M^1M^2{}_2O_4$ (M^1 = Cu; M^2 = Fe, Co, Cr) was studied. The relationship between the catalytic activity in CO, ethylbenzene, and propylene oxidation and the emissivity of the oxides was elucidated. The role of weakly bound oxygen and variable-valence ions in the exoemission and redox catalysis by mixed oxides is discussed.

Key words: exoemission, weakly bound oxygen, catalytic oxidation, carbon oxide, ethylbenzene, propylene, perovskites, spinel.

Mixed oxides with the perovskite (ABO_3) and spinel (AB_2O_4) structures are active catalysts of redox processes.[1—5] They are used, like model catalyst systems, to investigate the role of defects in the catalysis.[6] The perovskite and spinel structures contain large numbers of defects, *i.e.*, cationic vacancies.[7] A cationic vacancy on the surface can be regarded as an aggregate of coordinatively unsaturated anions with an increased mobility.[8] It was found by exoemission techniques[9] that weakly bound oxygen occurs on the surface of mixed oxides as a part of anions.[9] The catalytic activity of manganites, which are combinations of oxides with the spinel structure, correlates with the intensity of emission of negative charges.

The search for correlations between the electronic and catalytic properties of the catalysts is faced with substantial difficulties.[10] Weakly bound electrons can be located either on oxygen atoms[9] to give charged species of the $O_2{}^-$ and O^- type or on transition metal ions.[11]

The purpose of this work is to study the electronic properties of oxide catalysts with the perovskite structure by low-temperature (20—400 °C) exoemission (EE) and to compare the results with the published data[3] on the catalytic activity of these catalysts in the oxidation of CO, ethylbenzene (EB), and propylene (P). The $M^1M^2O_3$ perovskites (M^1 = La; M^2 = Co, Mn, Ni)* were used as investigation objects. For comparison, the emissivity of some $M^1M^2{}_2O_4$ oxides with the spinel structure was studied.

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Experimental

Perovskites were prepared by a method described previously,[12] namely, by precipitation of the La[M(C_2O_4)$_3$] oxalate complexes from solutions of metal nitrates by oxalic acid. The precipitates were dried and calcined for 6 h at 500 °C; the $CuCo_2O_4$ sample was heated at 350 °C. The presence of the perovskite or spinel structure was confirmed by IR spectroscopy[3] on a Specord M-80 spectrophotometer. The procedure of testing the catalytic activity of the samples was described previously.[3] The catalyst activities were compared at temperatures corresponding to 50% (for P) or 100% (for CO or EB) conversion (α) of the reactants.

The exoemission was recorded by a gas-flow Geiger counter of a Protoka reconstructed industrial setup.[13] Negative charges were recorded with a positive potential applied to the anode of the counter. Thermostimulated emission (TSE) was studied at a heating rate of 10 K min^{-1}. Experiments were carried out in a flow of the quenching counter gas, CH_4. The catalyst sample was 50 mg.

In the first series of experiments, the curve of "spontaneous" TSE mainly caused by thermodesorption of negative ions was recorded upon linear heating.[14] During the repeated heating, the TSE intensity decreased to a level close to the background. In the second series of tests, photothermostimulated emission (PTSE) was recorded while conducting a heating—cooling cycle. During heating and cooling, the samples were exposed to UV radiation with the wavelength $\lambda = 313$ nm ($E = 4$ eV) corresponding to the threshold of the photostimulated emission (PSE). In the third series, the samples were exposed to ^{90}Y—^{90}Sr β-radiation (dose 0.23 Gy) in air for repeated excitation and the TSE was recorded again.

Results and Discussion

Spontaneous thermostimulated emission. The TSE curves recorded during heating and subsequent spontaneous cooling of $LaCoO_3$ perovskite samples (Fig. 1) exhibit a broad TSE peak in a temperature range of 130—160 °C, which is typical of most of the oxides in question. We attributed this peak to a valence (charge) transformation of a loosely bound surface oxygen.[14] A similar TSE maximum in the region of ~150 °C was observed previously[9] for the catalysts we studied, namely, manganites with the spinel structure. In the case of the $LaMnO_3$ manganite (see Fig. 1), this maximum is less pronounced than for $LaCoO_3$; in this case, small TSE peaks are detectable near temperatures of 50, 140, 230, and 300 °C. During cooling and repeated heating of $LaCoO_3$ and $LaMnO_3$, sharp emission peaks are observed at $T \approx 250$—260 °C. At the same temperatures, 100% conversion of EB takes place on these samples (240 and 265 °C, respectively). The emission peaks observed during cooling can be assigned only to the temperatures of structural transitions on the sample surface; the energy evolved upon this transition induces activation of the exoemission centers and catalytic oxidation of EB. The same EE peak can be seen during repeated heating of $LaCoO_3$ and $LaMnO_3$ (see Fig. 1, *b*, peak *3*). The EE maxima observed during heating (TSE) or cooling and the photothermostimulated emission (PTSE) maxima can be related to temperatures of 100% conversion of CO, propylene, and ethylbenzene on $LaCoO_3$, $LaMnO_3$, $LaNiO_3$, and $LaCrO_3$ samples (Table 1).

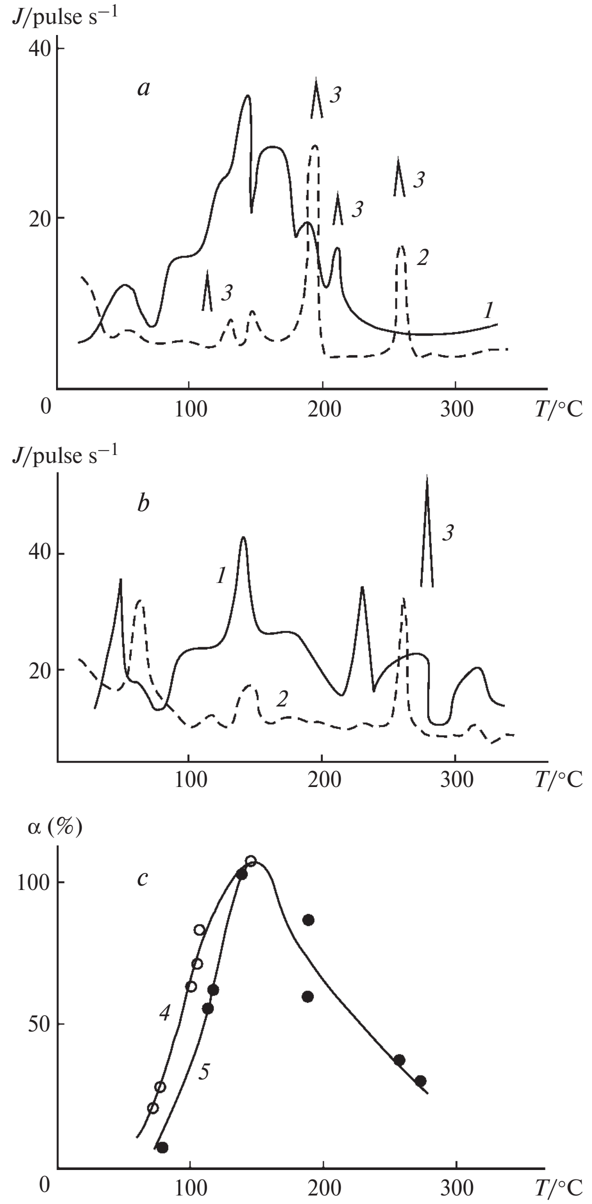

Fig. 1. Temperature dependence of the EE during heating (*1*) and subsequent cooling (*2*) for $LaCoO_3$ (*a*) and $LaMnO_3$ (*b*) and catalytic activity (α) of $LaCoO_3$ in CO oxidation in the pulse reactor[3] (*c*). Numeral *3* designates the main TSE peaks observed on repeated heating. Curve *4* and *5* show the total degree of CO conversion and its conversion into CO_2, respectively.

The temperature dependence of the total catalytic conversion (α) of CO on $LaCoO_3$ (*4*) and its transformation into CO_2 (*5*) for the reaction carried out in the pulsed reactor[3] is shown in Fig. 1, *c*. The plot indicates that once 100% conversion is achieved at ~140 °C, catalytic activity decreases at high temperatures. Evidently, this is due to side reactions.[3] The maximum in the catalytic activity curve (see Fig. 1, *c*) coincides with the TSE maximum for $LaCoO_3$ (see Fig. 1, *a*). This enables the conclusion that weakly bound electrons located, apparently, on the oxygen adsorbed on the surface are involved in CO oxidation.

In the case of $LaNiO_3$ (see Table 1), small TSE peaks (up to 25 pulse s^{-1}) were detected during the first heating only at temperatures of 150—170, 260, 280, and 310 °C; the peak at 150 °C was only 3 times as high as the oscillations in the background. During cooling and repeated heating, an emission peak (35 pulse s^{-1}) can be seen at a temperature of 280 °C, corresponding to 100% transformation of EB (290 °C). It follows from the data of Table 1 that the PTSE maxima also coincide satisfactorily with the temperatures of 100% conversion of CO and ethylbenzene and 50% conversion of propylene. Thus, in all the perovskites studied, the active centers responsible for ethylbenzne oxidation appear to be activated at the temperatures of structural transitions on the surface taking place during heating or cooling and giving rise to weakly bound electrons.

Table 1. Temperatures corresponding to the major TSE ($T_{max}{}^{TSE}$) and PTSE ($T_{max}{}^{PTSE}$) peaks for the initial and β-irradiated ($T_{max}{}^{irrad}$) perovskite samples and temperatures of 100% catalytic conversion of CO (T_{CO}) and ethylbenzene (T_{EB}), and 50% catalytic conversion of propylene (T_P)

Compound	T_{max}^{EE}	T_{max}^{PTSE}	T_{max}^{irrad}	T_{CO}	T_{EB}	T_P
			K			
$LaCoO_3$	130 190[b] 260[b] 260[a]	130[a] 120[b] 250[b] 250[a]	120 120[b] 215 260[b]	120	240	260
$LaMnO_3$	130 230 260[b] 270[a]	120 240—280	130 120[b] 260—280 290[b] 330	130	265	—
$LaNiO_3$	170[a] 275[b] 280[a]	110 210[c] 260—330[d]	130 230—270 310[b]	210	290	—
$LaCrO_3$	170 280—305 330[a]	240—280 310[b]	130 280 310—320[b]	260	310	340

[a] EE peaks recorded during the repeated heating.
[b] EE peaks recorded during the repeated cooling.
[c] Sharp decrease in the EE.
[d] Enhancement of the EE.

The valence state of surface oxygen is known[6,15] to govern the reaction mechanism and the catalyst activity and selectivity in oxidation reactions. The transformations of the gaseous, adsorbed, and surface lattice oxygen are described by the following equations:

$$O_2\text{ (gas)} \rightleftarrows O_2\text{ (phys.ads.)} \rightleftarrows O_2^-\text{ (chem.ads.)}, \qquad (1)$$

$$\updownarrows$$

$$O_2\text{ (gas)} \rightleftarrows O\text{ (dis.ads.)} \rightleftarrows O^-\text{ (ads.)} \rightleftarrows$$
$$\rightleftarrows O^{2-}\text{ (ads.)} \rightleftarrows O^{2-}\text{ (lattice)}. \qquad (2)$$

ESR and thrmodesorption studies and the Hall effect measurements demonstrated[7] that the O_2^- radical anions are stable in the region of equilibrium adsorption at $T \leq 175$ °C, while the O^- ions are stable at $T \geq 225$ °C. The oxygen thermodesorption curve was found to exhibit peaks at 185 and 285 °C, which are attributable to desorption of O_2^- and O^- ions, respectively.[16]

The TSE peak at 140—160 °C may correspond to the temperature of 100% conversion of CO and may be due to the emission of electrons and O_2^- ions according to the following reactions:[6,7]

$$O_2^-\text{ (ads.)} \longrightarrow O^-\text{ (ads.)} + O\text{ (ads.)}, \qquad (3)$$

$$2\,O^-\text{ (ads.)} + Q_r \longrightarrow O^-\uparrow + e\uparrow + O\text{ (ads.)}, \qquad (4)$$

where Q_r is the recombination energy. The TSE peaks at 260—280 °C, associated with the temperature of 100% conversion in ethylbenzne oxidation or 50% conversion in propylene oxidation, are due to the participation in the emission or catalysis of the O^- ions and electrons either liberated in reaction (4) or consumed in reaction (5)

$$O^-\text{ (ads.)} + e_{local} \rightleftarrows O_2^-\text{ (ads.)}, \qquad (5)$$

where e_{local} is an electron localized on a surface defect.

Reactions (1) and (2) are reversible. Process (4), which occurs at 260—280 °C and results in charge liberation during heating, can take place only under conditions of surface diffusion of O^- ions and recombination of these ions on the surface active sites, isolated energetically from the lattice, recombination energy being consumed for the emission of negative charges rather than scattered as phonons. Under conditions of our experiment, the probability of these processes is relatively low. The adsorbed O^- ions remain on the surface and participate in the catalytic oxidation of EB and P (see Ref. 16). However, during cooling, a phase transition described by reaction (5) takes place on the catalyst surface, resulting in an increase in the number of weakly bound electrons and surface O^- ions, some of which participate in the emission processes (T_{max} = 260—280 °C). These views are consistent with published data.[6,15,16] In the repeated process, the TSE at 260—280 °C is also observed during heating due to

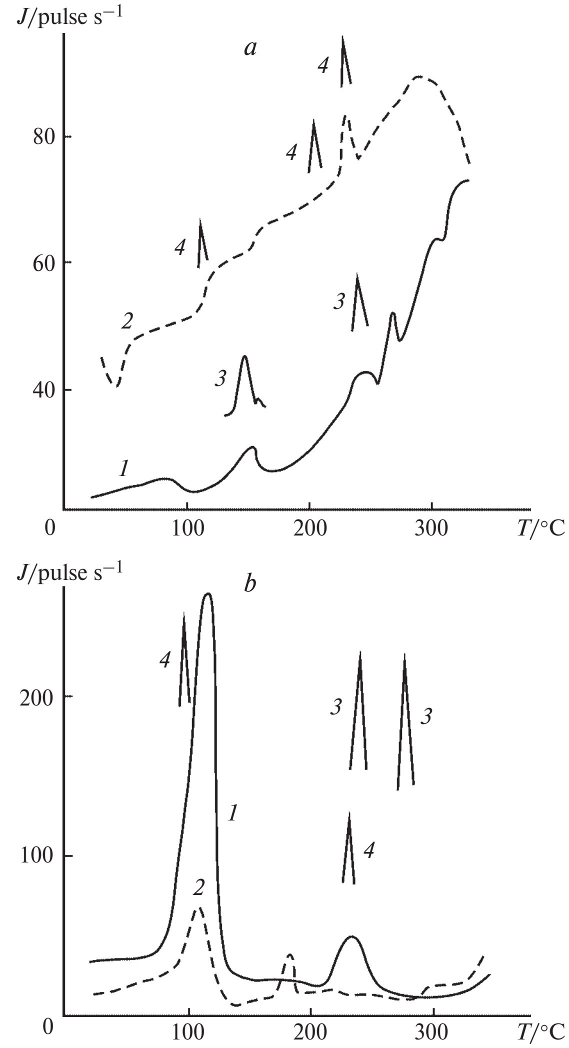

Fig. 2. TSE for $LaCoO_3$ (*a*) and $LaMnO_3$ (*b*) samples during heating (*1*) and cooling (*2*). Numerals *3* and *4* designate the main TSE peaks observed on repeated heating and cooling of the samples, respectively.

Table 2. Thresholds of the photoelectron sensitivity of perovskites based on the PSE data on exposure to UV light with different wavelengths at 20 °C

Compound	I/pulse s^{-1}					
	I[a]		II[b]		III[c]	
	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
$LaCoO_3$	6	120	30	1260	30	41000
$LaMnO_3$	19	90	12	270	20	290
$LaNiO_3$	15	450	100	146000	140	151000

[a] I: initial sample.

[b] II: the data were obtained after two heatings and one PTSE cycle.

[c] III: the data were obtained after two heatings and two PTSE cycles.

The λ_1 and λ_2 values are 313 and 257 nm, respectively.

the reversibility of reactions (1), (2) and to diffusion of the absorbed oxygen from the bulk toward the surface as O^- (or O_2^-) ions (see Figs. 1, 2 and Table 1). The high reactivity of the adsorbed O^- ions toward hydrocarbon oxidation and their desorption at 285 °C have been repeatedly noted in the literature.[16] A study of the catalytic activity in the pulse reactor showed[3] that more active catalysts ($LaCoO_3$) absorb more oxygen than less active catalysts ($LaMnO_3$), which is consistent with TSE data.

Photothermostimulated emission (PTSE). In recent years, there was an increased interest in the study of influence of the UV and high-energy (β-, γ-) radiation on the properties of catalysts. It was found that irradiation with high-energy electrons increases the activity of the Cu—Cr—Zn—Al catalyst in CO conversion.[17] This effect was interpreted[17] by assuming that an increase in the content of Al_2O_3 entails a change in the phase composition and a component redistribution over the surface. Exposure to UV or penetrating radiation is believed to increase the activity of solids in the catalytic redox transformations.[18] It was shown[19] that UV radiation induces low-temperature MoO_3/Al_2O_3-catalyzed selective reduction of NO by carbon monoxide to give N_2O; unlike the photochemical process, thermal process takes place at temperatures as high as 400 °C.

In this connection, it is of interest to study the electronic properties of perovskites by exoemission methods with exposure to UV light. The PSE threshold is located at $\lambda = 313$ nm ($E = 4$ eV) for all the samples studied. Table 2 presents the photoelectron sensitivity of perovskites expressed in EE intensity units (pulse s^{-1}). It can be seen from the Table that, according to PSE data, $LaNiO_3$ has the highest photosensitivity at ~20 °C, while $LaMnO_3$ has the lowest photosensitivity. A repeated linear heating slightly increases the PSE intensity compared to that of the initial sample but the enhancement of PSE observed on exposure to UV radiation with simultaneous heating (PTSE) is especially pronounced.

The data presented correspond to the PTSE curves for $LaCoO_3$ and $LaMnO_3$. The EE curves recorded during both heating and cooling of $LaCoO_3$ (see Fig. 2, *a*) point to the presence of a hysteresis over the whole range of temperatures studied, *i.e.*, to the structural transformations that occur in perovskite on exposure to UV radiation. The PTSE peaks at 240 °C (see Fig. 2, *a*, curves *1*, *2*) are arranged in the same way as in the case of TSE recorded for the initial samples (see Fig. 1, *a*) at a temperature of 100% conversion of ethylbenzene (240 °C). The separate, most intense PTSE peaks designated by numerals *3* and *4* refer to the repeated heating—cooling experiments. This confirms the assumption that the sites responsible for oxidation of ethylbenzene are activated upon electronic excitation during structural transformations on the surface because the intensity of the TSE peaks increases when the sample is re-heated.

In the first cycle of PTSE recording for $LaMnO_3$, hysteresis is scarcely observed (see Fig. 2, *b*); however, intense peaks appear at 110—130 °C. These temperatures are close to the temperature of 100% conversion of CO (130 °C). In addition, the emission increases somewhat at 265—300 °C, *i.e.*, in the temperature range typical of 100% conversion of EB (see Table 1). Sharper splashings of the PTSE currents were detected at 240 and 260 °C during the repeated heating of the sample; they match the temperatures of the highest activity of perovskites in EB conversion (see Fig. 2, *b*, peaks *3*). Comparison of Fig. 1, *b* and 2, *b* implies that UV radiation activates the EE, *i.e.*, the number of weakly bound negative charges grows 5—8-fold, and that increases the activity of the sites responsible for the oxidation of CO and EB during cooling or heating.

A more complex PTSE pattern was observed for the $LaNiO_3$ catalyst. In the second cycle, the PTSE intensity at temperatures of ≥ 210 °C sharply decreased (see Table 1). Note that at 210 °C, 100% conversion of CO on this catalyst was attained. The antiferromagnetic Curie point (the Néel point) for NiO is 250 °C; thus, second-order phase (magnetic) transitions can take place under our experimental conditions on the $LaNiO_3$ surface when it is enriched with nickel oxide, as has been observed for complex oxide catalysts.[17] For $T > 260$ °C, the emission current grew.

The effect of β-radiation on the TSE of perovskites. The results of TSE experiments conducted after exposure of $LaCoO_3$ and $MnCoO_3$ perovskites to β-radiation (dose 0.23 Gy) are presented in Fig. 3. It can be seen that the EE curves recorded during heating are similar to those observed for the initial samples (see Fig. 1, *a*, *b*), although the TSE intensity is somewhat higher for irradiated samples. A similar phenomenon, *i.e.*, the appearance of TSE maxima after β-irradiation of annealed samples, has been detected for manganites with the spinel structure.[9] During cooling of cobalt perovskites at 350—200 °C, hysteresis was observed, indicative of phase transitions induced by β-irradiation (see Fig. 3, *a*, *b*, curves *2*). The coincidence of the major TSE maxima (130—150 °C) in the initial and irradiated samples attests to the formation of the same TSE centers as a result of irradiation. In compliance with known views,[9] we believe that in this temperature range, the centers of electron and ion emission are formed by adsorbed oxygen (see reactions (1) and (2)). Heating of the initial samples resulted in oxygen desorption and in disappearance of the EE centers, while exposure to β-radiation in ambient atmosphere brings about radiation-induced adsorption. The emission occurs in conformity with reactions (3)—(5). Similar phenomena have also been observed for the $LaNiO_3$ and $LaCrO_3$ perovskites (see Table 1). The temperatures of the maxima coincided with the temperatures of 100% conversion of hydrocarbons. In terms of intensity, the main TSE maxima (at 130—140 °C) after β-irradiation were arranged in the same order as those for the initial samples, namely, $LaCoO_3 > LaMnO_3 > LaNiO_3$.

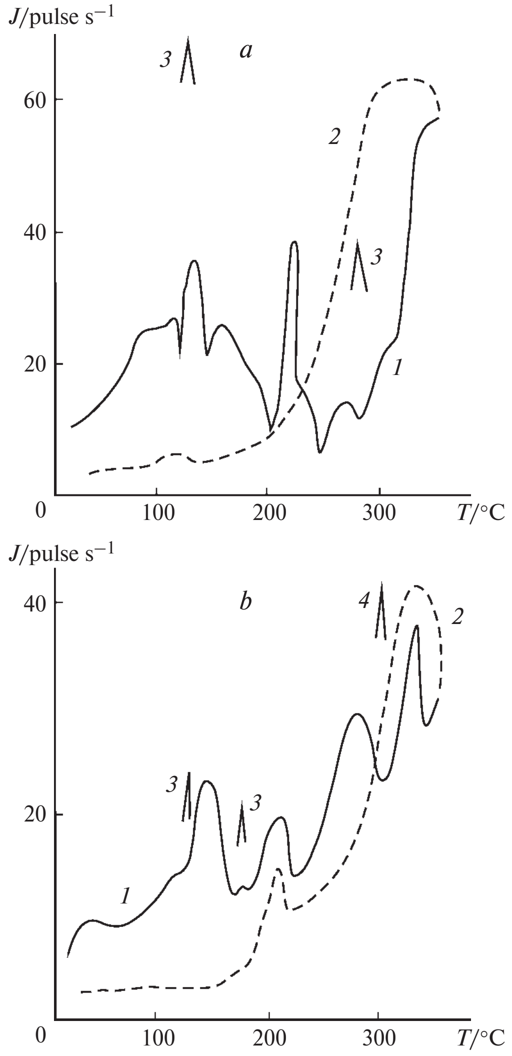

Fig. 3. TSE for β-irradiated $LaCoO_3$ (*a*) and $LaMnO_3$ (*b*) perovskites during heating (*1*) and cooling (*2*). Numerals *3* and *4* designate the TSE peaks for the repeated heating and cooling of the samples, respectively.

It is known[4] that in the temperature range where catalytic oxidation occurs (100—250 °C), the more active $LaCoO_3$ absorbs more oxygen than the less active $LaMnO_3$; this is consistent with our assumptions concerning the mechanisms of EE and catalytic oxidation involving charged oxygen species.

TSE of oxides with the spinel structure. Previously,[9] the emission capacity and the catalytic activity in CO oxidation have been studied for manganites with the spinel structure. In all cases, the TSE curves were found to ex-

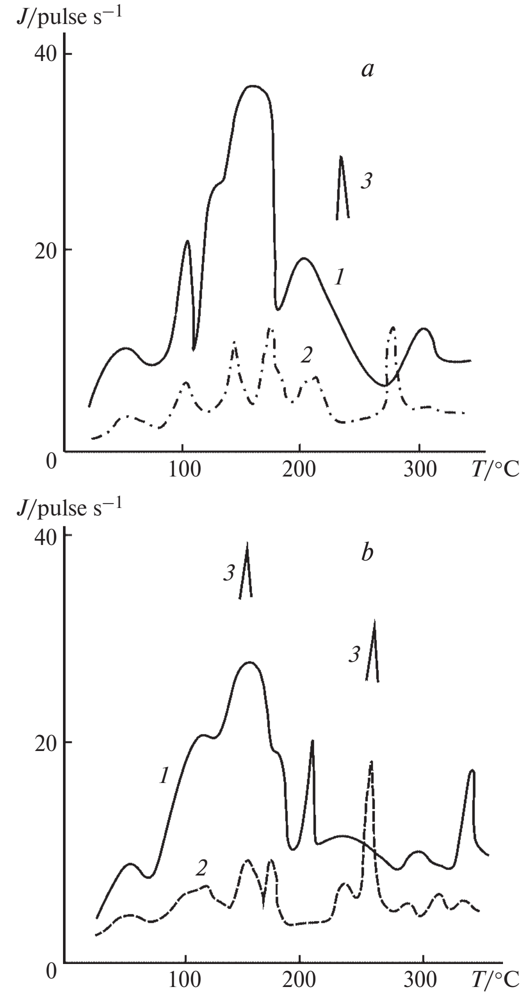

Fig. 4. TSE for the initial samples of the $CuCr_2O_4$ (*a*) and $CuFe_2O_4$ (*b*) spinels during the first (*1*) and repeated (*2*) heating of the samples. Numeral *3* designates the main TSE peaks observed on the repeated heating.

hibit a major clear-cut maximum at $T \approx$ 130—150 °C, which was attributed to the emission of electrons and oxygen ions according to reactions (1)—(5). A direct correlation between the emission intensity and catalytic activity of manganites was found. It can be seen from the temperature curves of emission recorded for the $CuCr_2O_4$ and $CuFe_2O_4$ samples (Fig. 4, *a*, *b*) during the first (curve *1*) and second (curve *2*) heating experiments and from the temperatures of the major TSE peaks and the temperatures of 100% conversion of CO and EB (Table 3) that in the case of spinel catalysts, these temperatures also coincide.

Presumably, weakly bound electrons emitted from the surface for the spinels studied are located not only on the adsorbed (weakly bound) oxygen atoms but also on variable-valence cations. In particular, in hopcalite, electron transitions between copper and manganese ions in different oxidation states by the Zener double exchange mechanism[20] can ensure participation of electrons in the oxidative catalysis[11]

$$Cu^{2+} + Mn^{3+} \rightleftarrows Cu^{+} + Mn^{4+}. \qquad (6)$$

Table 3. Temperatures of the major TSE peaks (T_{max}^{TSE}) and 100% conversion of CO (T_{CO}) and ethylbenzene (T_{EB}) for the spinels studied

Parameter	$CuCr_2O_4$	$CuFe_2O_4$
T_{CO}/°C	140	150
T_{EB}/°C	240	255
T_{max}^{TSE}/°C	150, 240*	150, 160**, 250*, 250**, 330

* EE peaks recorded during cooling.

** TSE peaks for the repeated heating.

Correlations between TSE and the catalytic activity of perovskites and spinels. Analysis of publications dealing with CO oxidation on Mn-containing octahedral molecular sieves doped with Ag^+, Co^{2+}, and Cu^{2+} ions indicates that the search for correlations between the structure of oxides, the activity in CO oxidation, and the content of active oxygen provides a lot of information concerning oxidation catalysts.[11] Thus a correlation between the catalytic activity and the Mn oxidation state was found: the activity increases with an increase in the content of Mn^{4+}. The dependences of the activity toward CO oxidation on the Mn^{4+} content and on the content of excess surface oxygen coincide.[21] Apparently, the charge displacement along the M—O—Mn bond (M = Co^{2+}, Ag^{1+}, Cu^{2+}) can be responsible for CO oxidation, *i.e.*, the mechanism of CO oxidation includes reversible electron transfer.

Of special interest is elucidation of correlations between the number of weakly bound negative charges emitted from the surface of complex oxides and the catalytic activity of the oxides. The TSE curves of perovskites did not show maxima at 140—160 °C as clearly defined as those in the case of spinels (manganites).[9] The total number of charges emitted in the temperature range of 20—130 °C for CO oxidation (Fig. 5, curve *1*) or 20—310 °C for ethylbenzene and propylene oxidation (see Fig. 5, curves *2* and *3*, respectively) was taken as a measure of emissivity of perovskites and spinels.

The catalytic activity for all the reactions studied correlates with the emissivity of perovskites (see Fig. 5). The catalytic activity and the EE intensity of spinels in CO and ethylbenzene oxidation (Fig. 6, curves *1* and *2*, respectively) were compared in a similar way. However, more detailed analysis shows that the activities of perovskites and spinels estimated from the temperature of 100% conversion of CO are close, although the emissivity of spinels is much higher than that of perovskites. This way of evaluation of the activity based on conversion does not always

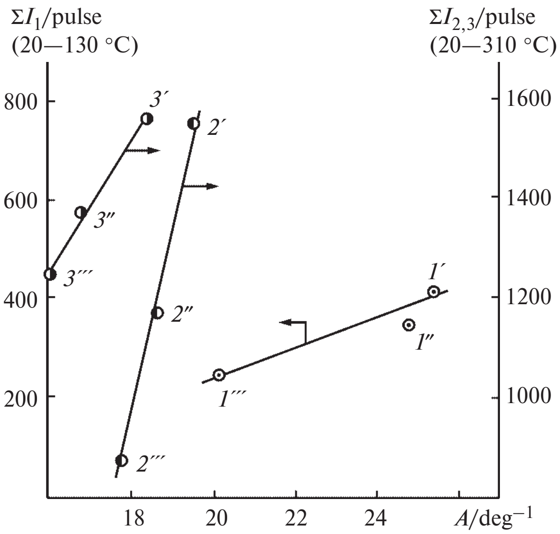

Fig. 5. Relationship between the emissivity (ΣI) and the catalytic activity (A) in CO (*1*), ethylbenzene (*2*), and propylene (*3*) oxidation defined as the temperature of 100% (for CO and ethylbenzene) or 50% (propylene) conversion of the reactant on the $LaCoO_3$ (*1′*, *2′*, *3′*), $LaMnO_3$ (*1″*, *2″*, *3″*), and $LaNiO_3$ (*1‴*, *2‴*, *3‴*) perovskites. The value reciprocal to the temperature of 100% (or 50%) conversion of the reactant was taken as the measure A of the activity.

reflect the number of active sites. For example, the spinel surface contains more active sites for oxidation than the perovskite surface;[3] this is consistent with an enhanced emissivity of spinels (*cf.* Figs. 5 and 6). Exoemission was measured under non-steady-state conditions in the pulsed mode; virtually each elementary event in the physicochemical process on the surface resulting in charge emission was recorded during these measurements. In this study, we used measurements of the catalytic activity in a flow-type setup.[3] In activity measurements in the pulse mode, the same oxidation states of CO and ethylbenzene were attained on perovskites at higher temperatures than on spinels; this corresponds to a higher emissivity of spinels. Conduction of oxidation reactions in the pulse reactor makes it possible to more comprehensively characterize the catalyst surface during interaction with a reactant.[3] In this case, better correlations between the activity toward oxidation and the EE are observed for compounds of various classes (spinels, perovskites).

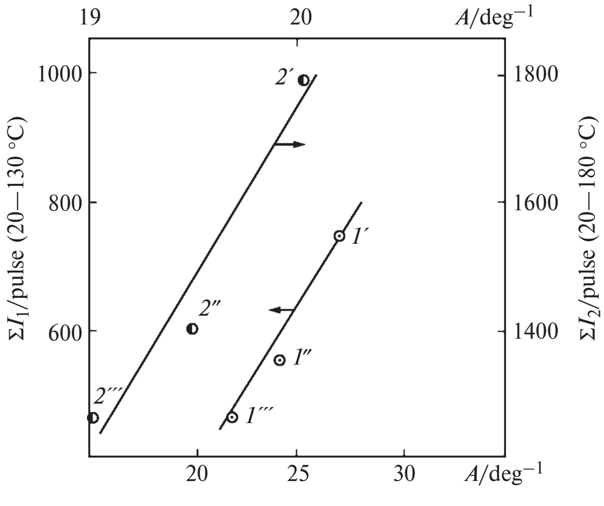

Fig. 6. Relationship between the emissivity (ΣI) and the catalytic activity (A) of spinels in CO (*1*) and ethylbenzene (*2*) oxidation defined as the temperature of 100% conversion of the reactant: $CuCo_2O_4$ (*1′*, *2′*), $CuCr_2O_4$ (*1″*, *2″*), $CuFe_2O_4$ (*1‴*, *2‴*). The value reciprocal to the temperature of 100% conversion of the reactant was taken as the measure A of the activity.

In view of the earlier data[9] indicating a good correlation between the catalytic activity and the emissivity of manganites with the spinel structure, it can be assumed that loosely bound electrons on the surface of oxide catalysts of different structures and different chemical compositions play an important role in oxidation reactions.

A study of CH_4 oxidation on perovskites by thermostimulated destruction using isotope heteromolecular exchange of oxygen with the $La_{1-x}M_xMnO_3$ surface demonstrated the presence of two types of active oxygen ions.[22] Catalysts with the perovskite structure contained adsorbed oxygen species, which are involved in reactions at low temperatures, and the lattice oxygen, which is activated at high temperatures. In our opinion, charged adsorbed oxygen species (O_2^-) participate in the oxidation of CO, while the lattice oxygen, which is activated to the greatest extent at temperatures of structural transitions (O^-_{surf}, O^{2-}_{surf}), participates in the oxidation of hydrocarbons.

Thus, exoemission experiments allow one to study the formation of the electronic structure and "excitation" of the active sites for the oxidation of hydrocarbons (in particular, ethylbenzene) in the structural phase transitions on the surface in the temperature range typical of catalytic reactions.

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