Weakly bound oxygen in the catalytic CO oxidation and exoemission from complex oxides having a spinel structure

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The catalytic activity of complex oxides $M^IM^{II}_2O_4$ (M^I = Cu, Ni, Co, Zn, or Mg; M^{II} = Mn or Cr) with a spinel structure in the oxidation of CO and the low-temperature (20—400 °C) exoemission of negative charges from their surface were investigated. A relationship between the catalytic activity and the emissivity of the systems under study was found. The role of the charged species of weakly bound oxygen in exoemission and oxidative catalysis by the complex oxides is discussed.

Key words: carbon monoxide, catalytic oxidation; spinel, exoemission; weakly bound oxygen.

The diversity of the mechanisms of the oxidation of carbon monoxide, particularly over oxide catalysts, is due to its high reactivity. Complex oxides with a spinel structure are very active in the oxidation of CO and hydrocarbons, and their activity is superior to the activity of the starting oxides.[1] The spinel structure of complex oxides includes two sublattices, tetrahedral and octahedral, with a great number of defects, which are cationic vacancies.[2] A cationic vacancy at the surface can be considered to be an aggregate of coordinatively unsaturated anions with high mobility.[3] Weakly bound oxygen (WBO) appears due to both chemisorption and the distortion of the spinel structure, which leads to the formation of cationic vacancies (V-sites), and is characterized by different bond energies with the surface.[4—6] WBO can occur at the surface as either charged or uncharged species. Identification of these species as well as the determination of the bond energy of WBO with the surface is a complicated problem. Radical species of oxygen and the temperature ranges of their stability are usually studied by ESR spectroscopy and temperature-programmed desorption (TPD).[7]

Low-temperature (from −196 to 430 °C) emission of electrons and ions (exoemission) from the surface of metals and oxides is due to the presence of WBO in the forms of O_2^-, O^-, O^{2-}, as well as hydroxyl groups and their clusters.[8—10] In this work, the catalytic activity of spinels MMn_2O_4 (M = Cu, Zn, Mg, Ni, or Co) in the oxidation of CO was studied and compared with the data on the thermally stimulated exoemission (TSE) of negative charges from the surfaces of these oxides.

Experimental

Catalysts were obtained by calcination of equimolar mixtures of nitrates or carbonates in air for 1 h at 150 °C, followed by an increase in temperature to 500 °C.[1] The spinel structure of the catalysts was confirmed by the IR spectra. The specific surface areas of samples determined by the BET method with the use of the low-temperature adsorption of krypton were within 8—12 $m^2 g^{-1}$.

The chemisorption of oxygen was studied at 100 °C on samples subjected to preliminary thermal-vacuum treatment ($p = 10^{-3}$ Pa) at 400 °C. The catalytic activity in the oxidation of CO was studied in a flow setup at a flow rate of 900 h^{-1}. The CO content in its mixture with air was equal to 5—6%. The composition of the reaction products was determined by GC. The catalytic activity was evaluated as the temperature of ~100% conversion of CO.

Exoemission was registered with a gas-flow Geiger counter from a reconstructed "Protoka" industrial setup.[11] The heating rate during the study of TSE was equal to 10 deg min^{-1}. The experiments were carried out in an atmosphere of methane, the quenching gas of the counter. When a positive potential (3.7 kV) was put into an anode of the counter, negative ions and electrons emitted by the surface of the sample were registered.

The curve of "spontaneous" TSE that was predominantly due to the thermal desorption of negative ions[9] was recorded in the first run with linear heating. When heating was repeated, the intensity of TSE decreased to a level close to the background. After that, the catalyst was β-irradiated with $^{90}Y—^{90}Sr$ (a dose was 0.2 Gr) in air for repeated excitation and the temperature dependence of exoemission was registered.

The IR spectra of solid samples were recorded on a Specord M-80 spectrophotometer.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1618—1621, September, 1997.

Results and Discussion

Figure 1, *a—d* presents the results of TSE from the starting samples (curves *1*), after repeated heating (*2*), and after β-irradiation (*3*). Because of the high emissivity of $CuMn_2O_4$ (see Fig. 1, *a*), TSE after repeated heating exceeded the background level. On the basis of previous studies of exoemission and thermal desorption,[8] one can assume that the main peak of TSE in the range of 130—160 °C for the samples under study is due to the emission of the CO_2^- and H_2O^- ions adsorbed on the surface sites, which include WBO in the form of O_2^-. The TSE process occurs at the expense of the recombination energy of desorbing active species, including charged species. It is noteworthy that because of the presence of organic impurities on the surface of the catalyst, WBO is desorbed, as a rule, as CO_2^- and additional thorough purification of the samples in a vacuum is necessary to detect oxygen.[12]

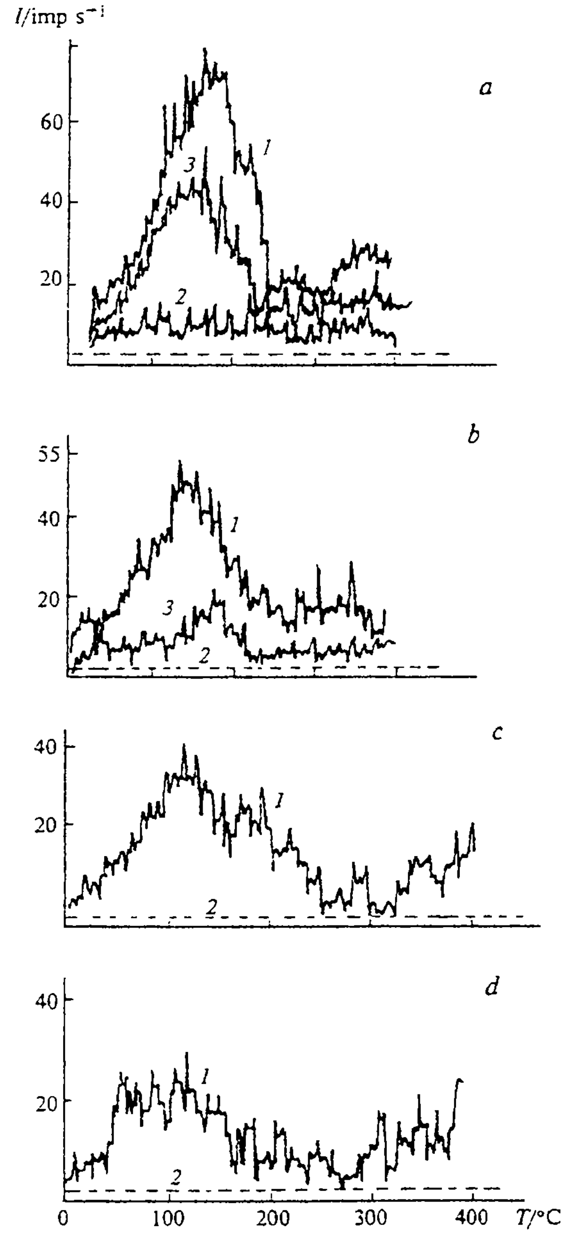

Fig. 1. Thermally stimulated exoemission from the surface of $CuMn_2O_4$ (*a*), $CoMn_2O_4$ (*b*), $NiMn_2O_4$ (*c*), and $ZnMn_2O_4$ (*d*): *1*, starting samples; *2*, after repeated heating; *3*, after β-irradiation; the dashed line is the background.

After desorption of the charged species, no TSE is observed in fact after repeated heating of the catalysts (see Fig. 1, *b—d*). However, TSE with the main peak at T_{max} = 130 to 160 °C appears again after β-irradiation (see Fig. 1, *a* and *b*, curves *3*). According to the results of recent studies of electron-stimulated desorption (ESD)[13] and radiation-induced instability,[14] the surface layer is destroyed by radiation. This process is accompanied by ion emission and the reduction of oxides. The scheme of the processes occurring as a result of β-irradiation of the lattice oxygen (O_{lat}^{2-}) can be presented as follows:

$$O^{2-}_{lat} \xrightarrow{E_\beta} O^-_{ads} + e_{loc} + \square\ , \qquad (1)$$

$$2\,O^-_{ads} \longrightarrow O^-_{2,ads} + e_{loc} + Q_{rec}\ , \qquad (2)$$

$$O^-_{2,ads} + Q_{rec} \longrightarrow O_2^-\uparrow, \qquad (3)$$

where E_β is the radiation energy, $\square$ is a vacancy, and Q_{rec} is the recombination energy. Under β-irradiation, the surface layer can be charged negatively and the electrons can be localized (e_{loc}) on neutral or positively charged surface centers.

Simultaneously with ESD, anionic defects are formed on which electrons are localized (F^+-sites), and then oxygen from the atmosphere ($O_{2,g}$) is adsorbed in the form of charged species:

$$\square + e \longrightarrow \boxed{e}\ , \qquad (4)$$

$$\boxed{e} + O_{2,g} \longrightarrow O^-_{2,ads}\ . \qquad (5)$$

As can be seen in Fig. 1, the peaks of TSE and ESD coincide. Hence, the same charged species of WBO are present at the surface. On the basis of the data of ESR spectroscopy and TPD, the authors of the majority of reports believe that the low-temperature (T < 175 °C) species of adsorbed oxygen is O_2^-; the desorption peak with T_{max} = 185 °C corresponds to this species. In the temperature range 170—280 °C, O^- is a stable species (see Refs. 15 and 16). The coincidence of the TSE peaks (T_{max} = 130 to 160 °C) of all oxides studied, both semiconductors and insulators, can be rationalized only by assuming that TSE occurs from the mobile layer of WBO. When T_{max} is achieved, the resonance (thermal)

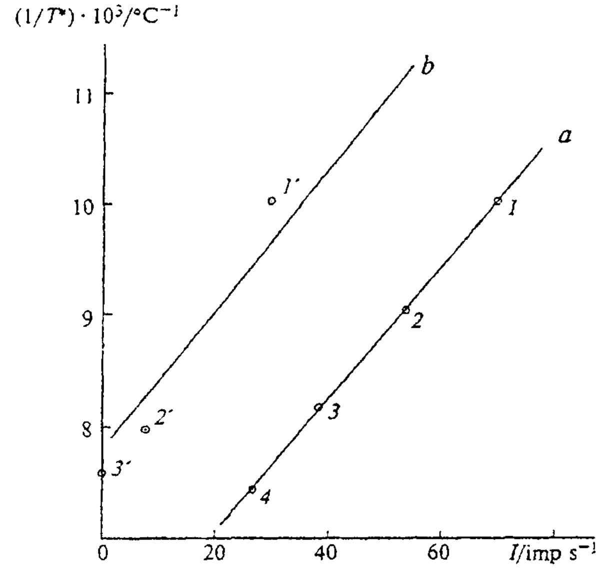

Fig. 2. Relationship between the activity of the catalysts in the oxidation of CO and the intensity of TSE from samples obtained from nitrates (*a*) and carbonates (*b*): *1*, *1′*, $CuMn_2O_4$; *2*, *2′*, $CoMn_2O_4$; *3*, $NiMn_2O_4$; *3′*, $Cu_{0.5}Mg_{0.5}Mn_2O_4$; *4*, $ZnMn_2O_4$.

excitation $O_2^- \xrightarrow{kT} {}^*O_2^-$ is observed. The relaxation processes result in TSE of electrons and O_2^- ions as well as of the adsorbed (bound with O_2^-) products in the form of neutral molecules or ions.

In the case under consideration, we deal with "resonance" decay of oxygen radical-ions in the electron-excited state ($^*O_2^-$), which leads to TSE of negative charges and the partial transformation of WBO into ions, *e.g.*, O^- at $T_{max} \approx 150$ °C.

The shift of the TSE peak to lower temperatures ($T \leq 100$ °C) (see Fig. 1, *c*, *d*) is due to the desorption of negatively charged water molecules.[8—10] The emission that is due to the transformation of the charged species of WBO ($O_2^- \rightarrow O^-$) at $T \approx 130$ to 160 °C is small and correlates with the low catalytic activity of these species (Fig. 2).

On the basis of the above-presented data, it is possible to expect a correlation between the catalytic activity of the catalysts studied in the oxidation of CO and their emissivity. Figure 2 shows the relationship between the maximum intensity of TSE ($T_{max} = 130$ to 160 °C) and $1/T^*$ (T^* is the temperature at which 100% oxidation of CO is achieved). As can be seen, there is a linear correlation between the catalytic activity and the emissivity of the catalytically active spinels.

The amount of oxygen (q) adsorbed at 100 °C and the maximum intensity of exoemission (I^*) were determined for $CuMn_2O_4$ and $CuCr_2O_4$.

Catalyst	q /μmol m^2	I^* /imp s^{-1}	T_{max} /°C	$(T^*)^{-1}$ /°C^{-1}
$CuMn_2O_4$	0.61	70	150	0.01
$CuCr_2O_4$	0.12	30	100—130	0.007

Here T_{max} is the temperature corresponding to the maximum TSE; T^* is the temperature of 100% conversion of CO.

The correspondence between the amount of oxygen chemisorbed and the intensity of emission from the samples confirms our suggestion that the same WBO species participate in both oxidative catalysis and exoemission. As O_2^- is the stable species of chemisorbed oxygen at $T < 175$ °C, according to Ref. 7, one can conclude that both the maximum TSE (at $T_{max} = 130$ to 160 °C) and the catalytic activity in the oxidation of CO in this temperature range are due to the same species of negatively charged oxygen, O_2^-.

Thus, WBO in the form of a negatively charged molecular species is formed when both cationic and anionic vacancies are present at the surface. Because the CO molecule is a donor of electrons,[17] it is adsorbed as a cation. According to the literature data,[1] the reaction proceeds in the adsorption layer *via* the Langmuir—Hinshelwood mechanism.

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Received July 1, 1996;
in revised form April 10, 1997