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In Situ Study of the Selective Oxidation of Methanol to Formaldehyde on Copper

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Abstract—Combined use of X-ray photoelectron spectroscopy (XPS) and *in situ* mass spectrometry made it possible to simultaneously obtain the O1*s* spectra and the mass spectrometric signal of formaldehyde ($m/z = 30$) in the course of heating (420–670 K) of polycrystalline foil in a flow of the reaction mixture of methanol and oxygen (with a total pressure of 0.1 mbar and a ratio of 3/1). It is shown that the O1*s* spectra contain two lines with E_b = 530.1 and 531.2 eV, whose relative intensities depend on the sample temperature. At a low temperature (420 K) the line with a lower binding energy dominates, whereas sample heating leads to a drastic decrease in its intensity and its replacement by a line with a higher value of E_b. A decrease in the intensity of the latter line occurs at $T > 550$ K, in the same temperature range as a drastic increase in the intensity of the formaldehyde signal. These lines were assigned on the basis of literature data and data obtained by the authors for the known forms of oxygen on copper and for the intermediate species of the reaction, such as methoxy and formate. The O1*s* line with E_b = 530.1 eV was assigned to methoxy groups, and the line with E_b = 531.2 eV was assigned to suboxide oxygen. The correlation of the intensity of the XPS signal of suboxide oxygen with the yield of formaldehyde was supported by stationary experiments using *in situ* XPS that prove its participation in the key step of the selective oxidation of methanol to formaldehyde.

INTRODUCTION

Selective oxidation of methanol to formaldehyde on copper has long been the focus of research because of its simplicity and because it can be considered as a model for many oxidation reactions of higher alcohols to the corresponding aldehydes. These reactions are carried out in industry in the presence of copper catalysts [1–9]. In the cited papers, surface-sensitive physical methods were applied that stipulated the strategy of studies: preliminary treatment of the clean copper surface to various adsorbed oxygen species and further testing of their reactivity toward methanol. However, it should be noted that this approach does not provide a solution to the pressure gap problem. Indeed, if the active form of oxygen is only formed under the reaction conditions, then it can be found in such experiments. Moreover, the active species may be at a weakly bound state, and the evacuation of the gas phase before obtaining spectral information may lead to the removal of the active species from the sample surface.

Analysis of published data [1–9] confirms that the problem of pressure gap for the catalytic system considered in this paper does exist for the following reasons:

—Before operation, the initial copper catalyst has to be activated;

—A pathway of methanol conversion depends on the methanol/oxygen ratio of the initial partial pressures in the reaction mixture and on the sequence of reactant supply;

—Stoichiometric copper oxides (Cu_2O and CuO) are unselective in formaldehyde synthesis; and

—Evacuation of the reaction medium or its cooling in order to freeze the active state of the copper surface leads to its transformation into copper(I) oxide.

These facts suggest that the state of adsorbed oxygen responsible for copper activity in the reaction of selective oxidation of methanol are formed under catalytic reaction conditions and this is a dynamic system which only exists in contact with the reaction medium. On the other hand, the high rate of the reaction (the reaction kinetics is limited by mass transfer) allows us to hope for the efficient formation of active sites at pressures lower than atmospheric.

The goal of this work was to study the surface of a copper sample by the XPS method in the course of catalytic methanol oxidation to identify the states of adsorbed oxygen responsible for the selective oxidation of methanol to formaldehyde. The catalytic activity of the copper surface was measured using mass spectrometry.

EXPERIMENTAL

All experiments were carried out using a VG ESCALAB “High Pressure” photoelectron spectrometer (Vacuum Generators, Great Britain) for recording electron spectra *in situ*. The possibility of recording photoelectron spectra at elevated pressures over the sample follows from the fact that the free path of electrons at a gas pressure of ~1 mbar is several millimeters

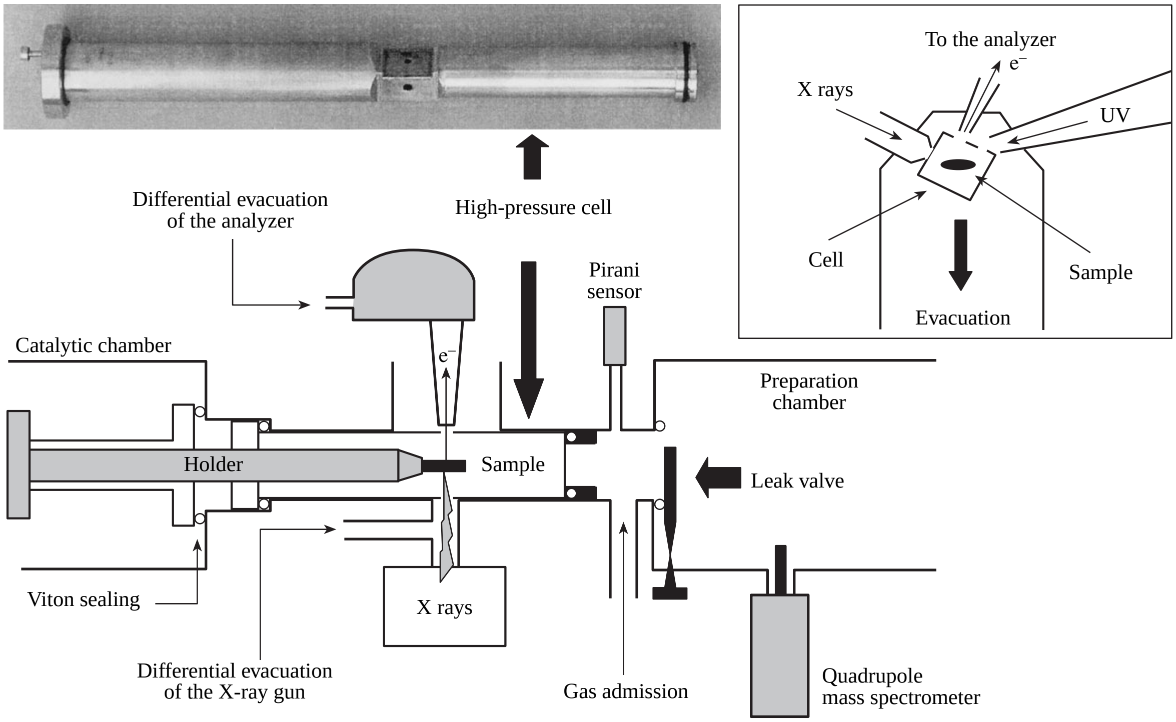

Fig. 1. High-temperature cell in the VG ESCALAB "high pressure" photoelectron spectrometer.

[10]. Correspondingly, to prevent substantial electron scattering in the gas, their path through the region of high pressures should be as short as possible. In the VG ESCALAB "high pressure" photoelectron spectrometer, this is achieved using a special high-pressure cell which is mounted in the analyzing chamber of the spectrometer using viton ring sealing (Fig. 1). This makes it possible to record photoelectron spectra at reaction mixture pressures of 1 mbar over the sample.

The pressure difference between the cell and other parts of the spectrometer is achieved by the presence of only three holes with a small diameter (<3 mm), which are the inlets for the X-ray and UV radiation and the outlet for photoelectrons to the analyzer and by the use of the two-stage differential evacuation of the spectrometer. The first stage involves the evacuation of the analyzer chamber by a high-performance diffusion pump. The second stage is independent evacuation of the X-ray radiation source, electrostatic lenses, and the analyzer by diffusion pumps. The latter provides a substantial pressure difference between the analyzer chamber and lenses due to which there is no substantial electron scattering in the electron lenses. The quantitative characteristics of the pressure difference between various parts of the spectrometer determined for oxygen are presented in the table.

Photoelectron spectra were recorded using nonmonochromated AlK_α radiation ($h\nu = 1486.6$ eV). The spectrometer was calibrated before experiments according to the positions of peaks of core levels Au4$f_{7/2}$ ($E_b = 84.00$ eV) and Cu2$p_{3/2}$ ($E_b = 932.7$ eV). For the detailed analysis of the chemical composition of the surface of the model catalyst, we decomposed the spectra into components. Upon the subtraction of the background spectrum using the Shirley method, the experimental curve decomposed into several lines corresponding to the photoemission of electrons from the inner levels of atoms in various chemical environments.

The composition of the gas phase in the cell was controlled by a quadrupole VG Q7B mass spectrometer (Fig. 1). The gas supply into the mass spectrometer was controlled by the leak valve. The reaction rate of selective methanol oxidation to formaldehyde was monitored by a change in the intensity of the mass spectrometric signal with $m/z = 30$ (H_2CO). Simultaneously, we recorded other signals as well (m/z): H_2 (2), H_2O (18), CO (28), CH_3OH (31), O_2 (32), and CO_2 (44).

A polycrystalline copper foil (99.99%) sample was mounted on the holder; the source of heat was a furnace

Pressure in different parts of the spectrometer

Pressure in the cell, mbar	Pressure in the analyzer chamber, mbar	Pressure in the X-ray tube, mbar
10^{-3}	10^{-6}	8×10^{-9}
5×10^{-3}	6×10^{-6}	4×10^{-8}
10^{-2}	10^{-5}	8×10^{-8}
5×10^{-2}	8×10^{-5}	5×10^{-7}
10^{-1}	2×10^{-4}	10^{-6}

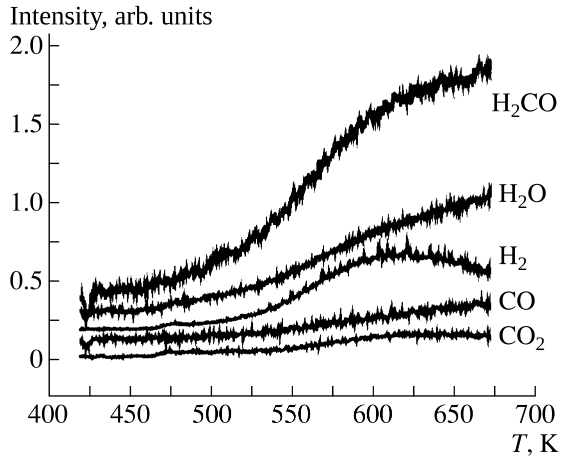

Fig. 2. Dependences of the intensities of mass spectrometric signals from the products of methanol oxidation on the sample temperature.

made of pyrolytic boron nitride (PBN, Sintec-Keramik), which is resistant to an oxidative medium [11]. The temperature was controlled using the chromel–alumel thermocouple attached to the sample by spot welding. The purity of the sample surface was controlled by XPS. The purity of gases was controlled by a quadruple mass spectrometer. The procedure of sample cleaning consisted in etching the foil surface by argon ions, and further oxygen adsorption at room temperature and fast heating of the foil in a vacuum to 900 K. No admixtures were detected upon sample cleaning and in the course of further experiments (exact to the sensitivity of the XPS method).

In Situ Experiments

Because clean copper is inactive in methanol oxidation, it was activated before the admission of the reaction mixture onto the sample. Activation consisted in the consecutive treatment of the copper foil in oxygen (20 min, 5 mbar, and 670 K) and in methanol (10 min, 0.2 mbar, and 670 K) [12]. The whole activation procedure (10 cycles) was carried out in the preparation chamber of the spectrometer. Upon activation, evacuation of the gas phase and cooling to $T = 420$ K, the sample was put into a high-pressure cell, where the stationary flow of the reaction mixture was maintained with a total pressure of 0.1 mbar and a O_2/CH_3OH reactant ratio of 1 : 3). Then, the sample was heated linearly with simultaneous registration of the complete set of mass spectra and photoelectron spectra O1*s* and $Cu2p_{3/2}$p3/2.

Figure 2 shows the dependences of the product yield on the sample temperature. The yield of the reaction product is characterized by the intensity of the corresponding mass spectrometric signal. In complete agreement with published data [9], the yield of the key reaction product, formaldehyde, is rather low in a range of temperatures close to room temperature and drastically increases at $T > 500$–550 K. Detailed analysis of the composition of products formed in the reaction and their ratios allowed us to draw some conclusions on the reactions occurring under these conditions. The reactions of selective and complete oxidation of methanol

$$2CH_3OH + O_2 \longrightarrow 2CH_2O + 2H_2O, \qquad \text{(I)}$$

$$CH_3OH + 3/2O_2 \longrightarrow CO_2 + H_2O \qquad \text{(II)}$$

are identified by the formation of formaldehyde, carbon dioxide, and water (Fig. 2). Carbon monoxide and hydrogen found in the reaction products suggested the occurrence dehydrogenation reactions:

$$CH_3OH \longrightarrow CH_2O + H_2, \qquad \text{(III)}$$

$$CH_3OH \longrightarrow CO + 2H_2. \qquad \text{(IV)}$$

The reaction with the formation of formaldehyde dominates. The low concentrations of CO and CO_2 compared to the concentration of formaldehyde in the reaction products are also notable. This implies that the selectivity of the sample toward formaldehyde, a key product, is high. The selectivity was determined by calculating the ratio of the formaldehyde signal intensity to the overall intensity of signals from all carbon-containing products: ~80%.

Automation of the spectrometer [13, 14] made it possible to record consecutively the XPS spectra O1*s* and $Cu2p_{3/2}$ and compare each spectrum with the sample temperature and the signal from the mass spectrometer. The sample heating ramp (0.2 K/s) was chosen to keep the temperature in the course of recording one spectrum within 10 K. Further analysis of spectra consisted in comparing, summing, and averaging several consecutive spectra provided that the shape of spectra remained the same in a certain temperature range. This made it possible to reduce the signal/noise ratio.

Figure 3 shows a series of spectra O1*s* recorded *in situ* in the course of the experiment for which mass spectrometric data are shown in Fig. 2. It can be seen that all the spectra consist of two signals with binding energies 530.1 and 531.2 eV, whose intensities change with the sample temperatures. Two spectra decomposed into components are given as an example. At the beginning of heating, the first line dominates (E_b = 530.1 eV). The second line grows with further heating to 520 K (E_b = 531.2 eV). Recall that, in the same temperature range, the intensity of the mass spectrometric signal characterizing formaldehyde also starts to increase (Fig. 2). However, before comparing the catalytic properties with the intensity of the signal O1*s*, we identified these signals.

Identification of Oxygen States

The signals O1*s* were identified *in situ* using the precision recording of the complete set of photoelectron signals (O1*s*, C1*s*, $Cu2p_{3/2}$, Cu*LVV*) at the initial

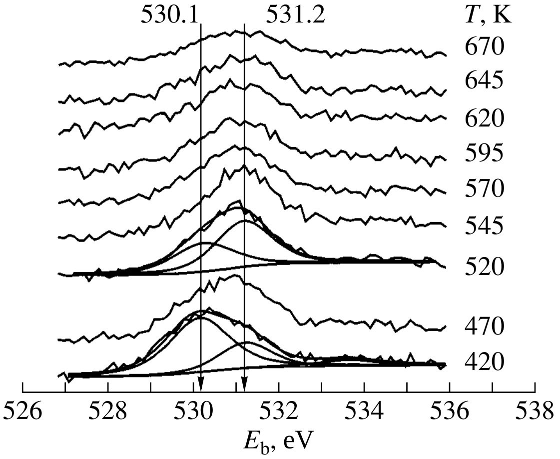

Fig. 3. The O1*s* spectrum of the methanol–oxygen system on copper at different temperatures.

(420 K) and final (670 K) temperatures and comparing them to the respective spectra of surface species known for the system under consideration [15–18]. The use of the Auger line of copper for the analysis of oxygen states instead of the photoelectron line Cu2$p_{3/2}$ was due to the higher sensitivity of the Cu*LVV* spectrum to the charge state of copper atoms. Nevertheless, the spectra Cu2$p_{3/2}$ were recorded in each experiment to determine their intensity. The intensities were used to calculate the concentrations of oxygen on the sample surface.

Figure 4 shows O1*s* photoelectron spectra and Cu*LVV* Auger spectra of various oxygen states involved in the composition of copper, CuO and Cu_2O, and oxygen adsorbed on the copper surface (O_{ads}). Adsorbed oxygen was obtained by O_2 adsorption at 300 K and 10^{-3} mbar for 5 min. A bulk Cu_2O sample was obtained by treating the clean copper surface with oxygen for 30 min at $T = 670$ K and $P_{O_2} = 5$ mbar. Sample treatment in more severe conditions ($P_{O_2} = 10$ mbar, $T = 720$ K, and 30 min) leads to the formation of CuO.

It can be seen that adsorbed atomic oxygen is characterized by the line O1*s* with $E_b = 529.7$ eV, oxygen in the composition of Cu_2O is characterized by the line with $E_b = 530.4$ eV, and oxygen in the composition of CuO is characterized by the line with $E_b = 529.6$ eV. These results are in complete agreement with literature data [15, 17] and were further used in identifying the oxygen state. The ratio of line intensities O1*s*/Cu2$p_{3/2}$ = 0.0145 obtained in our experiments also agrees with literature data: for adsorbed oxygen it is close to the analogous value (0.014) observed after the saturation ($\Theta = 0.5$ ML) of the Cu(100) surface with oxygen [16]. Taking into account the factor of atomic sensitivity, the ratio of intensities O1*s*/Cu2$p_{3/2}$ for Cu_2O suggests the stoichiometry O : Cu = 1 : 2.

In this system, several carbon-containing species can be formed which are intermediates in the catalytic reaction. Methoxy and formate species should be given attention first. It is well-known that these species are efficiently formed in the course of coadsorption of oxygen and methanol at temperatures close to room temperature. Under these conditions, both methoxy and formate groups are stable on the copper surface and can easily be identified by physical methods, such as XPS, TDS, and STM [5, 6]. Figure 5 shows C1*s* and O1*s* spectra recorded *in situ* in the course of O_2 and CH_3OH coadsorption at $T = 300$ K, a reactant ratio of 1 : 3, and a total pressure of 5×10^{-3} mbar. Such a low pressure was chosen to prevent copper surface oxidation and

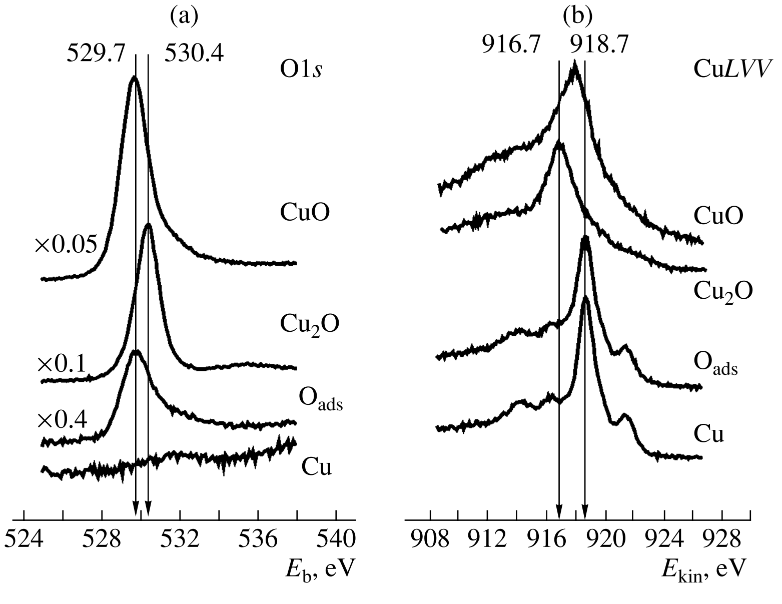

Fig. 4. (a) Photoelectron spectra O1*s* and Auger spectra Cu*LVV* obtained for the individual states of oxygen on the copper surface.

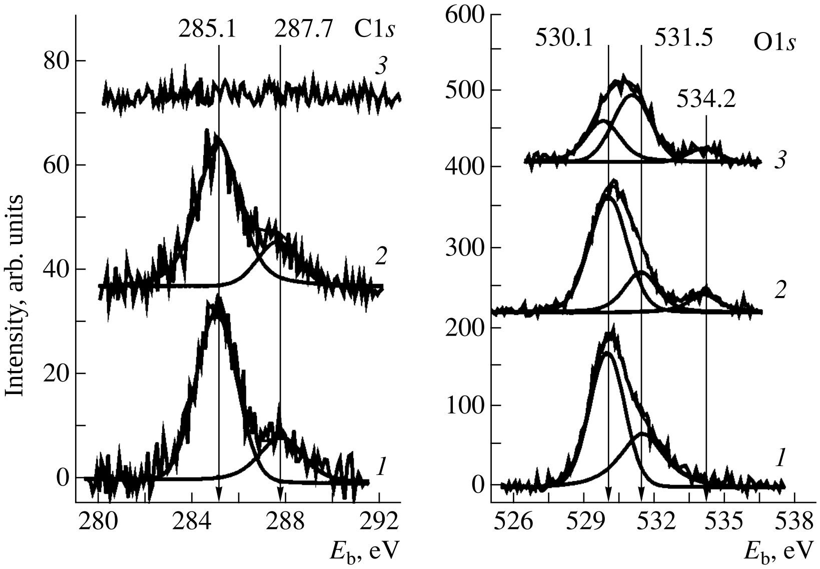

Fig. 5. Photoelectron spectra (a) C1*s* and (b) O1*s* recorded under stationary conditions at the (*2*) initial (420 K) and (*3*) final (670 K) temperature of the *in situ* experiment. Spectrum *1* was recorded after the model preparation of the methoxy and formate groups on the sample surface.

Cu_2O formation. In the C1*s* spectrum, two peaks with E_b = 285.2 and 287.7 eV were observed, and the O1*s* spectrum contained two peaks with E_b = 530.1 and 531.5 eV (Fig. 5). This led us to conclude that surface species that contain both carbon and oxygen are formed. The values of C1*s* and O1*s* peaks with binding energies of 285.2 and 530.1 eV are characteristic of methoxy groups, whereas the other two lines can be assigned to formate groups [6]. The O1*s*/C1*s* intensity ratio of the corresponding peaks is also close to the stoichiometric values for methoxy and formate groups.

Figure 5 also shows the C1*s* and O1*s* spectra recorded *in situ* before (T = 420 K) and after heating (T = 670 K) of the clean copper surface under conditions of catalytic reaction testing. It is seen that spectra recorded at 420 K (Fig. 5, spectrum *2*) are almost identical to the spectra of the copper surface containing a mixture of methoxy and formate groups. The only difference is a weak peak with $E_b \approx 534.5$ eV, which belongs to gas-phase methanol. Note also that the Auger spectrum Cu*LVV* is centered at E_{kin} = 918.7 eV pointing to the metallic state of copper. These data suggest that at T = 420 K the sample surface is mostly covered with methoxy groups and there are not many formate groups.

When identifying the states of oxygen in the O1*s* spectrum recorded at T = 670 K (Fig. 5, spectrum *3*), oxygen-containing species should only be taken into account, because no peaks are observed in the C1*s* spectrum. The second fact that should be taken into account is that in both cases (at 420 and 670 K) the Auger spectra do not contain signals belonging to copper ions. Small shifts in the values of binding energies of some components are also notable: the first line is centered at E_b = 529.8 eV (instead of 530.1 eV) and the second line is centered at E_b = 531.2 eV (instead of 531.5 eV). Taking all these facts into account, we assume that the component with the lower value of the binding energy in the O1*s* spectrum may belong to the adsorbed atomic oxygen.

The identification of the second O1*s* peak with E_b = 531.2 eV is a more complex task, because none of the oxygen states has close binding energies. Although the value of E_b is close, the absence of the corresponding C1*s* signal does not allow us to assign this O1*s* peak to formate. This line can be identified if we take into account results reported in [12], where the authors studied this system under similar conditions by *in situ* XANES. It was shown that metallic copper is active in the reaction of selective oxidation of methanol to formaldehyde if it contains oxygen in only one state, which, unlike all other oxide states of oxygen has no band in the XANES spectra near the absorption edge (photon energy of ~531 eV). This led the authors to make an assumption that copper suboxide is formed. Following this conclusion, it is logical to assign the O1*s* band with E_b = 531.2 eV to suboxide oxygen. The correctness of such an assignment is supported by two facts: the formation of this state occurs only under the action of the reaction medium and only on the metallic copper surface. The latter conclusion is based on the absence of the white line in the XANES spectra of the *L*-edge of copper absorption [9, 12], and the value of the kinetic energy of the Auger spectrum Cu*LVV* (918.7 eV) is typical of metallic copper as it was found in our experiments.

DISCUSSION

As follows from the above data, depending on the sample temperature, various species can exist on the copper surface: methoxy and formate species, adsorbed atomic oxygen, and oxygen in the composition of copper suboxide. To discuss their effect on the catalytic properties of copper in the reaction of selective oxidation of methanol to formaldehyde, it is necessary to compare their surface concentrations with the yield of formaldehyde.

Figure 6 shows the temperature dependence of the yield of formaldehyde (the intensity of the mass spectrometric signal) formed in the course of the reaction of oxygen and methanol (1 : 3) at a total pressure of 0.1 mbar. This is compared with the intensities of the signals with E_b ~ 530 and 531 eV, which are normalized with respect to the intensity of the Cu2*p* signal. As is known, an intensity ratio I I_{O1s}/I_{Cu2p} of 0.014 corresponds to 0.5 ML coverage. Note that, in the point with T = 420 K, the signal with a lower value of the binding energy refers to methoxy groups. At T = 670 K, it refers to the atomic adsorbed oxygen. At the same temperatures (420 and 670 K), the signals with high values of E_b refer to formate groups and suboxide oxygen, respectively. At the same time, at some intermediate temperatures, all the cited species may coexist before the adlayer would completely change its composition. Unfortunately, insufficient energy resolution of the spectrometer and the impossibility of registering many spectral regions in the course of relatively fast sample heating prevents the analysis of the intensities of separate signals in the course of heating. That is why Fig. 6 shows only integral (paired) dependences of the intensities of O1*s* signals on the temperature.

Nevertheless, drastic changes in the intensity observed in two temperature ranges, 450–520 K and >550 K, and analysis of literature data on the thermal stability of various surface species make it possible to draw some conclusions regarding their responsibilities for such a behavior. A drastic decrease in the intensity of the component with E_b ~ 530 eV at T > 450 K is most likely due to the disappearance of methoxy species, which decompose at temperatures that are a little higher than room temperature [6]. Suboxide oxygen is formed on the surface that is freed, and the concentration of this species practically reaches the monolayer coverage at T = 520 K. Further heating of the sample causes a gradual decrease in the concentration of suboxide oxygen, which is accompanied by an increase in the catalyst activity: the yield of formaldehyde gradually increases. This allows us to assume that it is the suboxide state of oxygen that is active in the formation of the key product of the reaction of selective methanol oxidation. A constantly high intensity of the signal with E_b ~ 530 eV in the temperature range 520–670 K most likely points to the existence of the adsorbed atomic oxygen under the reaction conditions. It is known that it is adsorbed atomic oxygen that substantially increases the ability of copper to adsorb methanol in the form of methoxy groups [19, 20]. The concentrations of other surface species are below the sensitivity of the XPS method, and this prevents the analysis of their effect on the catalytic activity of copper.

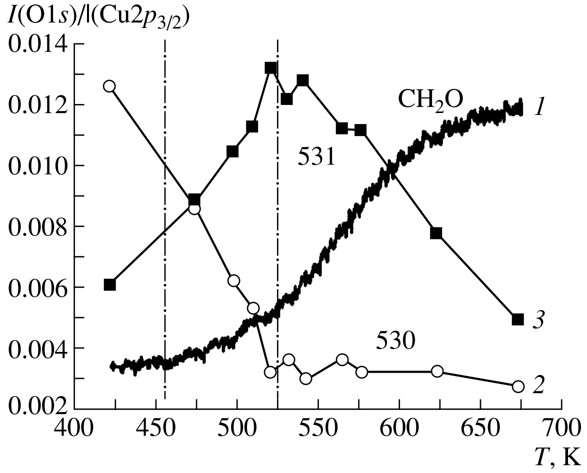

Fig. 6. The temperature dependence (in the course of methanol oxidation) of (*1*) the intensity of the mass spectrometric signal of formaldehyde, (*2*) the intensity of the signals O1*s* with E_b ~ 530 eV and (*3*) 531 eV normalized with respect to the intensity of the signal $Cu2p_{3/2}$.

CONCLUSION

Comparative analysis of the catalytic properties of copper and the composition of adsorbed layers allowed us to distinguish three temperature ranges where the sample behavior changes substantially (Fig. 6):

(I) The low-temperature range. In this temperature range the sample surface is covered by methoxy species and partly by formate species, which block the surface and prevent the adsorption of other reactants (e.g., oxygen). The catalyst remains inactive in all reaction pathways.

(II) The range of intermediate temperatures. In this range, the composition of the adsorbed layer changes. Methoxy and formate species leave the sample surface and are replaced by suboxide oxygen. The adsorbed layer becomes active toward formaldehyde formation.

(III) The high-temperature range. A drastic increase in the sample activity is accompanied by a substantial decrease in the concentration of suboxide oxygen, which is probably the species that is active in the selective oxidation of methanol to formaldehyde.

The correlation of catalytic properties of copper in the reaction of methanol oxidation to formaldehyde with the concentration of suboxide oxygen motivates a further detailed study of its nature by a complex of surface-sensitive methods.

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