Physicochemical investigation of the copper and silver catalysts of the ethylene glycol oxidation

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Abstract

The copper and silver catalysts of ethylene glycol (EG) oxidation into glyoxal have been investigated by means of X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA) methods. The data presented in this work show that two types of the carbon deposits, which accompany glyoxal synthesis, are formed. First type of deposits are the graphite-like structures, which can be formed on Cu surface at lean content of oxygen in the reaction mixture. Second type of deposits is the oxycarbon structure, which grows as filaments. Both morphology and the chemical composition of oxycarbon deposits depend strongly on the reaction mixture. Oxygen in the reaction mixture leads to the predominant formation of the oxycarbon filaments on the oxidized metal surface. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Selective ethylene glycol (EG) oxidation on silver and copper catalysts is the most perspective method of the glyoxal synthesis. In industry, glyoxal is widely used for production of the important organic compounds [1]. One of the main problems of EG oxidation process into glyoxal is the coke formation giving rise to deactivation of the catalyst surface [2,3]. In contrast to the selective methanol oxidation into formaldehyde [4], the coke formation is observed during EG oxidation process on the massive metal catalysts. It is associated with the high reaction ability of EG and glyoxal in the polycondensation processes.

We have previously established [2] that the double-layer Cu–Ag catalytic system shows the best efficiency in the process. However, during the oxidation reaction of EG the intense coke formation process decreasing both the activity and the life term of the catalysts takes place on the surface. The process of the coke formation on a massive metal Cu and Ag catalysts has not yet been investigated in the literature. In this work, series of catalysts have been analyzed after different extent of deactivation. The influence of external parameters (temperature and composition of the reaction mixture) of the EG

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oxidation process on the coke formation has been studied on massive Ag and Cu catalysts.

To study the catalyst morphology, nature and states of carbon in the coke deposits we used a scanning electron microscopy (SEM), thermal gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) together with catalytic methods.

2. Experimental

The sample of massive Ag catalyst was prepared by calcination of the mixture of electrolytic crystals with an organic support for 2 h at 923–973 K in air [5]. Cu catalyst was prepared by electrolytic deposition on the cellular support with the following erase of organic base [6].

The coke formation was studied in a flowing catalytic reactor with the use of the McBain balance. This reactor makes it possible to observe the increase of the coke deposits on the catalyst surface directly during the EG oxidation process. To prevent the convection flows and alcohol condensation, the quartz spiral was separated from the heating catalytic reactor by the water cooler. B-630 cathetometer was being used for registration of the quartz spiral tension while the increase of the coke deposits on the catalyst was leading to the growth of sample weight during the catalytic process. The measurement error of a catalyst weight was 0.001 g. The determination of the coke deposit content was carried out according to the equation:

$$C_{PY} = \frac{h_0 - h}{Rg} 100\%,$$

where C is the coke deposits, wt.%; h_0 is the initial tension of quartz spiral, mm.; h is the quartz spiral tension during the catalytic experiment, mm; R is the spiral sensitivity, mm/mg; g is the catalyst weight, mg.

The XPS were recorded using a VG ES-CALAB electron spectrometer. XP spectra were taken with AlK$_\alpha$ radiation ($h\nu = 1486.6$ eV). Experimental resolution characterized by full width at half maximum (FWHM) of Ag3d$_{5/2}$ line is 1.3 eV if pass energy of analyzer is equal to 20 eV. Spectra were calibrated against $E_b(Ag3d_{5/2}) = 368.1$ eV and $E_b(Cu2p_{3/2}) = 932.7$ [7]. Quantitative calculations from XPS data were made in view of atomic sensitivity factors [7].

SEM investigations were performed with aid of scanning electron microscope BS-350 (TESLA) equipped with electron gun 16 kV. The samples were mounted by means of silver glue and were covered by gold film (thickness of 100 Å) to exclude a charging effect.

The thermal graphic analysis was carried out using derivatograph Q-1500 in the airflow at the temperature interval of 298–1173 K.

3. Results

3.1. Carbon deposition

In Fig. 1, the dependence of the coke formation on the reaction conditions is presented. According to the obtained data, the coke formation increases monotonically with the temperature rise in the interval of 673–973 K on both Ag and Cu catalysts (Fig. 1a). However, the quantity of the coke deposits on Cu is significantly higher then on Ag. This fact may be associated with the difference of the coke formation mechanisms on the surface of Ag and Cu catalysts.

Dependence of the coke formation on the variation of oxygen content in the reaction mixture has a more complicated character (Fig. 1b). Under the conditions of oxygen absence in the reaction mixture, the coke deposits are not formed on the Ag surface. On the Cu catalyst, the quantity of the coke deposits is also not so high (1.7 wt.%). According to previous work [8], EG is not converted into glyoxal on the clean Ag surface. Unlike Ag, the EG dehydro-
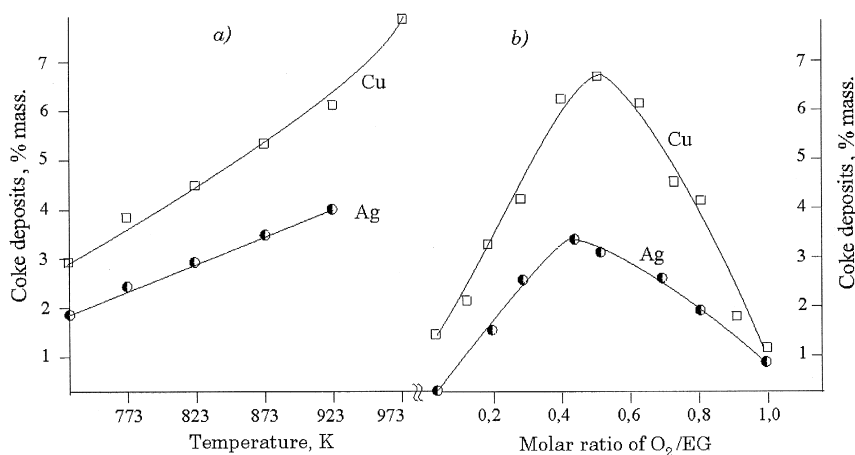
Fig. 1. The coke deposition on Ag and Cu catalysts depending on temperature (a) and O_2/EG ratio (b). Concentration of EG in water solution = 60 wt.%, molar ratio N_2/EG = 4, molar ratio of O_2/EG = 0.5 (a), temperature = 873 K (b).

genation into glyoxal on the clean Cu surface takes place [9], since the coke formation on the clean Cu surface becomes possible under the oxygen absence.

The increase of the carbon amount with the oxygen content from 0.1 to 0.5 (molar ratio of O_2/EG) is observed. This deposition is associated with the formation process of glyoxal (Fig. 1), which is the basic coke-forming agent.

The further increase of oxygen content in the reaction mixture higher than O_2/EG ~ 0.6 leads to a decrease of the coke deposits on the catalyst surface. At the O_2/EG ratio equal to 1.0, the steady state amount of carbon deposits is about 1 wt.%. Obviously, at such conditions, the destruction of coke deposits occurs under the effect of oxygen.

3.2. XPS data

In Figs. 2 and 3, C1s and O1s spectra of the silver and copper samples investigated before and after the action of the reaction mixture are presented. As seen from Fig.2, the silver sample before treatment contains two oxygen species with E_b(O1s) = 531.5 eV, 533.1 eV and carbon species, where the main component is characterized by E_b(C1s) = 284.4 eV. We attribute oxygen feature with E_b(O1s) = 531.5 to oxygen

located in distorted lattice of Ag surface [10]. Peak with E_b(O1s) = 533.1 eV can be related with the adsorbed water and carbon containing
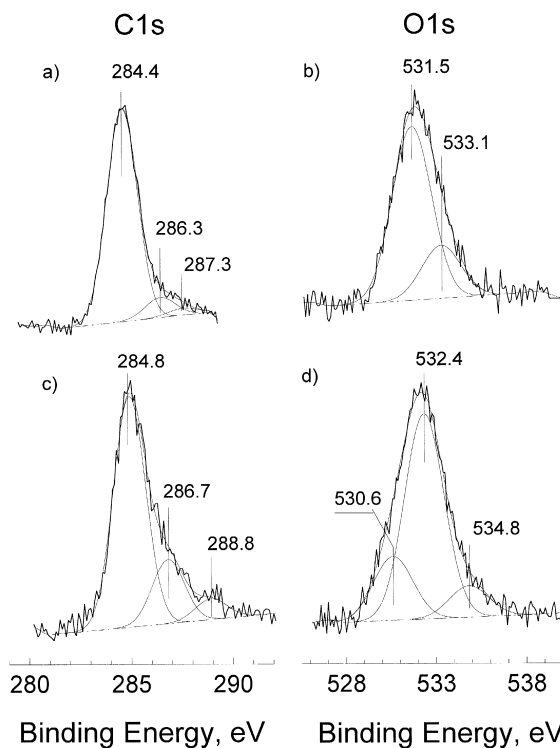

Fig. 2. C1s (curves a,c) and O1s (curves b,d) spectra obtained before (a,b) and after (c,d) the action of reaction mixture on silver catalyst at 773 K (O_2/EG = 1.0, EG/H_2O = 0.4). Spectra are presented without normalization.
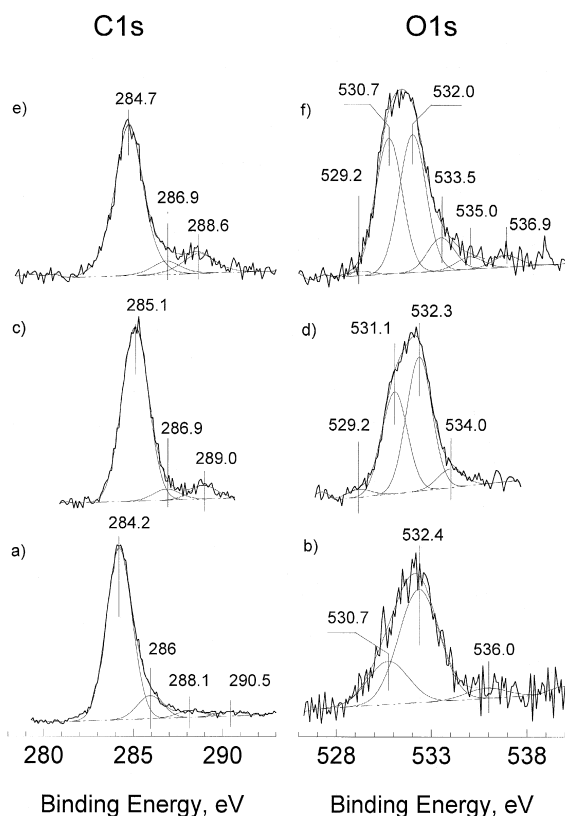
Fig. 3. C1s (curves a,c,e) and O1s (curves b,d,f) spectra obtained after the action of reaction mixture on copper catalyst at 600 K. (a,b) Reaction mixture with $O_2/EG = 0.0$, $EG/H_2O = 0.6$; (c,d) reaction mixture with $O_2/EG = 0.3$, $EG/H_2O = 0.4$; (e,f) reaction mixture with $O_2/EG = 1.0$, $EG/H_2O = 0.6$. Spectra are presented without normalization.

species [7,11]. Main carbon species are no doubt related with elementary amorphous carbon or small graphite particles. The treatment by the reaction mixture at 773 K leads to a substantial increase of carbon and oxygen. As a result of this catalytic treatment, the O/C ratio determined from XPS data is about 0.8.

Spectra b,c of Fig. 2 indicate new states of oxygen and carbon in comparison with initial sample. First of all, the positive shift of C1s line from 284.4 to 284.8 eV is observed. This shift is due to the incorporation of oxygen into carbon deposits. Also, there is a significant increase of oxygen containing species with $E_b(C1s) = 286.7$ eV, 288.8 eV [7,11]. In their groups, oxygen is determined by $E_b(O1s) =$

530.6 eV while the main component with $E_b(O1s) = 532.4$ eV is attributed to oxygen inside the carbon deposit structures. Thus, XPS spectra demonstrate that carbon deposits contain not only carbon, but they consist of oxycarbon structures.

XPS data obtained from Cu catalysts confirm the above conclusions concerning the oxycarbon deposits. In Fig. 3, the C1s and O1s spectra depending on the reaction mixture composition (variation of O_2/EG) are presented (see Fig. 1b for comparison). One can see from Fig. 3 that the treatment with EG only produces C1s spectrum (curve a) where the main peak with $E_b(C1s) = 284.2$ eV together with the satellite line (BE = 290.5) can be reliably associated with a graphite-like structures.

The variation of the reaction mixture composition leads to the essential changes in C1s spectra (Fig. 3, curves c,e). Firstly, the chemical shift of main component $0.5 \div 0.9$ eV is observed. Secondly, the position and intensity of the supplementary carbon lines in the oxygen containing groups are varied. Curve fitting of the O1s spectra allowed to distinguish two components with $E_b(O1s) = 530.7 \div 531.1$ eV and $532.0 \div 532.4$ eV, which correspond to oxygen in the Cu_2O surface layer [7,11] and in the carbon deposits, respectively. The peak with $E_b(O1s) = 529.2$ eV characterizes CuO oxide. Another low intense lines can be ascribed to oxygen atoms in the composition of carbon–oxygen groups in oxycarbon structure.

3.3. SEM data

The Ag, Cu samples represent the entire open-work object plaited from the threads with the diameter of 20–30 μm for Ag and 200–300 μm for Cu (Fig. 4a,b). Their threads form the emptiness (the diameter of 100–500 μm) in the Cu crystal. The thread surface consists of the uniformly distributed hemispheres with the diameter of 50–100 μm. Pores of different dimension in the various directions penetrate the crystal Cu threads. One can see from SEM
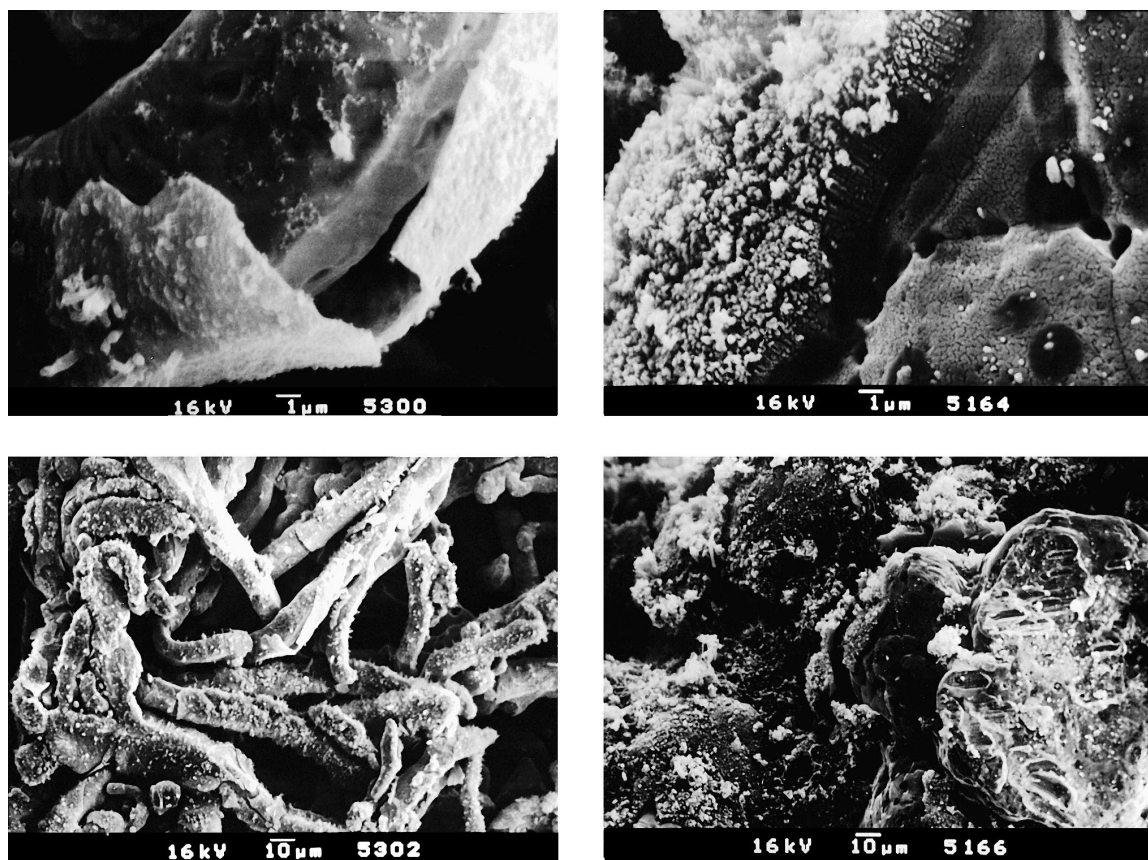
Fig. 4. SEM images of the surface of silver (a,c) and copper (b,d) catalysts after the action of reaction mixture. (a,c) $T = 898$ K, $O_2/EG = 1.0$, $EG/H_2O = 0.4$; (b,d) $T = 873$ K, $O_2/EG = 0.5$, $EG/H_2O = 0.6$.

pictures that the thread surface consists of alloyed metallic Cu crystallites 10 μm in size, and it forms the dendrite structure. The crystallites have the large quantity of defects. Thus, the Cu, Ag crystals of catalysts are characterized by the branched and connected pore structure that leads to both the formation of developed surface and the light access of reagents to the active centers of the catalyst surface.

In the result of the catalysis action, the surface of the Ag, Cu samples are covered by thick films of the carbon-containing deposits (Fig. 4c,d). The thickness of film on Ag catalyst is 0.5 μm while it is about 3 μm on the Cu catalyst surface. On the Ag surface, the deposited carbon film looks as a compact crust (Fig. 4c). One can see that this crust consists of carbon filaments tightly plaited. The morphol-

ogy of carbon deposits on Cu catalysts is different one. The deposited film on the Cu catalysts consists of carbon filaments tight-fitting to each other, which are perpendicular to the surface (Fig. 4d).
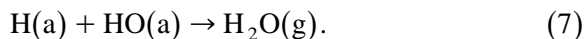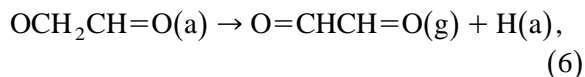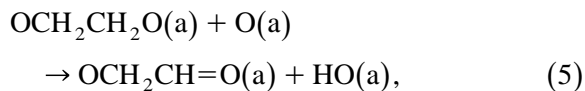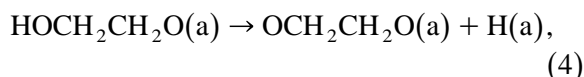
3.4. TGA data

The influence of oxygen content in the reaction mixture on the structure and composition of the carbon deposits on the Cu catalyst surface has been investigated by the thermal graphic analysis method. The narrow exothermic peaks with the $T_{max} \sim 723$ and 753 K correspond to the burning of the graphite-like carbon formed under the action of oxygen absence in the reaction mixture. The increase of the oxygen content in the reaction mixture up to the O_2/EG

molar ratio of 0.2 leads to the broadening of the exothermic peak with $T_{max} \sim 723$ K aside of the lower temperatures. Further increase of the oxygen content up to $O_2/EG \sim 0.4$–0.5 leads to the peak shift to low temperatures up to 653 K. TG analysis made for Ag samples after the treatment by reaction mixture ($O_2/EG = 0.2$–1.0) shows burning of the coke deposits at 623–723 K.

4. Discussion

The investigation of carbon deposits on Cu and Ag catalysts of selective oxidation of EG by complex of physicochemical methods reveals its complicated morphology and chemical composition. We would pay attention to two important features of carbon deposits. First feature is the formation of carbon filaments on both Ag and Cu surfaces. Second peculiarity is based on XPS data, which give the evidence of inclusion of large amount of oxygen inside the carbon deposits, so they are not pure carbon deposits but rather oxycarbon ones. SEM, XPS and TGA methods demonstrate that nature of these deposits is the same for both investigated types of catalysts. Then, it was determined that treatment of catalyst by only EG results in graphite-like (not oxycarbon) structures in the case of Cu catalysts. There is no effect in the case of Ag catalyst. Admission of oxygen to the reaction mixture results in significant acceleration of carbon deposition (Fig. 1b). We think that oxygen plays an activation role in the EG transformation process according to the following mechanism:

$$O_2 \rightarrow 2O(a), \tag{1}$$

$$HOCH_2CH_2OH(g) \rightarrow HOCH_2CH_2O(a), \tag{2}$$

$$HOCH_2CH_2OH(a) + O(a)$$
$$\rightarrow HOCH_2CH_2O(a) + HO(a), \tag{3}$$

$$HOCH_2CH_2O(a) \rightarrow OCH_2CH_2O(a) + H(a), \tag{4}$$

$$OCH_2CH_2O(a) + O(a)$$
$$\rightarrow OCH_2CH=O(a) + HO(a), \tag{5}$$

$$OCH_2CH=O(a) \rightarrow O=CHCH=O(g) + H(a), \tag{6}$$

$$H(a) + HO(a) \rightarrow H_2O(g). \tag{7}$$
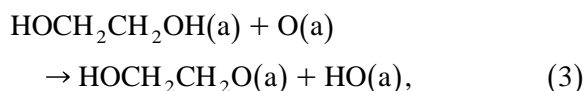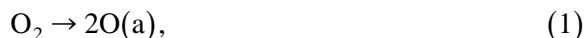
If we take into account that the coke formation correlates with the glyoxal rate formation, the presence of oxygen is necessary for both the major processes: EG oxidation into glyoxal and the secondary coke formation. Thus, the formation of the coke deposits is most likely determined with the formation of the oxidation products, mainly by glyoxal. As the composition of the carbon deposits depends on the variation of the reaction mixture, it is reasonably to propose that oxygen atoms from O_2 immediately participate in the formation of oxycarbon structures.

The growth of the oxycarbon structure occurs as filaments. The reaction mixture composition influences essentially on both the morphology and the chemical composition of the forming filaments. Under the conditions of the low oxygen content in the reaction mixture (the molar ratio of $O_2/EG = 0.2$), the formation of filaments and graphite-like structures takes place on the Cu surface. The graphite-like structures ($T_{max} \sim 753$ K in TGA) cover the unoxidized metal patches of the Cu surface while the oxycarbon filaments are formed on the oxidized surface area. Further increase of the oxygen content in the reaction mixture leads to both the total disappearance of the graphite-like deposits and the predominance of the oxycarbon deposit type ($T_{max} \approx 653$ K).

According to catalytic data, the decrease of the deposits amount on the catalyst surface as oxygen content increases up to $O_2/EG = 0.5$–0.8 is accompanied by the glyoxal selectivity growth. One may propose that efficient burning out leads to the increase of the active Cu surface that intensifies the glyoxal formation process. On the other hand, it is impossible to exclude that the oxycarbon layer is simply the source of an additional glyoxal at such conditions. On the

decomposition of such filament structure under the oxygen action, the glyoxal appearance in the reaction products is possible. This assumption is in agreement with data reported in Ref. [1]. The authors proposed that in the presence of oxygen-containing reaction mixtures the coke formation could not take place because of self-regeneration process only.

It is important to notice that the coke formation on a massive Ag surface was not observed during the methanol oxidation process into formaldehyde [4]. It seems to be one of the main differences between methanol oxidation and EG oxidation underlying an important role of glyoxal in mechanism of the coke deposition.

5. Conclusions

The copper and silver catalysts of EG oxidation to glyoxal have been investigated by complex of physical methods of the surface analysis. The data presented in this work show that two types of the carbon deposits, which accompany glyoxal synthesis, are formed. The first type of deposits is the graphite-like structures that can be formed on Cu surface at lean content of oxygen in the reaction mixture. Second type of deposits is the oxycarbon, which grows as filaments. Both morphology and the chemical composition of oxycarbon deposits depend strongly on the reaction mixture. Oxygen in the reaction mixture leads to the predominant formation of the oxycarbon filaments on the oxidized metal surface.

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