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Special Features of the State of Copper(II) Oxide and Its Electric Conductivity in Porous Glass

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Abstract—Controllable accumulation of copper(II) oxide in porous glass was carried out by repeated impregnation of the carrier by $Cu(NO_3)_2$ aqueous solutions with subsequent thermal decomposition of the salt. The results of measuring electric conductivity of a series of modified plates in combination with the data on the optical and X-ray electron spectroscopy make it possible to characterize two trends in the oxide distribution on a silica surface. In the case of its cyclic accumulation by small portions, a two-dimensional structure of monolayer filling the surface is presumably formed in a narrow range of CuO concentration, whereas the increase in the "step" of the accumulation gives rise to the formation and growth of island oxide particles.

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A wide set of unique materials, from dielectrics up to high-temperature superconductors, were obtained on the basis of transition metal oxides [1]. In the course of intensive development of chemistry and physics of nanosize functional elements and devices of electronics a problem arises of the directed synthesis and study of special properties of systems lacking a formed zone structure [1–5]. Of a basic interest are the specificity of exchange and transfer of electrons in the case of small number of structural units (10^{15}–10^{16} unit cm^{-2}) forming oxides of *d*-elements in the initial stage of filling the surface of dielectric carriers with these units. The determination of the nature of electric conductivity variation, which has an independent value, is intended to clear the problem of the form of existence and special features of behavior of oxides depending on the size of deposited particles.

The data on the spectroscopic study of copper(II) oxide and its electric conductivity measured in the course of its gradual accumulation on a porous glass surface are presented and compared in the present work. The glass was synthesized according to the procedure [5] in the form of thin (1 mm) plates, membranes penetrated by channels with an effective radius of ~70 nm. A significant volume of the pore space (V_p 0.34 $cm^3\ g^{-1}$) and the specific surface area (S_{sp} 22 $m^2\ g^{-1}$) of glass plates provide a possibility for reliable weight determination of the copper oxide content in them, which makes much easier its planned accumulation and determination of the nature of its distribution in the carrier.

Copper oxide was deposited by impregnating glass with copper(II) nitrate solutions, subsequent removal of water, and thermal decomposition of the salt. Gradual (step-by-step) accumulation of CuO mass was achieved by multiple repetition of impregnation-decomposition operations. Molar amount of $Cu(NO_3)_2$ (and, hence, of copper oxide) added per 1 g of glass in one "cycle" linearly depends on the concentration of the impregnating solution *c* and the volume of carrier pores V_p.

$$Q = cV_p\gamma. \quad (1)$$

The value of $\gamma \le 1$ reflects a degree of filling pore space with a solution. The calculation of *Q* in the case of ideal filling pores with a 0.15 M solution gives the value of 0.51×10^{-4} mol g^{-1}, whereas averaging of the experimental results gives the value of $(0.41\pm0.05)\times10^{-4}$ mol g^{-1}. The corresponding value of $\gamma \sim 0.8$ points in the first approximation to inaccessibility of a part of pores for the impregnating solution. It is necessary to note, however, that the assumed factor does not manifest itself in filling pores with water, as this is the way which was used to determine their volume V_p 0.34 $cm^3\ g^{-1}$. A possible reason for γ decrease on the impregnation of the carrier by a

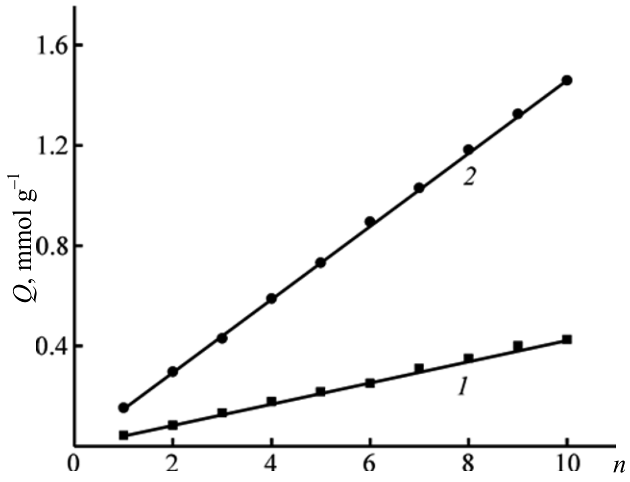

Fig. 1. Dependence of the amount of copper(II) oxide (*Q*) in porous glass on the number of accumulating cycles (*n*) using impregnating $Cu(NO_3)_2$ solutions, *c* (*1*) 0.15 and (*2*) 0.5 M.

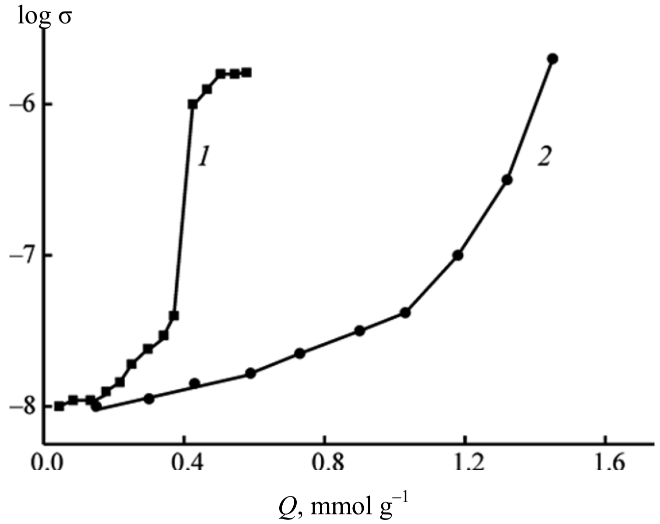

Fig. 2. Change in electric conductivity of porous glass as copper oxide is accumulated in it in (*1*) "small step" and (*2*) "long step" modes.

solution is the presence of a water layer with a lowered dissolving ability on the silica surface [6–8]. The increase in the impregnating solution concentration up to 0.5 M leads to reliably determinable increase in the average value of the coefficient up to the value $\gamma \sim 0.9$ as a result of a partial destruction of a near-wall water layer by an electrolyte [6–8].

Cyclic repetition of impregnation-thermolysis operations with the use of $Cu(NO_3)_2$ solutions (*c* 0.15 and 0.5 M) leads to an increase in the amount of copper oxide in glass according to equation (1) at γ 0.8 and 0.9. "Step-by-step" growths in *Q* in the two cases differ approximately from each other by a factor of 3.5 (Fig. 1). Retention of linear dependence in the case of the oxide accumulation points to insignificance of decrease in the carrier pore volume caused by it. In fact, the theoretical limit of CuO amount defined by the volume of pores in glass V_p 0.34 $cm^3\ g^{-1}$, in view of the reference value 6.45 g cm^{-3} of oxide density [9], is 2.19 g g^{-1}. Thus, even the maximal value of *Q* reached in our experiments (0.07 g g^{-1}) corresponds to filling only ~3% of pore space with the oxide.

Results of measuring electric conductivity σ provide essential information on the character of filling surface of porous glass by copper oxide. In the case of dry initial glass the value $\sigma < 10^{-9}\ \Omega^{-1}\ cm^{-1}$ appears outside the measuring capability. The application of minute oxide portions provides the occurrence of primary channels of through conductivity, thus the shape of the dependence log σ(*Q*) reflecting oxide accumulation "by small steps" (Fig. 2) points to special features of its structure formation. A gradual increase in the number of fixed polyhedra of copper(II) oxide [and (or) their low-branched ensembles, clusters] in the initial portion of the curve is accompanied by a smooth increase in conductivity. However a slight increase in the amount of oxide up to $Q > 0.37$ mmol g^{-1} causes a distinctly expressed jump of σ (Fig. 2). The narrow range of process occurring recorded in this way characterizes a high probability of the presumable formation of a two-dimensional structure of the conducting oxide layer, which is close to a monolayer structure. The estimation of the average number of $[CuO_6]$ polyhedra on an elementary area under condition of their planar distribution (2) in view of the known value of a specific surface area of the carrier can support this conclusion.

$$n = QN/S_{sp}. \qquad (2)$$

Here *N* is Avogadro number.

In such an approximation, when *Q* values of 0.37 and 0.42 mmol g^{-1} limiting the range of process occurring (Fig. 2) are reached, one structural $[CuO_6]$ unit falls on an area of 10 Å^2. Not exaggerating the importance of this result, we have to point out its correspondence to the possibility of dense stacking of polyhedra on the surface. Thus, there is a reason to believe that the completion of the formation of copper(II) oxide monolayer in the range *Q* 0.37–0.42 mmol g^{-1} is accompanied by an increase in collective electronic

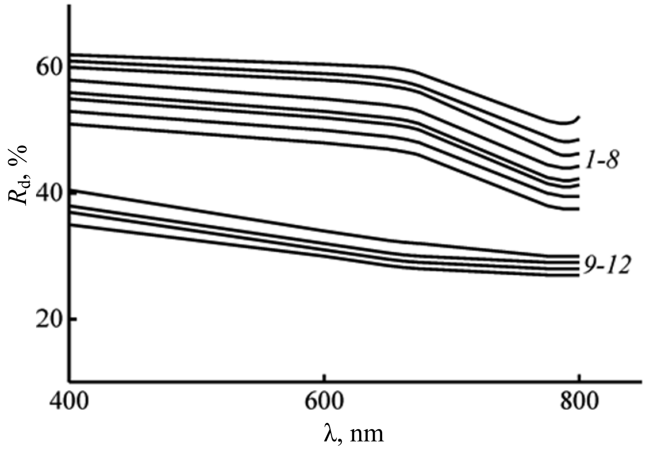

Fig. 3. Spectral distribution of diffuse reflection coefficients of a series of porous glasses modified by copper(II) oxide in the "small step" mode. Figures designate the number of carried out cycles of oxide accumulating.

interactions and, hence, by a sharp increase in conductivity. A possibility of the aggregation leading to the formation of an island (three-dimensional) structure can be excluded in this case, as the islands in the realizable range of low oxide contents in glass inevitably would be separated from each other, which contradicts the well pronounced step in the log σ(Q) dependence.

The monolayer of copper(II)-oxide polyhedra fixed on the walls of glass through channels in the course of accumulating oxide by "small steps" represents a surface analog of copper silicate. The formation of numerous "anchor" Si–O–Cu bonds with a carrier as well as Cu–O–Cu bridges during the coupling of polyhedra in a tangential direction appears energetically preferable in comparison with the normal (in relation to the surface) growth direction. In this connection it seems quite probable that the action of the specified structural features in certain conditions can appear insufficient to "retain" copper oxide aggregation into three-dimensional particles. The increase in the amount of the salt entered in the pore volume in the impregnation stage (increase in the oxide weight during its decomposition) can lead to the primary formation of island structures.

To check this assumption, we increased the concentration of impregnating $Cu(NO_3)_2$ solution up to 0.5 M. The transition to "long steps" (Fig. 1) essentially changes the shape of the dependence log σ(Q) (Fig. 2). In this case the initial curve part of slow increase in conductivity is strongly stretched, and the region of the process appears wide and poorly expressed. As a surface of the carrier is filled, the lowered conductivity of capsulated oxide manifests itself clearly, and to reach values of $\sigma \sim 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$ it is necessary to add its amount three times as much as is required in the "small step" procedure. Obviously, the increase in the amount of oxide applied at a time leads to a significant increase in its "volume" weight, i.e. to a presumable formation and the subsequent growth of three-dimensional particles. The essential restriction on the possibility of the formation of contacts between the latter appears up to the copper oxide concentration noticeably greater than the value corresponding to a monolayer filling of the surface of porous glass channels with the oxide.

Changes in the diffuse reflection spectra accompanying the copper oxide accumulation in the carrier (Fig. 3) are indicative. After the first cycle of its application in "small steps" a weak absorption band with a maximum about 780 nm arises, which is characteristic of pseudooctahedral oxygen surrounding of copper(II) [10]. A gradual increase in the oxide weight is accompanied by widening the band and by gradual increase in its intensity, and when the CuO amount of Q 0.37 mmol g^{-1} is reached (the ninth step of application, Fig. 3), its significant strengthening up to the continuous absorption covering the whole visible area is observed.

The character of electric conductivity variation (Fig. 2) suggests that the evolution of optical spectra at gradual CuO accumulation reflects progressing coupling of $3d$-electrons of copper(II) atoms and their spontaneous "collectivization" in the monolayer region. Unlike it, the appearance and growth of oxide islands at the "long step" accumulation (c 0.5 M) is seen from the primary recording of a wide structureless band and subsequent monotonous absorption strengthening. It is necessary to note that the observed widening, the absence of the band resolution, and a high intensity of the spectra are only partly connected with the specificity of recording in reflected light and with the quality of a spectrometer. A principal cause of the specified features seems to be the high degree of the $3d_\pi$–$2p_\pi$ coupling along the Cu–O–Cu bonds and the solid phase electron-vibration interactions; furthermore, the possibility of the delocalization of $3d$-electrons over Cu···Cu bonds is not excluded.

Dimensional features of the variation of copper oxide electronic structure during step-by-step increase in its amount in glass are also reflected in the X-ray electron spectra. The most intensive bands of electron

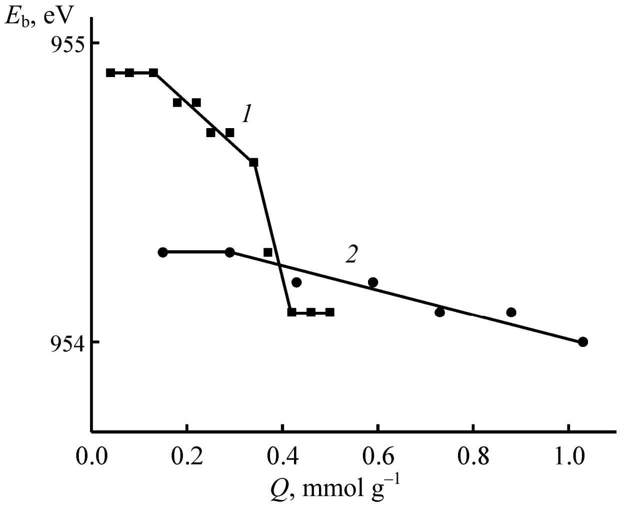

Fig. 4. Dependence of the position of maxima of bands of copper $2p_{1/2}$ state ionization on the amount of CuO oxide entered into porous glass in modes of (*1*) small steps and (*2*) long steps.

detachment from filled copper shells are observed in the case of its internal $2p$-states; the increase in the corresponding values of bond energy E_b is regarded as a result of increasing positive charge on the metal atom [11]. Spectra of all synthesized samples contain two bands corresponding to the ionization of $2p_{1/2}$ and $2p_{3/2}$ states of copper with a distance of 20 eV between the maxima.

Changes in the bond energy E_b ($2p_{1/2}$) with repetition of cycles of the oxide synthesis in the modes of small and long steps are shown in Fig. 4. In the first case high values of E_b ($2p_{1/2}$) are recorded, which in general corresponds to a substantial increase in a positive effective charge on copper atoms. The increase in the amount of CuO is accompanied first by an insignificant displacement of maxima of the counting to a side of smaller energies, however on reaching Q 0.37–0.42 mmol g^{-1} a clear decrease in E_b values is observed. A probable reason of this dependence is the electron-acceptor power of the silica carrier [12, 13], which is most noticeable in the initial section of the oxide accumulation. An appreciable weakening of the polarizing action of a glass surface is reached upon strengthening collective interactions in the narrow range of CuO concentration, where a monolayer is formed. It results in a decrease in a positive charge on copper atoms and hence in E_b values. Island structures, formed by “long step” accumulation of the oxide, experience the electron-acceptor action of the surface to a much smaller degree. This is responsible for rather low E_b values recorded in the spectra and for their weak decrease with increasing CuO mass (Fig. 4).

EXPERIMENTAL

The degree of copper oxidation in the composition of deposited oxide was determined by the characteristic band of detachment of internal $2p$-electrons in the X-ray electron spectra recorded on an ES-2401 spectrometer (MgK_α exciting radiation with an energy of 1253.6 eV). Optical spectra in visible region were taken in the diffuse reflection mode on an SF-16 instrument.

Porous glass plates were impregnated with 0.15 and 0.5 M copper(II) nitrate solutions. The duration of the impregnation was 30 min, which ensured the maximal filling of pore space with the solution; the excess of the solution was removed from the external surface of plates by compressed air. Dehydration and subsequent thermal decomposition of the salt in pore space were carried out in the mode of linear temperature rise from room temperature up to 400°C at a rate of 5 ged min^{-1} with a subsequent exposure to 400°C for 1 h. Measurements of weight losses during the thermolysis reliably testified to the formation of CuO oxide on the silica surface. The gradual accumulation of the oxide mass in a glass was provided by a multiple repetition of impregnation-decomposition operations.

Measurement of electric conductivity of modified porous glasses. To decrease the contact resistance we covered plates under study with a layer (thickness of ~1 mm) of graphite powder with the average size of particles 10–20 μm. Then samples were placed between clamping (with a constant force of 200 g cm^{-2}) flat polished graphite electrodes with copper leads entered in them. Electric resistance was measured at the frequency of 1 kHz using an E7−11 universal measuring instrument (in some cases an R-5058 bridge); recorded R values were converted to the values of specific conductivity (σ) taking into account the real sizes of samples (3).

$$\sigma(\Omega^{-1}\ \mathrm{cm}^{-1}) = l/RS. \quad (3)$$

Here l is thickness of a glass plate (cm), S is its area (cm^2).

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