State of the Cu electrode surface studied by X-ray photoelectron and Auger spectroscopies

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Annealing of the copper plate in flame was found (by XPS and X-ray Auger spectroscopy) to enrich the surface copper layers in oxygen in the forms of Cu_2O and adsorbed oxygen. The changes in the surface layers of the copper cathode due to annealing can be the origin of the earlier found enhancement of its activity in the electrocatalytic hydrogenation of citral and *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines (R = Me, All, Ph). This method of the copper electrode pre-treatment provides its long durability, an insignificant decrease in the electrocatalytic activity in time, and the reproducibility of the electrocatalytic hydrogenation of unsaturated organic compounds.

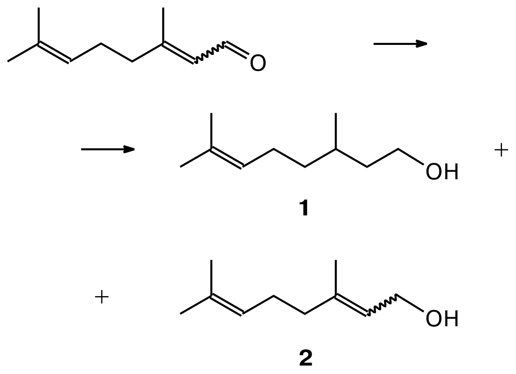
Key words: copper cathode, annealing, X-ray photoelectron spectroscopy, X-ray Auger electron spectroscopy, surface, electrocatalytic hydrogenation, electrocatalytic activity.

The nature of the cathode material and the state of its surface are known[1,2] to exert a substantial effect on the mechanism, direction, and efficiency of electrocatalytic hydrogenation (ECH). Therefore, the pre-treatment of the electrode surface is very important. Traditional methods of electrode activation are[3] the mechanical or chemical treatment, application of an asymmetric alternating current (cathode-anodic polarization), and addition of metal salts to an electrolysis solution.

Metallic copper, whose atoms have no vacant d-orbitals in the ground state, exhibits[4] the catalytic activity in hydrogenation only after its activation due to the appearance of excited valent states. As a rule, the electrocatalytic activity of copper is substantially enhanced when used in combination with other metals. For example, iron and copper are close in activity in hydrogen evolution, and the implantation of iron with copper ions decreases the hydrogen overvoltage to values lower than those on both individual metals.[5] The Cu, CuCo, CuSn, CuZn, and Cu_3Sn skeleton catalysts and electrolytic powders prepared by the combined precipitation of Cu with Ni and Cu with Zn were successfully used[6] in the electrochemical reduction of the acetylene bond of dimethylethynylcarbinol. Acetylene compounds were reduced[3] to ethylene compounds on the copper and copper-silver electrodes, and the copper cathode was recommended to preliminarily anneal in the burner flame to develop the active surface.

We have shown earlier[7] that the yield and ratio of compounds **1** and **2** in the ECH of citral in 40% aqueous DMF in the presence of 0.1 *M* KCl (Scheme 1) are changed substantially depending on the method of pre-treatment of the massive Cu cathode. The most efficient method of Cu cathode preparation is annealing in the gas burner flame followed by the removal of copper oxide with dilute HNO_3 (overall yield of products **1** and **2** was 86%, molar ratio **1** : **2** was 2.3). The optimization of ECH conditions (composition of an electrolysis solution) provided[8] citronellol **1** in a rather high yield at the overall yield of products ~90% and **1** : **2** ratio of 4.8.

Scheme 1



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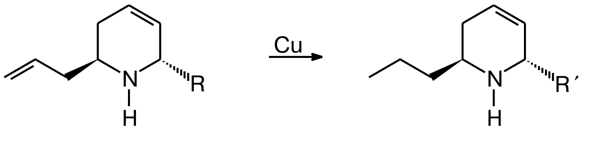
Such a pre-treatment of the Cu cathode is also efficient in the ECH of *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines **3a—c** (R = Me, All, Ph). It has been shown[9] that only allyl substituents can be selectively hydrogenated on the annealed Cu electrode to give the corresponding piperideines **4a—c** (Scheme 2).

Scheme 2



3a—c **4a—c**

R = Me (**3a**), All (**3b**), Ph (**3c**) R′ = Me (**4a**), Pr (**4b**), Ph (**4c**)

We can propose that annealing of the Cu electrode in the burner flame followed by treatment with dilute HNO_3 changes the state of its surface, increasing noticeably the catalytic activity in the ECH of unsaturated organic compounds. It seems interesting to study the cathode surface by physicochemical methods after its annealing. One of the most popular and efficient methods for analysis of the electrode surface (massive metals) is Auger spectroscopy.[1] In this work we studied by XPS and X-ray Auger electron spectroscopy (XAES) the state of the surfaces of the non-annealed, annealed, and previously used in ECH copper cathodes.

Experimental

Copper (special purity grade, 11-4 TsMTU-03-9-69 trade mark, cathode plates obtained by electrolytic copper fining) with the content of the main substance $\geq$99.995% and an electrotechnical copper (M-0 trade mark) wire with the $\geq$99.95% purity and oxygen content $\leq 3.5 \cdot 10^{-3}$% were used as the cathode and reference samples.

The following cathodes were used for the ECH of citral[7,8] and *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines (R = Me, All, Ph)[9]: a cylindrical copper plate 0.5 mm thick with the 95-cm^2 working surface area (S_w) or a spiral copper wire (d = 2.4 mm) with $S_w \approx 74$ cm^2. Before each electrolysis, the copper cathode was stored in the oxidation zone of the blast burner flame for ~3 min. After cooling in air, copper oxide formed on the surface was removed with dilute HNO_3 (1 : 10), and the electrode was washed with water. After this procedure, the copper surface became red, uniform, and slightly rough.

The X-ray photoelectronic Cu2p$_{3/2}$ and Auger electronic CuL$_3$VV spectra were detected at −50 °C on a Kratos XSAM-800 spectrometer using Mg-Kα radiation (1253.6 eV). The C1s line with the binding energy (E_b) 285.0 eV chosen as standard corresponds to adsorbed hydrocarbons of the oil of a diffusion vacuum pump. The relative concentrations of Cu^0 and Cu$^+$ in the surface layers with the thickness $\leq$30 Å analyzed by XPS were estimated by the ratio of peak heights in the CuL$_3$VV Auger spectra with the kinetic energy (E_{kin}) 918 and 916 eV, respectively, taking into account the contribution of the CuL$_3$M$_{45}$M$_{45}$ Auger satellite to the Cu^0 peak, whose position coincides with the main transition of Cu$^+$. The surface was bombarded with high-energy Ar$^+$ ions (2.5 keV) *in situ* in the spectrometer chamber at an argon pressure of $4 \cdot 10^{-7}$ Torr.

Three samples of the copper plate 6×13 mm^2 in size were comparatively analysed by XPS and XAES: a new plate with a thickness of 0.2 mm (**A**), the same plate after fivefold standard treatment by annealing (**B**); a fragment of the plate used as a cathode in ECH experiments for two years and multiply annealed (**C**). All three samples **A—C** were washed with dilute HNO_3, rinsed with water, and placed in ethanol under argon. After spectra recording, samples **A** and **B** were left in air without a solvent for 1 day and then analyzed repeatedly.

The samples were bombarded with the high-energy Ar$^+$ ions for 3, 5, and 15 min, detecting the Cu2p$_{3/2}$ and CuL$_3$VV lines after each stage of bombardment.

Results and Discussion

The state of copper (Cu^0, Cu$^+$, and Cu^{2+}) in the X-ray photoelectronic (XPS) spectra is usually identified by comparison of the XPS spectra of Cu2p$_{3/2}$ electrons and X-ray Auger electronic spectra of the CuL$_3$VV transitions. The shift of the core level of Cu2p$_{3/2}$ toward higher binding energies and the occurrence of the "shake-up" satellite, whose E_b is higher by ~7.8 eV, in the XPS spectrum indicate the presence of the Cu^{2+} ion. The Cu$^+$ and Cu^0 copper states are characterized by the same binding energies of the Cu2p$_{3/2}$ electrons in the XPS spectra and can be distinguished only by the line shape in the X-ray-excited Auger electronic spectra.

The XPS spectra of Cu2p$_{3/2}$ electrons (Fig. 1) of all three samples stored in ethanol under argon contain peaks with $E_b \approx 932.5$ eV corresponding to Cu^0 and Cu$^+$ and do not contain peaks of the satellite with $E_b \approx 940$ eV, indicating that Cu^{2+} is absent from their surface. Therefore, CuO formed due to annealing (samples **B** and **C**) or by the air oxygen (sample **A**) is removed completely from the copper plate surface with dilute HNO_3. This treatment has no effect on the composition of the surface and near-surface layers (Table 1). The Auger electronic spectra of these samples (Fig. 2) indicate that the surface layers of the samples contain copper in two states: Cu$^+$ and Cu^0. The calculation of the relative content of each species shows that the surface of non-annealed sample **A** contains a smaller amount of lower copper oxide (27% of the total amount) than samples **B** and **C** (38 and 45%, respectively, see Table 1). Thus, annealing increases the amount of lower copper oxide in the surface layers. Unlike sample **A**, the surface layers of samples **B** and **C** contain, along with oxygen in the form of Cu_2O ($E_b \approx 532$ eV), another oxygen species with $E_b \approx 530.4$—530.9 eV, whose fraction is ~50%. The XPS peak of oxygen with E_b of the 1s electrons

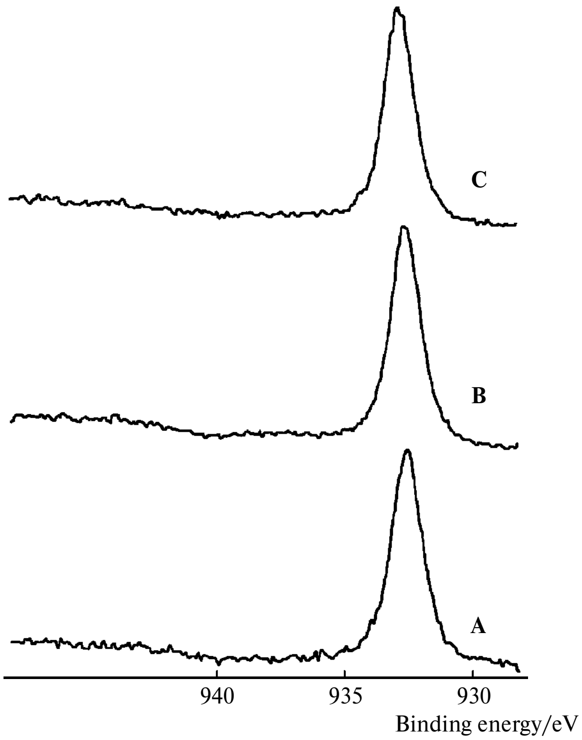


Fig. 1. XPS spectra of Cu2p$_{3/2}$: a new copper plate (**A**), a copper plate annealed 5 times in the burner flame (**B**), and a fragment of the multiply annealed cathodic plate used in ECH (**C**).

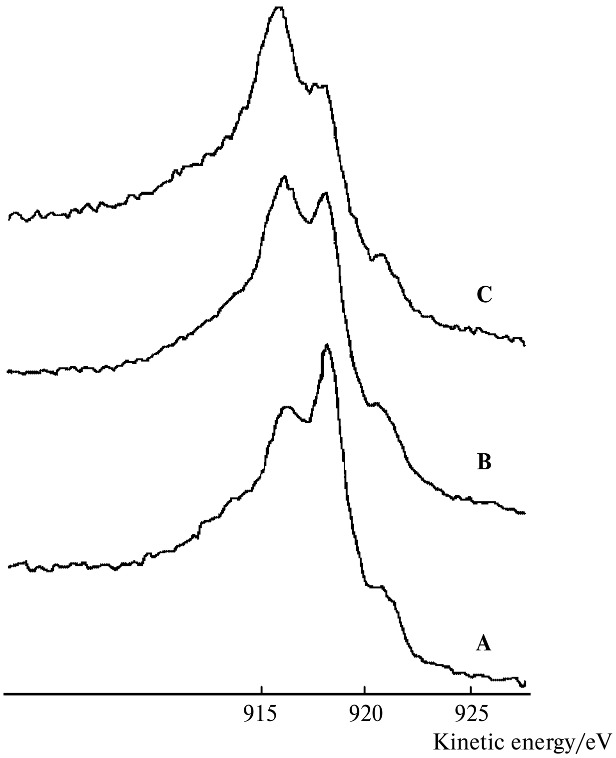


Fig. 2. X-ray Auger electronic spectra of CuL$_3$VV: a new copper plate (**A**), a copper plate annealed 5 times in the burner flame (**B**), and a fragment of the multiply annealed cathodic plate used in ECH (**C**).

equal to 530.4—530.9 eV characterizes non-corrosion chemisorption and can be assigned[10] to atomic adsorbed oxygen or oxygen inserted in the copper lattice. The latter appears, likely, due to annealing in air. A similar fact of oxygen penetration inside the crystalline lattice of the

Table 1. Surface composition and state of the copper electrode according to the X-ray electron spectroscopic data

Sample	Conditions of storage	Duration of Ar$^+$ bombardment/min	E_b/eV		E_{kin}(CuL$_3$VV)/eV			Content (%)		
			Cu2p$_{3/2}$	O1s	1	2	3	Cu^{2+}	Cu$^+$	Cu^0
A	EtOH, Ar	—	932.5	532.2	—	916.3	918.1	—	27.0	73.0
	In air	—	933.1	532.2	914.8	916.0	Shoulder	100	—	—
		3	933.0	532.7	–	916.2	918.0	–	38.0	62.0
		5	933.0	932.8	–	916.1	918.1	–	29.0	71.0
		15	933.0	532.9	–	916.1	918.1	–	16.0	84.0
B	EtOH, Ar	–	932.5	530.9 (45%), 532.6 (55%)	–	916.1	918.1	–	38.0	62.0
	In air	–	933.4	532.2	914.8	916.2	Shoulder	100	–	–
		3	932.7	532.7	–	916.2	918.4	–	19.0	81.0
		5	932.7	532.7	–	916.1	918.3	–	15.0	85.0
		15	932.7	532.5	–	916.1	918.2	–	8.0	92.0
C	EtOH, Ar	–	932.7	530.8 (45%), 532.5 (55%)	–	916.2	918.0	–	44.0	56.0
		3	932.7	530.4 (40%), 532.3 (60%)	–	916.2	918.2	–	24.0	76.0
		5	932.7	530.6 (55%), 532.8 (45%)	–	916.2	918.2	–	20.0	80.0
		15	932.8	530.6 (60%), 532.6 (40%)	–	916.2	918.1	–	17.0	83.0

smooth plate to form dissolved oxygen during the oxygen-hydrogen treatment is considered[2] to be established rather reliably.

Storage of samples **A** and **B** in air results in the 100% oxidation of the surface copper atoms to the state of Cu^{2+}, which is indicated by the appearance of a peak at 914.8 eV in the Auger spectra and a satellite in the XPS $Cu2p_{3/2}$ spectra (see Table 1). This change in the surface state under the air oxygen action indicates that the cathode should be used in the electrochemical process immediately after pre-treatment or its necessary storage in a solvent under argon.

The data on a change in the copper content in different valent states, depending on the duration of ion etching of the surface of the samples studied, are presented in Fig. 3. During the bombardment of the surface with the Ar^+ ion, the concentration of copper oxides can decrease due to both the removal of the surface layers and ion-induced reduction. Under our conditions, the 5-min Ar^+ ion bombardment removes the surface layer with a thickness of 100—300 Å.

It is seen from the data in Table 1 and Fig. 3 that the surface of samples **A** and **B** is completely liberated from copper(II) oxide after the first 3 min of Ar^+ ion bombardment. A considerable portion of Cu_2O is also removed from the surface layers in 15 min. The results of ion bombardment of non-annealed sample **A** indicate a considerable amount of Cu_2O in the surface and near-surface layers. It is most likely that oxygen penetrates into the near-surface layers also at room temperature when the copper plate is stored in air for a long time. It was unexpected that the Cu_2O content in the deeper near-surface layers of sample **B** annealed for five times is halved compared to that in sample **A**, which was not annealed in the burner flame.

It seems that the flame annealing of the copper plate results in the enrichment of the surface layer in oxygen in the forms of Cu_2O and the adsorbed and inserted oxygen. At the same time, the decrease in the Cu_2O concentration in deeper layers in annealed sample **B** indicates, probably, structural changes in the metal due to annealing.

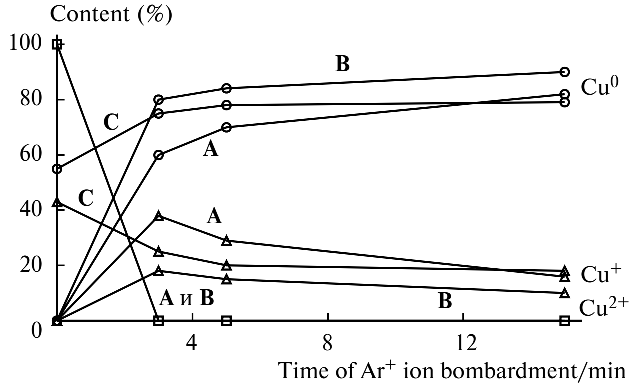


Fig. 3. Depth of the profile of the copper oxide samples: a new copper plate (**A**), a copper plate annealed 5 times in the burner flame (**B**), and a fragment of the multiply annealed cathodic plate used in ECH (**C**).

The influence of the structure and state of the metallic catalyst surface on its adsorption and electrocatalytic properties were discussed in detail.[1,5] As a rule, the thermal treatment of electrodes results[2] in surface smoothening and formation of more ordered and stable structures. Based on the data on the physicochemical properties of copper, we assumed[7] that the enhancement of the catalytic activity of the annealed Cu cathode is related to recrystallization processes.

We measured the temperatures of the external and internal surfaces of the cylindrical Cu electrode by a chromel—alumel thermocouple during its annealing. After 1 min, the whole surface of the Cu electrode becomes uniformly red, and its temperature reaches 340—360 °C. During the next 2 min, the color and texture of the surface remain unchanged and the temperature does not increase. According to Bochvar´s rule,[11] the temperature of recrystallization of copper is ~370 °C. It has also been shown[11] that at this temperature in the pure deformed copper the sizes of crystallite grains increase rapidly from $2 \cdot 10^{-5}$ to $2.5 \cdot 10^{-4}$ cm in the initial short time interval, and their final size is independent of the degree of deformation of the starting sample.

Thus, two parallel processes occur, most likely, during annealing: formation of additional defects of the crystalline lattice due to inserted oxygen and Cu_2O and recrystallization — enlargement of crystal grains, *i.e.*, formation of smooth regions. The removal of inserted oxygen under the ECH conditions should result in the appearance of new adsorption sites. Thus, two types of active sites with different structures are formed, probably, on the surface of the Cu cathode.

A comparison of the adsorption and kinetic data for olefin electroreduction on smooth platinum suggested[12] that the atomic hydrogen and the molecules of organic substances are adsorbed on different adsorption sites. The interaction of olefin with the atomic hydrogen occurs at the boundaries of these regions and determines the rate of the whole process.

A comparative study of different classes of organic compounds showed[13] that the tendency to π-adsorption is a general regularity. The adsorption rate of organic compounds (*e.g.*, benzene and phenylacetic acid) on smooth platinum is higher than that on the platinated surface,[14] and a special arrangement of the adsorption sites and their structural correspondence to the adsorbed molecules are necessary for the efficient ECH of complex organic compounds.

When the annealed Cu cathode is used, the potential of hydrogen evolution from an aqueous-organic medium decreases (by 200—300 mV), and defects of the crystalline copper lattice can be sites of adsorption of hydrogen evolved on the cathode. It is likely that the formation of smooth regions on the annealed Cu cathode surface due to recrystallization favors the π-adsorption of large organic molecules. Therefore, no competition for the adsorption site should appear between the organic molecule and atomic hydrogen during ECH, which can finally be a reason for the sharp increase in the electrocatalytic activity of the Cu electrode after annealing.

When the massive metal is an electrode-catalyst, its biography is very significant, *i.e.*, method of preparation (forging, molding, punching, *etc.*[3]), because structures with different concentrations of defects of the crystalline lattice can be formed. In the case of the ECH of citral, we used[7] the cylindrical Cu cathode (refined copper) and also the cathode-spiral of a copper wire. The cathode-spiral was 5 times subjected to the standard treatment. Nevertheless, the yields of products and ratio of citronellol **1** and isomeric nerol and geraniol **2** were similar to those with the annealed cylindrical Cu cathode. Therefore, the biographic defects of the metal generated during preparation are eliminated during annealing, and the electrocatalytic properties of copper are standardized.

After the prolonged (for two years) work with the cylindrical Cu cathode we found some decrease in its efficiency in the ECH of citral, although the potential of hydrogen evolution shifted toward positive values. The surface of the Cu cathode became noticeably darker and more friable. The sample of this cathode (**C**) was studied by XPS and XAES.

As can be seen from the data in Table 1, the Cu_2O content in the near-surface layer of sample **C** is higher than that in sample **B** but is lower than that in sample **A**. However, the fraction of dissolved (inserted) oxygen with $E_b \approx 530.4$—530.9 eV in sample **C** is ~50% and does not decrease despite a considerable decrease in the total amount of oxygen present in the examined surface layers. It is most likely that the structure ordering decreases and the concentration of defects of the crystalline lattice increases due to the prolonged use of the multiply annealed Cu cathode in ECH. It is known[15] that the cations of the supporting electrolyte (alkaline metals) are inevitably incorporated into the cathode during electrolysis. It was also shown[16] that the Cl^- anions are adsorbed and included into the crystalline lattice of metallic copper as evidenced by the characteristic coloration of the flame during annealing. The adsorbed organic compounds and chlorine are removed from the cathode during annealing. However, the concentration of defects of the crystalline lattice increases, that is, the defects are accumulated during multiple annealing.

The thorough mechanical purification of the cylindrical Cu cathode surface to gain the lustrous surface followed by annealing (3—5 times) resulted in the complete recovery of its catalytic activity.

A high reproducibility of the EHC results should be mentioned when the described method of electrode preparation is used. Moreover, special experiments on the ECH of citral showed that this electrode can be used in prolonged electrolysis: we carried out four experiments for 2 days without the intermediate treatment of the cathode. The efficiency of the annealed Cu cathode decreased insignificantly: in the fourth run the total yield of products **1** and **2** is only by 5% lower than that in the first entry. The ratio of products **1** and **2** also slightly decreased, and the time necessary for the complete consumption of the starting citral increased by ~1.5 times. By contrast, it is known[3] that the reducing activity of the Ni cathode during cyanamide electroreduction is halved already after 10 min of electrolysis. The fast loss of the electrocatalytic activity is especially characteristic of electrodes with the sponged or electrodeposited surface layers.

Thus, the combination of published data and results of studying the Cu cathode surface by the XPS and XAES methods makes it possible to assert that the enrichment of the surface copper layers in oxygen in the form of Cu_2O and atomic adsorbed oxygen and structural changes by the elevated temperature result in an increase in the electrocatalytic activity of the Cu electrode during ECH. Annealing in the burner flame of the Cu cathode is a fast and convenient method providing well reproducible results for the preparation of the electrode for ECH.

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