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Structure and Catalytic Properties of a Cu²⁺-Containing Hydrogel of Zirconium Dioxide

E. G. Kovaleva*, L. S. Molochnikov*, V. G. Kharchuk, O. V. Kuznetsova**,
A. B. Shishmakov**, M. Yu. Yanchenko***, L. Yu. Buldakova***, I. N. Zhdanov*,
Yu. V. Mikushina**, and L. A. Petrov****

* Ural State Forestry Engineering University, Yekaterinburg, Russia
** Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, Yekaterinburg, Russia
*** Institute of Solid-State Chemistry, Ural Division, Russian Academy of Sciences, Yekaterinburg, 620219 Russia
Received July 4, 2003

Abstract—The distribution of Cu^{2+} ions in ZrO_2 and sulfated ZrO_2 hydrogel phases was studied by EPR spectroscopy and voltammetry. The formation of the following three types of copper structures was observed: mononuclear Cu^{2+} complexes (**A**), magnetic associates (**B**), and Cu^{2+} compounds (**C**) that gave no EPR signals under the conditions used in the spectroscopic measurements. The specific catalytic activity of various Cu^{2+} compounds in the liquid-phase reaction of 2,3,5-trimethyl-1,4-hydroquinone oxidation was determined. The copper complexes **C** were found to exhibit the highest catalytic activity.

INTRODUCTION

The capability for self-organization and evolution is a fundamental property of highly dispersed systems, including gels—in particular, element dioxide hydrogels. This property is related to thermodynamic nonequilibrium and the excess energy of a developed interface between solid nanoparticles; this is responsible for a trend towards free energy minimization and system stabilization. The resulting flexible structured hydrate network and highly organized near-surface element dioxide hydrogel layers provide unique conditions for the formation of surface metal complexes capable of driving catalytic reactions in a certain direction. Moreover, because of the unique properties of hydrogels (such as enhanced chemical stability, accessibility of active surface centers over the entire reaction volume, capability for intense heat and mass exchange in the absence of brittle fracture, ease of separation from reaction products, and possibility of multiple regeneration), use of hydrogels in heterogeneous catalysis is of scientific and practical interest.

Previously, we found that a new polyfunctional heterogeneous system, which includes Cu^{2+}-containing SiO_2, SnO_2, and TiO_2 hydrogels, consists of different copper structures that are catalytically active centers in hydroxyarene oxidation reactions [1–4]. In this context, the structure and distribution of copper structures on the surface of hydrogels is one of the determining factors of the system.

The aim of this work was to study the structure and distribution of various copper structures on the surface of ZrO_2 and sulfated ZrO_2 hydrogels (it is well known that their unhydrated analogs exhibit considerable cat-

alytic and sorption activity [5, 6]) and to determine their catalytic activity in the liquid-phase oxidation reaction of 2,3,5-trimethyl-1,4-hydroquinone as a model hydroxyarenes.

EXPERIMENTAL

The test materials were Cu^{2+}-containing hydrogels of ZrO_2 (**I**) and sulfated ZrO_2 (**II**). The gels with the specific surface area $S_{sp} = 250 \pm 12$ m²/g were synthesized by the hydrolysis of a 0.28 M aqueous $ZrSO_4$ solution with a 2 M KOH solution to pH 7.5 or 5.0 for gels **I** and **II**, respectively, followed by repeated washing with distilled water. After this washing, the continuous phase had pH 7.0. The values of S_{sp} were determined from the adsorption of an inert gas. The composition of hydrogel **II** (the $-SO_3H$ group concentration was 17 wt %, and the Zr/S element ratio was 3 : 1) was determined using elemental analysis, IR spectroscopy (on a Specord M-80 spectrometer), and potentiometric titration (with the use of a pH 121 meter) [7, 8].

The oxidation of 2,3,5-trimethyl-1,4-hydroquinone was experimentally studied in a thermostatted reactor equipped with a reflux condenser and a bubbler for introducing air via stirring (at a stirrer speed higher than 2 s⁻¹ and an air flow rate of 6.2 l/h) to insure the occurrence of the process in the kinetic region. The reaction was performed in 10 ml of an aqueous methanol solution (water/methanol ratio of 1 : 1, by volume) at 50°C with a thermostatting accuracy of ±0.2°C. An aqueous solution of copper chloride (5.9×10^{-5} mol of $CuCl_2 \cdot 2H_2O$), 0.28×10^{-4}–1.6×10^{-2} mol of gels **I** and **II**, and a substrate (6.6×10^{-4} mol) solution in methanol were placed in the reactor and stirred. The substrate solution

was introduced with the delay required for the complete sorption of copper(II) by gels **I** and **II**.

We found that 5.9×10^{-5} mol of $CuCl_2 \cdot 2H_2O$ was completely sorbed within ~45 s on 1.2×10^{-3} (or more) mol of ZrO_2, which forms hydrogel **I**, and on 3.7×10^{-3} (or more) mol of sulfated ZrO_2, which forms hydrogel **II**. The concentration of Cu^{2+} ions in the phase of test gels was determined by atomic absorption spectrometry on a Perkin-Elmer 403 spectrometer. The concentration of Cu^{2+} ions in the phase of gels **I** and **II** was varied by introducing various amounts of these gels into the reaction zone. The concentrations of Cu^{2+} ions in gels **I** and **II** were varied within the ranges 5×10^{-2}–2×10^{-1} and 3×10^{-2}–2×10^{-1} mmol/g gel.

Under the above conditions of stirring, 6.6×10^{-4} mol of 2,3,5-trimethyl-1,4-hydroquinone was completely sorbed on 1.2×10^{-3} (or more) mol of gels **I** and **II** in 10 ml of an aqueous methanol solution within ~60 s. The sorption values of the substrate on the test gels were found by the quantitative determination of the substrate in mother liquors after separating the gel phase. The procedure of GLC analysis on a Chrom-4 chromatograph was analogous to that described elsewhere [9].

The kinetic measurements were performed by sampling and the GLC determination of the starting compound in the samples [9]. The resulting functions of substrate concentrations were approximated by polynomials. The initial reaction rates w_0 were calculated using numerical differentiation and interpolation techniques. The determination error of w_0 was no higher than 10%. The initial rates of substrate consumption $w_{0,A}$, $w_{0,B}$, and $w_{0,C}$ in the interaction with mononuclear Cu^{2+} complexes (**A**), magnetic associates (**B**), and Cu^{2+} compounds (**C**) that do not give EPR signals, respectively, were calculated by solving combined algebraic equations of the form

$$w_{0,i} = w_{0,A}n_{i,A} + w_{0,B}n_{i,B} + w_{0,C}n_{i,C},$$

where $w_{0,i}$ is the initial reaction rate at i equal to the ratio of the amount of Cu^{2+} to the amount of the gel; and $n_{i,A}$, $n_{i,B}$, and $n_{i,C}$ are the fractions of complexes **A**, **B**, and **C**, respectively, at the Cu^{2+} concentration $[Cu^{2+}]_i$ in the gel phase. The calculation was performed with consideration of the w_0 of a parallel reaction of substrate oxidation by oxygen. The determination error in $w_{0(A,B,C)}$ was no higher than 15%.

Because the EPR spectra of moist samples are difficult to measure, we measured the EPR spectra of Cu^{2+} on the surface of gels that were filtered off and dried at room temperature.[1] The EPR spectra were measured on

[1] The sample drying conditions under which the complexes did not undergo structural changes, and the ratio between various Cu^{2+} species remained unaffected, were found in preliminary experiments. The EPR spectrum began to change, as compared to that of a hydrogel solution vitrified at 77 K, which sorbed Cu^{2+} ions (the ratio water/methanol = 1 : 1), only when the samples were dried at a temperature higher than 333 K.
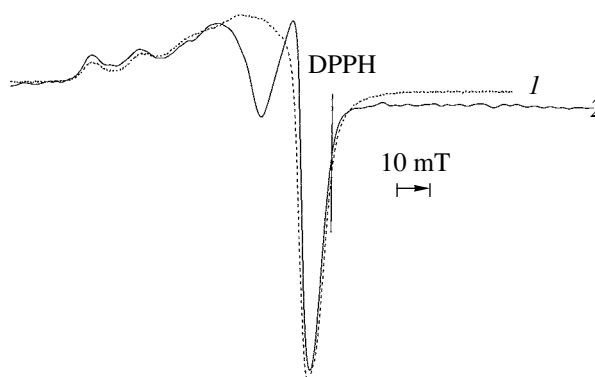
Fig. 1. EPR spectra of Cu^{2+} ions in hydrogels (*1*) **I** and (*2*) **II** at $[Cu^{2+}] < 0.03$ mmol/g gel and $T = 293$ K.

a PS 110.X 3-cm EPR radiospectrometer (Belarus) at room temperature in thin-walled round quartz ampules ($d = 4$ mm). The treatment and analysis of the EPR spectra were performed with the use of the software package of the spectrometer.

The voltammetric measurements were performed with the use of a PU-1 polarograph. The potential sweep rate was 20 mV/s. An electroactive carbon-paste electrode was used as an indicator electrode; the apparent surface area of this electrode was 0.07 cm^2. The active part of the electrode consisted of a mixture of the test compound, spectroscopically pure graphite, and Vaseline oil as a binder in a weight ratio of 1 : 4 : 2, respectively. To stabilize the true surface of the electrode, the test substances and graphite were sifted, and fractions with a particle size of ≤ 63 μm were taken [10].

A glassy carbon crucible served as an auxiliary electrode, and an EVL-1M1 saturated silver–silver chloride electrode served as a reference electrode. A solution of $CH_3OH + H_2O$ (1 : 1) + 0.025 M HCl was used as a supporting electrolyte. The voltammograms were measured over a potential range from +0.4 to –2.0 V.

RESULTS AND DISCUSSION

EPR spectroscopy. We found that three types of copper structures (**A**, **B**, and **C**) were formed on the surface of the test hydrogels. The anisotropic EPR spectra of copper, resolved in a parallel orientation with the parameters $g_\parallel = 2.332 \pm 0.005$ and $A_\parallel = 13.6 \pm 0.3$ mT (Fig. 1), suggest the formation of complexes **A** of the same structure in hydrogels **I** and **II**. These complexes were formed even at small amounts of adsorbed copper ($[Cu^{2+}] < 0.03$ mmol/g gel). The parameters of the EPR spectra of Cu^{2+} in these gels are consistent with those observed in freshly precipitated aluminum and gallium hydroxides [11] and in the Na^+ form of carboxylic cation exchangers [12, 13]; they suggest that the closest
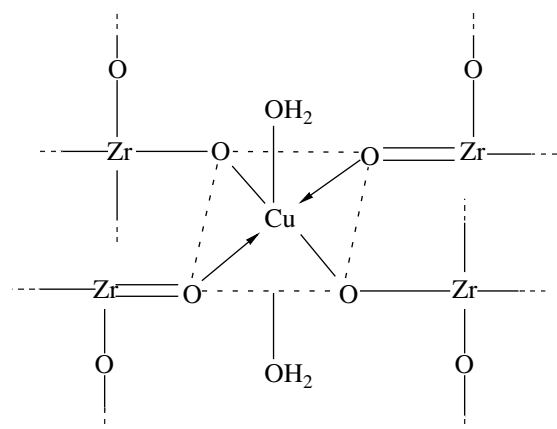
Fig. 2. Structure of mononuclear Cu^{2+} complexes formed on the surface of test gels **I** and **II**.
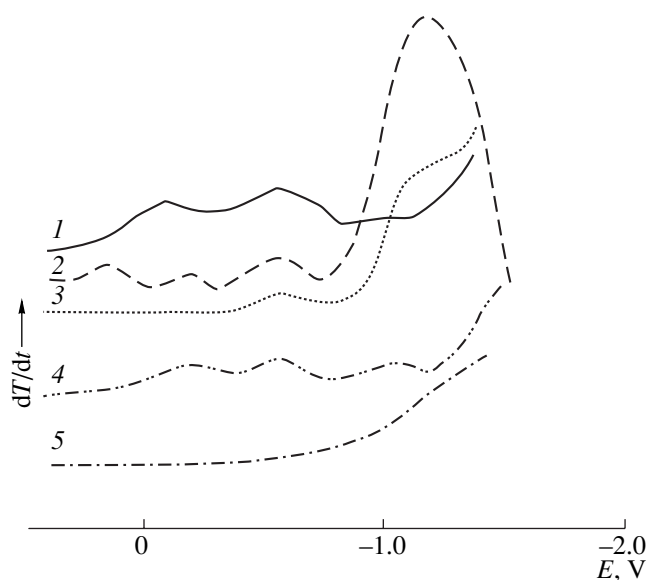

Fig. 3. Electrochemical behavior of Cu^{2+} ions on the surface of hydrogels **I** and **II**: (*1*) Cu^{2+}—electroactive carbon-paste electrode, (*2*) Cu^{2+}—gel **II**, (*3*) gel **II**, (*4*) Cu^{2+}—gel **I**, and (*5*) gel **I**.
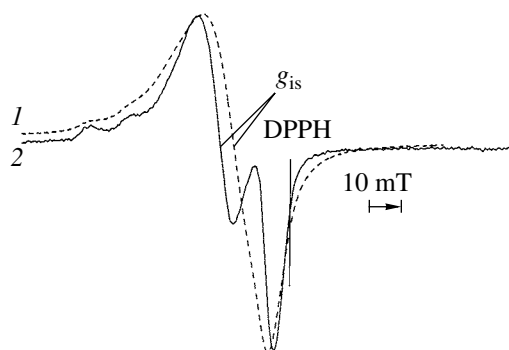

Fig. 4. EPR spectra of Cu^{2+} ions in hydrogels at $T = 293$ K: (*1*) **I** ($[Cu^{2+}] = 1.67$ mmol/g gel) and (*2*) **II** ($[Cu^{2+}] = 2.5$ mmol/g gel).

environment of the Cu^{2+} ions consists of the oxygen atoms of a zirconia matrix of hydrogels and water molecules (Fig. 2).

In a previous study of sulfo cation exchangers [14], it was found that the sulfo group does not enter the first coordination sphere of Cu^{2+} ions and, consequently, has no effect on the parameters of the EPR spectra. Therefore, it would not be expected that the presence of sulfo groups in hydrogel **II** would manifest itself in the EPR parameters of copper complexes. However, it is likely that sulfo groups participate in the formation of the second coordination sphere of a portion of copper complexes in this gel to make the water molecules in the first coordination sphere of Cu^{2+} ions more mobile. This conclusion follows from the appearance of a peak with a potential of +0.14 shifted toward positive potentials in the curve of copper reduction on hydrogel **II**, as compared with hydrogel **I** and the electroactive carbon-paste electrode (Fig. 3). An increase in $[Cu^{2+}]$ resulted in the formation of compounds **B** with an increased local concentration of copper ions on the surface of the gels. This is evident from the appearance of an almost symmetrical line with the averaged g-factor (g_{is}) equal to 2.150 ± 0.01 (in the case of gel **II**) and 2.130 ± 0.01 (in the case of gel **I**), along with an anisotropic signal (Fig. 4). The difference in the anisotropic signal parameters for the two hydrogels is indicative of the different structures of compounds **B**. On the surface of hydrogel **II**, compounds **B** are formed that are the associates of closely spaced and exchange-interacting complexes **A**, because the averaged g-factor coincides with the value of $g_{av} = (g_{\parallel} + 2g_{\perp})/3$ for complexes **A**. It is our opinion that structures **B** formed on the surface of gel **I** are the associates of Cu^{2+} ions, which do not form an individual phase of $Cu(OH)_2$ and are not arranged in complexes **A** with oxygen in a zirconia matrix. In our opinion, this is an intermediate species in which the aqua hydroxo complexes of copper are linked with each other and, at particular sites, with inorganic polymer chains. Complexes **A**, which were formed at the initial stage of sorption, took part as growth sites in the formation of compounds **B** in gel **I**. This follows from a dramatic decrease in the concentration of complexes **A** and a simultaneous increase in the concentration of compounds **B** in gel **I** (Fig. 5b, curves *3*, *5*).

The formation of structurally different compounds **B** in the test hydrogels can be explained by different compositions of these hydrogels. The presence of sulfo groups in the structure of hydrogel **II** affects the acidity of the medium and, evidently, considerably decreases the probability of the partial hydrolysis of copper ions. The participation of sulfo groups in complexation may also be responsible for the formation of magnetic associates **B** from individual complexes **A** in gel **II**. In these associates, the chemical bonds in the individual copper complexes that form these associates are weakened. It
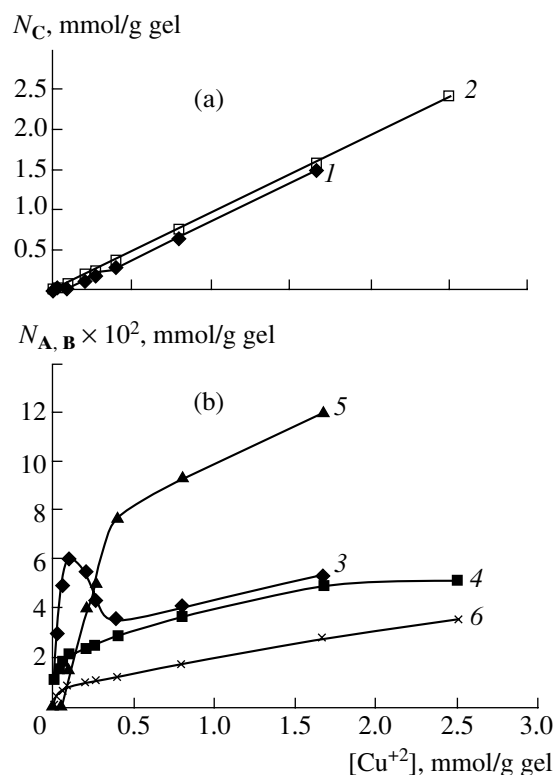
Fig. 5. Absolute amounts of copper structures (a) (*1*, *2*) **C**, (b) (*3*, *4*) **A** and (*5*, *6*) **B** on the surfaces of test gels (*1*, *3*, and *5*) **I** and (*2*, *4*, and *6*) **II** as functions of the concentration of sorbed Cu^{2+} ions.

Fig. 6. Fractions of copper structures (*1*, *2*) **A**, (*3*, *4*) **B**, and (*5*, *6*) **C** in the total concentration of Cu^{2+} ions sorbed on the surfaces of test gels (*1*, *3*, and *5*) **I** and (*2*, *4*, and *6*) **II**.

is most likely that this fact is responsible for the appearance of a peak with a potential of +0.14 in the voltammetric curve of Cu^{2+}-containing gel **II** (Fig. 3).

An inconsistency between the spectroscopic and sorption data for the test gels over the entire range of Cu^{2+} sorption suggests the formation of compounds **C**, the absolute amount of which on the surface of gels **I** and **II** increases with $[Cu^{2+}]$ (Fig. 5a). By analogy with similar structures formed in ion exchangers [11, 14], these compounds can be a separate phase of $Cu(OH)_2$ or polynuclear Cu^{2+} compounds with bridging OH^- groups.

An analysis of the EPR spectra of the test gels demonstrated that, as the concentration of Cu^{2+} in the gels was increased up to the exhaustion of their exchange capacity, both complexes **A** and compounds **B** occurred on their surfaces (Fig. 5b). We established this fact only for the ZrO_2 hydrogels. In the case of previously studied Cu^{2+}-containing hydrogels of SnO_2 and TiO_2, complexes **A** were gradually converted into compounds **B** with increasing $[Cu^{2+}]$; this was supported by the complete conversion of anisotropic spectra into isotropic spectra [4]. Various quantitative ratios between the compounds **A**, **B**, and **C** were reached by varying the value of $[Cu^{2+}]$. The fractions of these compounds in the total sorbed copper contents of the gel surfaces were
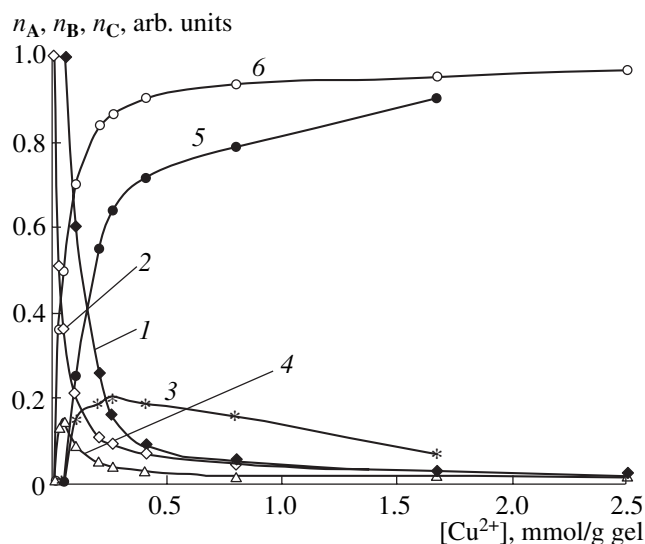
determined by the computer separation of EPR signals. Figure 6 demonstrates the corresponding curves for the test gels. It can be seen in Fig. 6 that the fraction of complexes **A** (n_A) on the surface of hydrogels decreased with $[Cu^{2+}]$ (curves *1*, *2*); the fraction of compounds **B** (n_B) initially increased only slightly and then decreased, passing through a maximum (curves *3*, *4*), whereas the fraction of compounds **C** (n_C) steadily increased (curves *5*, *6*).

In our opinion, such behavior (Figs. 5, 6) reflects the nonuniform distribution of Cu^{2+} localization sites on the surface of the test gels. There are areas with the predominant localization of complexes **A** and of compounds **B** and **C**. Complexes **A** are formed at low gel surface coverages with Cu^{2+} ions. As $[Cu^{2+}]$ increased, the formation of these complexes was practically finished, and the formation of compounds **B** and **C** occurred. In this case, the number of the localization sites of compounds **B** was much smaller than that of compounds **C**. A decrease in the functions $n_B = f([Cu^{2+}])$ with increasing $[Cu^{2+}]$ in the test hydrogels was due to the saturation of the hydrogels with structures **B** with increasing gel coverage by structures **C**. Note that the absolute amounts of structures **A**, **B**, and **C** ($N_{A, B, C}$, mmol/g gel) (Figs. 5a, 5b) and their fractions (Fig. 6) at the same value of $[Cu^{2+}]$ were different for gels **I** and **II**. In gel **I**, greater concentrations of compounds **B** were detected compared with gel **II**. We also found that compounds **B** and **C** in gel **II** began to appear at lower $[Cu^{2+}]$ compared with gel **I**. It is likely that sulfo groups are also the sites of growth for the formation of structures **B** in hydrogel **II**; this fact is responsible for the appearance of these structures at smaller degrees of gel saturation with Cu^{2+} ions. The
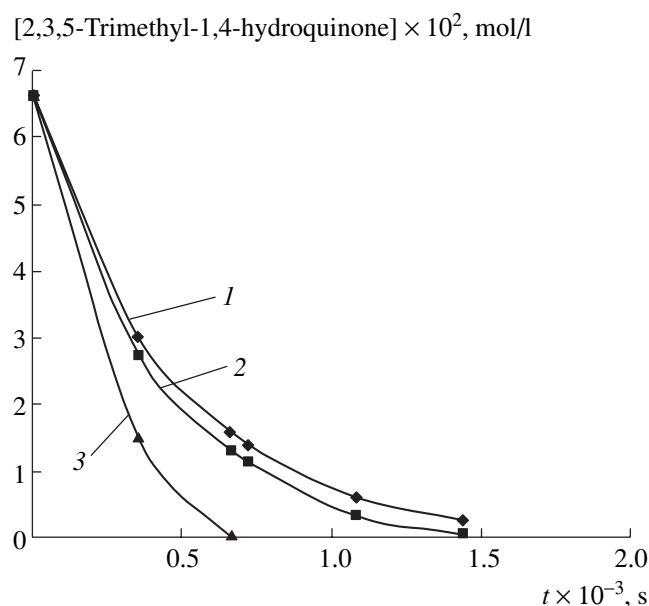
[2,3,5-Trimethyl-1,4-hydroquinone] $\times 10^2$, mol/l

Fig. 7. Kinetic curves of substrate consumption in the oxidation of 2,3,5-trimethyl-1,4-hydroquinone with atmospheric oxygen in the presence of (*1*) a CuCl$_2$ · 2H$_2$O solution or in gels (*2*) **I** and (*3*) **II**.

introduction of sulfo groups also provided a more uniform coverage of this hydrogel with complexes **A** (Fig. 5b).

Voltammetry. An analysis of Cu^{2+} reduction curves at the electroactive carbon-paste electrodes containing hydrogels **I** and **II** (Fig. 3) demonstrated that (a) the Cu$^{2+} \longrightarrow$ Cu$^+$ reduction ($E_{peak} = -0.20$ V) at an electroactive carbon-paste electrode containing hydrogel **I** was hindered compared with that at a carbon-paste electrode without gels **I** and **II** ($E_{peak} = -0.10$ V), because the Cu$^{2+} \longrightarrow$ Cu$^+$ reduction potential was shifted to a negative region; (b) two peaks (with potentials of +0.14 and –0.20 V, respectively) corresponded to the Cu$^{2+} \longrightarrow$ Cu$^+$ reduction at an electroactive carbon-paste electrode containing hydrogel **II**; one of these electrodes exhibited the same potential as that of hydrogel **I**, whereas the other potential was shifted to a positive region to suggest easy Cu^{2+} reduction; (c) a peak with a potential of –0.55 V, which exhibited the same potential in all of the three curves, corresponded to the Cu$^+ \longrightarrow$ Cu^0 reduction. It is well known that the formation of stable complex compounds results in a shift of the reduction potential toward negative values. Therefore, we believe that the occurrence of a peak with a potential of –0.20 V, which is shifted toward negative values, in the voltammetric curves of hydrogels is due to the fact that sorbed Cu^{2+} ions form a strong compound in hydrogel phases. The appearance of a peak with a potential of +0.14 V in the reduction curve of copper(II) sorbed by hydrogel **II** can be explained in two different ways: the shift of a peak toward a positive

region, compared with the peak of Cu^{2+} reduction at an electroactive carbon-paste electrode containing no gels, can reflect either the formation of a strong Cu$^+$ compound, which results from the reduction of Cu^{2+} ions, or the formation of a more mobile Cu^{2+} compound in a hydrogel, compared with the Cu^{2+} compound that occurs in solution [15]. In the former case, a peak, due to the Cu$^+ \longrightarrow$ Cu^0 reduction and shifted toward the region of negative potentials, would appear; however, we did not detect this peak in the experimental voltammetric curve. We believe that the peak with a potential of +0.14 V reflects the presence of Cu^{2+} compounds with the sulfo group in hydrogel **II**; the structure of these compounds was discussed above.

Peaks that were detected in voltammograms and not discussed in the text are not related to the reduction of copper ions.

Catalysis. The liquid-phase oxidative dehydrogenation of 2,3,5-trimethyl-1,4-hydroquinone occurred in accordance with the following reaction scheme:

2,3,5-trimethyl-1,4-hydroquinone   2,3,5-trimethyl-1,4-benzoquinone
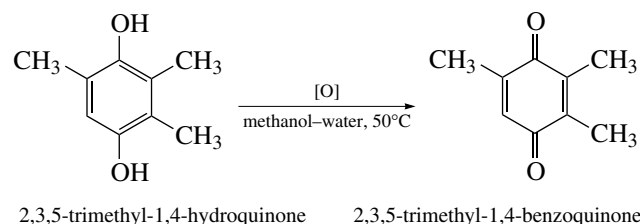
This reaction occurred with the quantitative yield of 2,3,5-trimethyl-1,4-benzoquinone. We found that the test hydrogels in the absence of copper inhibited the oxidative hydrogenation process.

Substrate oxidation on Cu^{2+}-containing hydrogels **I** and **II** accelerated the reaction, as evidenced from the kinetic curves of substrate consumption (Fig. 7). It can be seen in Fig. 7 that the catalytic activity of the Cu^{2+}-containing hydrogel **II** in the above reaction was higher than that of hydrogel **I**. We associate this fact with structural differences between the test hydrogels, with different structures of compounds **B** in the test hydrogels, and with the distributions of compounds **A**, **B**, and **C** on their surfaces.

With the use of the dependence of the initial rates of 2,3,5-trimethyl-1,4-hydroquinone oxidation (w_0) on [Cu^{2+}] for the set of copper structures (Fig. 8), we determined the specific initial rates of substrate oxidation ($w_{0, A}$, $w_{0, B}$, and $w_{0, C}$) by these structures; these initial rates characterize their individual reactivities (see table). Data on the fractional concentrations of various copper structures were used in the calculations (Fig. 6).

It can be seen in the table that individual Cu^{2+} ions in gels are much less active than in solution. This is not surprising, because the accessibility of Cu^{2+} ions to a substrate in solution is much higher than in gels. A comparison of data on the initial specific rates $w_{0(A, B, C)}$ of 2,3,5-trimethyl-1,4-hydroquinone oxidation by vari-
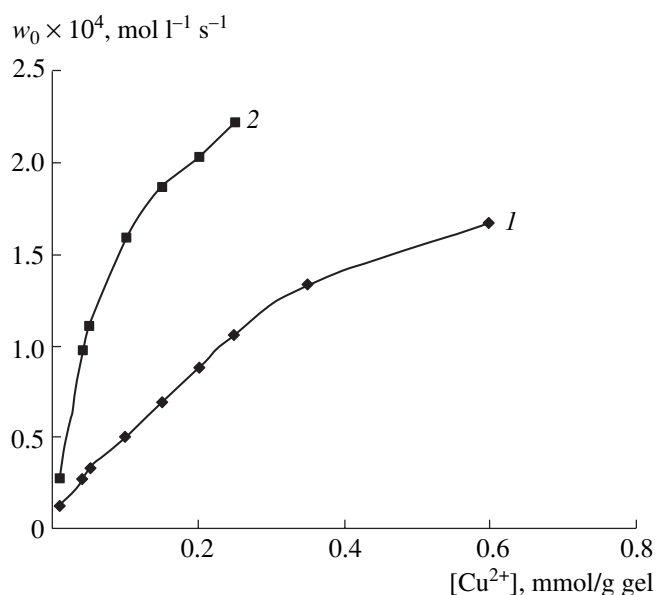
$w_0 \times 10^4$, mol l^{-1} s^{-1}

Fig. 8. Initial rates of 2,3,5-trimethyl-1,4-hydroquinone oxidation as functions of the concentration of sorbed Cu^{2+} ions on the surfaces of test gels (*1*) **I** and (*2*) **II**.

ous copper structures demonstrated a higher catalytic activity of Cu^{2+} ions bound in compounds **C** and **B**, compared with complexes **A**. Compounds **C** in heterogeneous catalysts exhibit a higher activity than that of Cu^{2+} ions in solution. This may be due to an increased mobility of electrons in these polynuclear copper(II) complexes with bridging OH$^-$ groups and to the possibility of electron density transfer in them. Previously [16, 17], a correlation between the mobility of electrons and the catalytic activity of Cu^{2+} was found using microwave conductivity measurements. The acceleration of dehydrogenation was explained by the fact that, in this case, the reactions of hydroquinone oxidation and oxygen reduction can be spatially separated.

Initial specific rates of 2,3,5-trimethyl-1,4-hydroquinone oxidation by copper compounds **A**, **B**, and **C**

Gel	$w_0 \times 10^4$, mol l^{-1} s^{-1}			
	$w_{0,A} \pm 0.03$	$w_{0,B} \pm 0.04$	$w_{0,C} \pm 0.04$	$w_0 \pm 0.16$ (oxidation with Cu^{2+} ions in solution)
Without gel	–		–	0.54
Gel **I**	0.10	0.30	0.70	–
Gel **II**	0.10	0.40	0.80	–

It is our opinion that compounds **C** in the test hydrogel phases exhibited a large specific surface area, and that the Cu^{2+} ions in them were much more accessible to hydroquinone compared with Cu^{2+} ions in compounds **B**. It is likely that, if it was possible to take into account Cu^{2+} ions that actually participated in the catalytic process in compounds **B**, their initial specific rates would be at least no lower than those for compounds **C**. The productivity of the process, which manifests itself in the calculated values of initial specific rates, increases as a result of the increasing number of Cu^{2+} ions that actually participate in catalysis.

The high catalytic activity of Cu^{2+}-containing hydrogel **II** correlates with the voltammetric data on the formation of copper complexes, which undergo more reversible reduction.

Thus, the interaction of Cu^{2+} ions with the test hydrogels essentially depends on the composition of these gels and on the concentration of copper on their surfaces. The presence of the sulfo group in the structure of hydrogels is responsible for the fractional distribution of various copper compounds on the surface and for the high catalytic activity of these compounds in the oxidative dehydrogenation reaction of 2,3,5-trimethyl-1,4-hydroquinone.

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