

# Copper Complexes Stabilized by Chitosans: Peculiarities of the Structure, Redox, and Catalytic Properties

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**Abstract**—Peculiarities of the structure and physicochemical properties of copper–chitosan complexes prepared by different methods were studied by IR, UV-visible, ESR spectroscopy, and electron microscopy. The catalytic activity of redox copper centers stabilized by the chitosan matrix in the reactions of oxidation of *o*- and *p*-dihydroxybenzenes in an aqueous medium was determined. Quantitative ESR measurements provide evidence for the localization of virtually all copper ions introduced in the initial heterogeneous chitosan samples with copper contents below 1.5 wt % in the form of isolated  $\text{Cu}^{2+}$  ions in square planar coordination. The chitosan matrix was shown to strongly bind copper ions under conditions of redox transformations in the catalytic tests or upon prolonged heating in boiling water. Reoxidation of the samples with  $\text{H}_2\text{O}_2$  results in quantitative restoration of the initial ESR signal of Cu(II). Heterogenized copper–chitosan samples exhibited high activity and stability in the catalytic oxidation of dihydroxybenzenes into quinones, whereas the homogeneous system was characterized by irreversible poisoning due to formation of copper–hydroquinone complexes. Preparation of the binary composite system with a thin heterogeneous copper–chitosan film supported on a macroporous silica allows one to dramatically enhance the specific catalytic activity and the efficiency of the active component. Such an approach may turn out to be useful in the synthesis of supported chitosan catalyst with a low noble metal content.

Chitosan (*N*-deacetylated chitin, poly(1-4)-*N*-acetyl- $\beta$ -*D*-glucosamine) is a biodegradable polysaccharide containing various functional groups. This polymer is known to possess unique adsorption properties with respect to diverse ions, or even atoms, of metals. On one hand such a polymeric matrix capable of irreversibly binding different ions attracts attention basically as an effective system for removal of heavy metal cations from diluted aqueous solutions [1–5]. Literature data on the physicochemical properties of metal complexes with chitosan are available [6–9]. On the other hand, the systems obtained by immobilization of cations on the chitosan matrix can be considered as a new generation of ecologically friendly catalysts. In general, ions and complexes of transition metals immobilized on polymeric matrices are promising catalysts due to the favorable combination of the properties of homogeneous and heterogeneous systems. However, there are only a few publications devoted to the use of metal complexes stabilized by chitosan in heterogeneous catalytic properties [10–12] and information about the application of chitosan complexes in catalytic oxidation is virtually missing.

The goal of this study has to prepare various complexes of copper with chitosan, to perform a detailed investigation of their properties and morphology, and to evaluate the catalytic activity of the redox sites of such complexes in the reaction of oxidation of *o*- and *p*-dihydroxybenzenes.

## EXPERIMENTAL

### Reagents

**Unmodified chitosan.** As-received chitosan made from crab shells (Korea, molecular weight 100000–150000, deacetylation degree 70%, moisture content 3 wt %) was used for preparation of catalysts without further purification.

Glutaric aldehyde (25 vol % aqueous solution, reagent grade) was chosen as a cross-linking agent. SPAN-60 (sorbitane stearate, Fluka AG), used as an emulsifier, and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  were of analytical-grade purity (Fluka AG).

**Modified chitosan.** Conventional procedures described elsewhere [13–15] were applied for preparation of chitosan modified with glutaric aldehyde.

Initially chitosan was dissolved in 0.1 M HCl to prepare a solution with a chitosan concentration of 1.5 wt %, then 60 ml of the solution obtained was added to 60 ml of hexane containing 5 wt % of SPAN-60 emulsifier. The mixture was stirred at 60°C at 3000 rpm until formation of an emulsion. Then the stirring rate was decreased to 500 rpm, and 13 ml of the 25% aqueous solution of glutaric aldehyde were added by drops for 1 h (the molar ratio of glutaric aldehyde : amino group of chitosan, GA/ $\text{NH}_2$ , was 0.64). The stirring rate of 500 rpm was maintained for 4 h until com-

pletion of the cross-linking procedure. In order to remove SPAN-60, the polymer obtained was filtered and washed several times with distilled water at 80°C and hexane at 55°C. Then the polymer was dried in air for 48 h.

### Preparation of Catalysts

**Homogeneous copper–chitosan complex.** The calculated amount of  $\text{CuCl}_2$  was added to a 1.5 wt % solution of chitosan in 0.1 M HCl at room temperature, and the mixture was stirred until the formation of a transparent greenish gel-like mixture. For the FTIR spectroscopic study, the solution of the homogeneous copper–chitosan complex was placed on quartz plates and air-dried for 48 h.

**Coprecipitation method.** A greenish solution of the homogeneous copper–chitosan complex (0.5–9 wt %) was prepared as described above. Then the solution obtained was added by drops to a 0.5 M NaOH solution. Spherical globules formed were filtered and washed with distilled water until they obtained a neutral pH 7 and then dried in air for 48 h.

**Adsorption method.** A 1.5 wt % solution of chitosan in 0.1 M HCl was added by drops to a 0.5 M NaOH solution. Spherical globules formed were filtered off, washed with distilled water until neutral pH, and then air-dried for 48 h. The polymer particles thus obtained (1 g) were placed in 20 ml of an aqueous solution containing the calculated amount of  $\text{CuCl}_2$ . The mixture was stirred for 20 min, then the catalyst particles were filtered, washed several times with distilled water and dried in air for 24 h.

**Immobilization of the copper–chitosan complex on the surface of porous  $\text{SiO}_2$  (KSK).** A weighed amount (1 g) of amorphous  $\text{SiO}_2$  (KSK, particle size, 0.25–1 mm, surface area 330  $\text{m}^2/\text{g}$ , water incipient wetness capacity, 1.2 ml/g) was impregnated by 1.2 ml of the solution of the homogeneous copper–chitosan complex prepared using the above procedure. The system thus prepared was placed for 15 min in a 0.5 M NaOH solution. Then siliga gel with heterogenized copper–chitosan complex was filtered off, washed repeatedly with distilled water (until neutral pH), and dried in air for 24 h and then in a vacuum for 10 h.

**Immobilization of the copper–chitosan complex on the surface of mesoporous MCM-41 carrier.** A weighed amount (1 g) of the MCM-41 support (pure  $\text{SiO}_2$  with unidimensional channels, diameter of channels, ~4 nm, surface area 1040  $\text{m}^2/\text{g}$ , water incipient wetness capacity, 4.6 ml/g) was impregnated by 4.6 ml of the solution of the homogeneous copper–chitosan complex. The system thus prepared was treated with 1.5 ml of a 25% solution of glutaric aldehyde for 3 h, washed repeatedly with distilled water (until complete

removal of glutaric aldehyde), and filtered. The sample obtained was dried in air for 48 h and then in a vacuum for 24 h.

**Copper complex with chitosan modified with glutaric aldehyde.** The homogeneous copper–chitosan complex, prepared as described above, was added to an equivalent volume of hexane containing 5 wt % of SPAN-60. Then the same procedure was used as described above for the preparation of modified chitosan.

### Study of Catalytic Properties of the Prepared Samples in Oxidation of *o*- and *p*-Dihydroxybenzenes

Copper–chitosan complexes (6.5 wt % Cu) were tested as catalysts of oxidation of isomeric *o*- and *p*-dihydroxybenzenes by oxygen in air into the corresponding quinones. The catalyst loading was placed into a glass flask with an aqueous solution of dihydroxybenzene (the substrate : catalyst molar ratio, 10 : 1), and the mixture was stirred with a magnetic stirrer. Samples of the reaction mixture were periodically withdrawn for analysis. The reaction was monitored by measuring the intensities of the UV absorption bands of the quinones formed (Specord M-40 UV–visible spectrometer, the bands at 390 and 428 nm for hydroquinone and catechol, respectively). The concentrations were expressed in arbitrary units of the absorbance  $\ln(T)$  that are proportional to the product concentrations.

### IR and UV-visible Spectroscopic Study

Transmission FTIR spectra were recorded at 20°C using a Nicolet Protege 460 spectrometer in the range of 4000–400  $\text{cm}^{-1}$  at a resolution of 8  $\text{cm}^{-1}$  and Matteson Galaxy Series FTIR 5000 spectrometer in the range of 4000–600  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ . In the first case, particles of chitosan samples were crushed and ground in a mortar, then the fine powder was mixed with KBr, pressed into a thin wafer, and placed in the sample holder of the spectrometer. The OMNIC program was used for the treatment of the spectra. In the second case, the chitosan samples were ground with a drop of perfluorinated oil in an agate mortar, then the fine suspension was placed between the NaCl windows and the spectra were taken [13]. The same sample was used for recording UV–visible transmission spectra using Perkin–Elmer UV–visible Lambda 18 spectrometer (wavelength range, 250–800 nm, resolution, 1 nm). The use of the perfluorinated oil allows one to suppress light scattering, which is quite significant for dry powders, especially in the UV range [13]. The spectrum of pure chitosan was subtracted from the UV-visible spectra of the copper-containing samples, in order to discriminate the bands attributed to copper centers. IR spectra of the samples dispersed in perfluorinated oil

were treated using the WIN-FIRST program (correction of the baseline, subtraction of the spectrum of perfluorinated oil). Intense bands of perfluorinated oil are observed in the region of 1300–1100 cm<sup>-1</sup> and do not overlap with the bands of OH, NH, and CH groups of chitosan in the region of 4000–2000 cm<sup>-1</sup>.

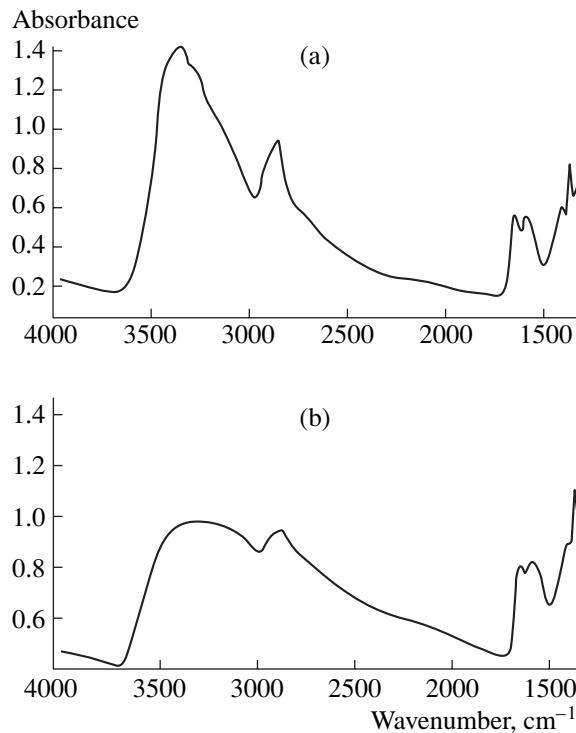
### ESR Study

ESR spectra were recorded using a Bruker ESR 300 spectrometer equipped with a 4104OR resonator and quartz Dewar vessel in the X band ( $\lambda \approx 3.2$  cm) at 20°C and -196°C. The ESR spectra were measured at the microwave power of 6.35 mW and amplitude of modulation 2.0 G in the range of 2000–4000 G (5 scans with the sweep time of 42 s) or 100–4600 G (2 scans at the sweep time of 84 s). Bruker ESP 300E and WIN-EPR (version 901.201) programs were used for treatment of the spectra (correction of the baseline, double integration). DPPH and frozen solutions of Cu(NO<sub>3</sub>)<sub>2</sub> were used as standards to determine the *g*-values and for quantitative analysis of Cu<sup>2+</sup> ions observed by ESR.

Particles of the weighed catalyst were placed in quartz ampules to fill the necessary volume (diameter, 3.5 mm, height, 15 mm), evacuated for 10 min until the pressure in the vacuum system reached 0.03 Torr at 20°C, and sealed off. ESR spectra were measured at 20°C and normalized by the weight of the sample. Then the ampules were opened to air and the measurements repeated. Then the sample particles were saturated with water and kept overnight. Then the ampules were placed in liquid nitrogen and spectra were taken at -196°C. To derive the fraction of ESR-detectable Cu<sup>2+</sup> ions in the samples under study, the spectra were compared to those of the frozen solutions of Cu(NO<sub>3</sub>)<sub>2</sub> [14, 15]. The samples were studied in series and the ampules were placed in the same position in the resonator chamber in order to increase the accuracy of the quantitative measurements.

## RESULTS AND DISCUSSION

IR spectra of the initial chitosan and copper–chitosan complex (1.5 wt %) prepared by coprecipitation are presented in Fig. 1. The spectrum of the initial chitosan (Fig. 1a) is virtually the same as the spectra reported in the paper [16] devoted to IR-spectroscopic studies of chitin and chitosan. Obviously, the presence of copper in the complex causes significant changes in the shape of the broad band at 3700–1700 cm<sup>-1</sup> assigned to different types of OH and NH vibrations in polymers. Coordination of the chitosan matrix with Cu<sup>2+</sup> ions results in substantial changes of the vibration frequencies in this region with a shift toward low frequencies. Thus, even for low-percentage samples, the interaction of copper ions with the polymer matrix turns out to be strong enough for perturbation of O–H and N–H bonds in chitosan. The effect of the broadening of absorption bands is higher for the samples with copper content 9 wt %;

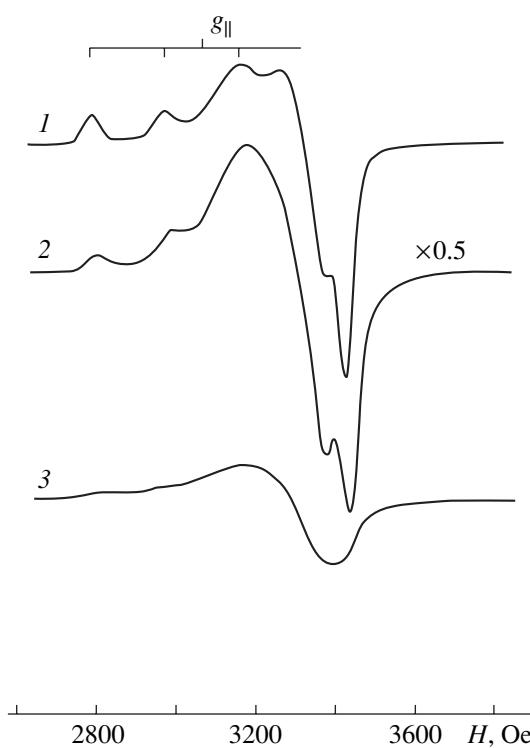


**Fig. 1.** IR spectra of (a) the initial chitosan and (b) the 1.5% Cu/chitosan sample in the region of vibrations of OH, NH, and CH groups.

however, the quantitative analysis is hardly possible in this case. It is worthwhile noting that the spectrum of the complex with copper content 1.5 wt % prepared by impregnation of wet chitosan globules with a copper(II) solution is identical to the spectrum of the sample obtained by coprecipitation (Fig. 1b). Hence, absorption of copper(II) ions by chitosan leads to binding of copper similar to the samples prepared from the homogeneous complex.

Besides broadening of the OH and NH absorption bands, introduction of copper in chitosan results in the appearance of a strong absorption band at 470 cm<sup>-1</sup> presumably ascribed to the stretching vibrations of the Cu–N bonds [17]. For the dried thin films of homogeneous copper-containing complexes, this band is observed at 466 cm<sup>-1</sup>. The values of the frequencies may indicate the formation of chelate copper complexes with chitosan ( $\nu = 472$  cm<sup>-1</sup>) [17]. The spectrum of the sample after the catalytic reaction contains a shoulder at 590 cm<sup>-1</sup> that may be related to the formation of bonds between NH<sub>2</sub> groups of chitosan and Cu(I) ions [17].

Comparison of the IR spectrum of chitosan modified with glutaric aldehyde with that of the copper complex with this polymer (0.5 wt % Cu) shows that introduction of copper causes broadening of the bands of OH and NH vibrations similarly to the unmodified polymer. However, unlike the blue complex prepared from the initial chitosan, the copper complex with chi-



**Fig. 2.** ESR spectra of different starting Cu/chitosan samples taken at 20°C: (1) coprecipitated 0.5% Cu/chitosan, (2) coprecipitated 1.5% Cu/chitosan, (3) 0.5% Cu/chitosan prepared by the adsorption method.

tosan modified with glutaric aldehyde is dark-brown. Therefore, we can assume that a considerable part of copper ions is reduced by the aldehyde in the course of the preparation. Nevertheless, binding of copper by the polymer matrix leads to a broadening of the absorption bands of OH and NH groups.

It stems from the IR-spectroscopic data that immobilization of copper on chitosan results in the formation of a rather stable complex. This conclusion is in agreement with the literature data on the capability of chitosan to irreversibly bind copper ions from diluted aqueous solutions [3–5]. However, two important questions arise in studying the use of copper-containing chitosan systems as heterogeneous catalysts: (1) whether or not the active Cu(II) sites are resistant toward decomposition and leaching in the course of the catalytic reaction and (2) if there are some peculiarities in the redox properties of copper centers immobilized on the chitosan matrix?

The loss of copper in the catalytic process cannot be significant, because the analysis of the liquid phase does not reveal any detectable concentrations of copper ions in the solution after catalysis. Quantitative analysis by the ESR method allows one to gain more detailed

information about the state and peculiar features of Cu(II) centers.

ESR spectra of three copper-containing chitosan samples are shown in Fig. 2. The signal of the precipitated complex (0.5 wt % Cu) is typical for magnetically isolated Cu(II) ions. The parameters of the hyperfine structure (HFS) ( $g_{\parallel} = 2.24$ ,  $A_{\parallel} = 179$  G,  $g_{\perp} = 2.045$ ) indicate that copper is stabilized in a local crystal field of a low symmetry close to the planar-square coordination [15]. Unfortunately, no signals of the additional hyperfine structure due to splitting on nitrogen atoms of the ligands are observed in the ESR spectra of Cu(II) in chitosan (Fig. 2). Thus, we cannot determine experimentally the number of N and O atoms in the coordination sphere of the copper ion. It follows, however, from DFT calculations [18] that the structure of disaccharide with copper, which contains simultaneously the  $\text{NH}_2$  and  $\text{CH}_2\text{OH}$  groups of the neighboring chitosan rings, is optimal. Presumably, the coordination sphere of the Cu(II) ion includes two  $\text{NH}_2$  and two  $\text{CH}_2\text{OH}$  groups. This hypothesis is supported by the literature data: ESR spectra with identical HFS parameters were found [3, 8, 19–21]. In the case of the samples kept overnight in distilled water, substantial swelling of the spherical globules of the copper–chitosan complex was observed (the diameter of the particles increased 2–2.5 times). However, no respective changes in the shape or intensity of the ESR signal were noticed. Thus, water molecules penetrating the interior of the polymer do not act as extra ligands coordinating copper(II) ions. Quantitative analysis of the ESR spectra, with the frozen  $\text{Cu}(\text{NO}_3)_2$  solution being used as a calibration standard [14, 15], gives the value of  $5.0 \pm 0.5$  mg of Cu(II) per 1 g of chitosan, i.e. almost all the introduced copper ions in the low-percentage sample are ESR-detectable isolated cations. The ESR signal of the sample with copper content 1.5 wt % (Fig. 2, curve 2) is similar to the spectrum presented in Fig. 2, curve 1, whereas its absolute intensity corresponds to a copper content of  $14.0 \pm 1.4$  mg Cu(II) per 1 g of polymer. Therefore, virtually all the copper ions in the precipitated samples with copper content below 1.5 wt % are isolated and contribute to the ESR signal intensity. Even in the case of the precipitated sample with the maximum copper content (9 wt %), the intensity of the ESR signal corresponds to about 2/3 of the total amount of introduced copper (Fig. 3, curve 1). However, in this case, the components of the hyperfine structure are not well resolved because of the interaction between paramagnetic copper ions (Fig. 3, curve 1).

The resolution of the HFS components in the spectrum of the low-percentage sample (0.5 wt %) prepared by the adsorption method (Fig. 2, curve 3) is not as good as in the case of the precipitated sample (Fig. 2, curve 1). The integral intensity of the signal corresponds to  $\sim 4$  mg of Cu(II) per 1 g of chitosan (80% of the introduced ions are detected by ESR). Most proba-

bly, the distribution of Cu(II) ions in the bulk of the impregnated globules is not uniform. However, even in this case, copper ions concentrated in subsurface layers are separated and do not form clusters with Cu–O–Cu bonds.

For the sample with copper content 0.5% on chitosan modified with glutaric aldehyde, a very weak ESR signal of Cu(II) is observed. This is indicative of the reduction of the main part of the introduced copper ions during treatment with the aldehyde. These data and the IR spectroscopic results provide evidence for rather strong complex formation between copper and chitosan sufficient for the stabilization of Cu(I) or Cu(0) species.

Special experiments were carried out to study the copper losses in the course of the catalytic process. As was already mentioned, the copper content in the liquid phase was below the detection limit. At the same time, it was noticed that catalytic tests or prolonged boiling in water cause significant changes in the color of the samples. It was of interest, therefore, to monitor the dynamics of the transformation of the Cu(II) ESR signal when the complex is subjected to various treatments.

ESR spectra of Cu(II) (Fig. 3) were taken at different stages of treatment of the precipitated sample with 9.0 wt % Cu in distilled water at 101°C. The sample loading was placed in a glass beaker (5 ml) containing 4 ml of water, sealed, and heated at a constant temperature (101°C) for a specified time interval. Upon cooling to room temperature, the sample was filtered, placed in an ESR ampule, and dried in a vacuum at room temperature. The corresponding changes in the integral intensity of the Cu(II) ESR signal are shown in Fig. 4. Hydrothermal treatment of the sample for 75 min provokes a 4-fold decrease in the signal intensity (Fig. 4) without any changes in the parameters of the signal. However, a further 3-min treatment of the sample at room temperature with a 1% aqueous solution of H<sub>2</sub>O<sub>2</sub> results in growth of the intensity to the starting value. Complete restoration of the signal (cf. Fig. 3, curve 1) unequivocally proves that quantitative reoxidation of all copper ions to Cu(II) occurs.

Hydrothermal treatment was also carried out for the sample containing 1.5 wt % Cu. Similarly to the above-described effects, boiling of the sample in water caused a dramatic (4-fold) decrease in the intensity of the Cu(II) ESR signal, whereas reoxidation with H<sub>2</sub>O<sub>2</sub> at 20°C led to a quantitative restoration of the initial signal. Thus, heating of the copper–chitosan complexes in distilled water results in reduction of a considerable part of the copper ions by the polymer matrix, presumably, with the participation of the reactive amino groups. The reduced active centers are stabilized by the matrix and can be quantitatively reoxidized to yield the starting complex. Oxidation of the amino groups of the ligand in the complex is possible during the interaction

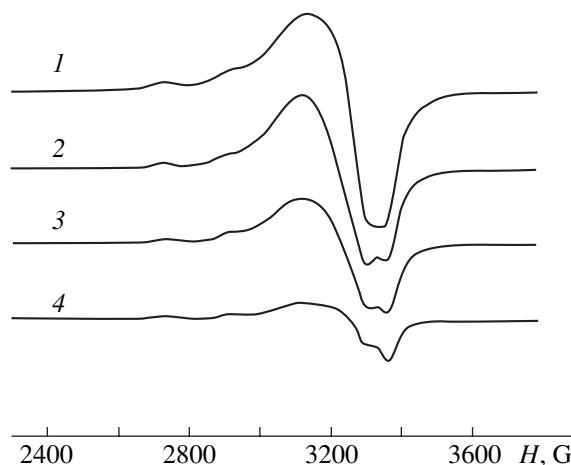
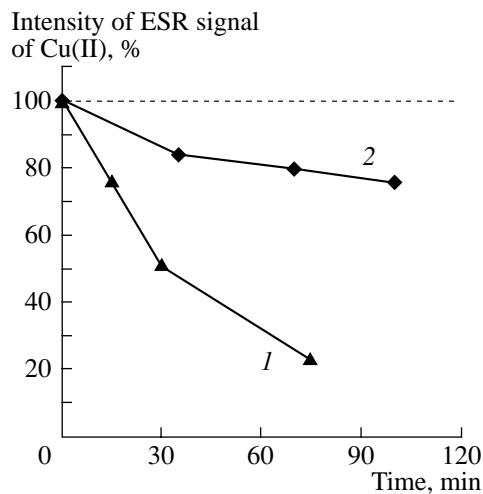


Fig. 3. ESR spectra of the 9% Cu/chitosan sample taken at 20°C at different stages of the treatment: (1) initial sample, (2–4) after hydrothermal treatment for 15, 30, and 70 min, respectively.

with H<sub>2</sub>O<sub>2</sub>, but we did not pay attention to the study of this reaction. The variation in the UV spectra during the redox transformations of complexes in water are presented in Fig. 5.

Thus, since the organic support is capable of reducing the Cu(II) centers upon heating chitosan in water, the question arises about the role of water in this process. The experiment was repeated with dry globules of the sample containing 9 wt % Cu, which was heated in an atmosphere of nitrogen. The sample loading was placed in a glass beaker (5 ml), purged with dry nitrogen, sealed, and heated at 101°C for a specified time interval. Such a thermal treatment in dry conditions, i.e. in a more dense and rigid polymer matrix, results in a significantly less pronounced reduction of Cu(II) in chitosan (Fig. 4). A still weaker effect was found upon heating the copper–chitosan complex at 80°C in liquid benzene. Obviously, swelling in water (with the size of globules increasing 2–2.5 times) provides the elasticity of the polymer matrix and is favorable for the interaction between the Cu(II) centers and the reactive groups of chitosan. Thus, water appears to be a perfect reaction media for the systems under study. Furthermore, the quantitative reoxidation of copper in the interior of the swollen chitosan particles with a diluted solution of H<sub>2</sub>O<sub>2</sub> provides evidence for the high extent of the permeability of the swollen polymer.

As was indicated above, the samples experience significant changes after their catalytic transformations. For all the samples the intensity of the Cu(II) ESR signal decreases by 30–40% while the parameters of the signal remain unchanged. Thus, the dynamic equilibrium Cu(II)  $\longleftrightarrow$  Cu(I) in the catalysts is substantially shifted toward the reduced state in the course of testing, meaning that the reoxidation stage is not fast under the reaction conditions. A new narrow ESR signal

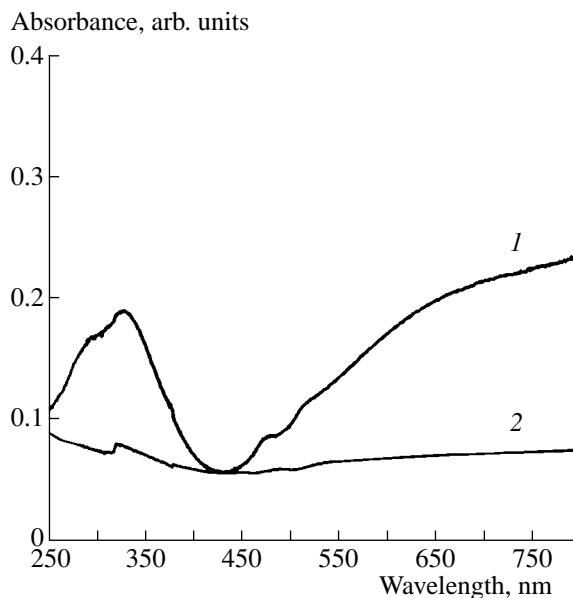


**Fig. 4.** Changes in the integral intensity of the ESR spectra of Cu(II) caused by the thermal treatment of the 9% Cu/chitosan sample at 101°C: (1) swelled globules in water, (2) dry globules in an  $N_2$  atmosphere.

with  $g \approx 2.005$  and  $\Delta H \approx 6$  G appears in the spectra of the Cu/chitosan and Cu/chitosan/SiO<sub>2</sub> samples after the catalytic reaction, in addition to the Cu(II) signal discussed above. The interpretation of this signal, observed on a broad background of the intense Cu(II) ESR signal, is a difficult problem. A narrow symmetric singlet with  $g \approx 2.002$  may appear as a result of the formation of a quinone cation radical. However, scrupulous inspection of this part of the spectrum allowed us to notice that the main signal with  $g = 2.005$  looks somewhat asymmetric, and two weak shoulders with  $g = 2.010$  and 2.000 can be revealed. A specific triplet with such parameters may indicate the stabilization of a paramagnetic species  $O_2^-$  on the catalytic site [22]. Additional studies may shed some light upon this problem and provide new data for an unambiguous interpretation.

From the viewpoint of the utilization of the samples under study in catalysis, of particular importance is the problem of accessibility of the catalytic sites in the bulk of the polymer globules. The contribution of the main part of the active centers localized in the interior of the polymer globules with a diameter of 2–3 mm may be insignificant. Therefore, thin-layer (egg-shell) catalysts were prepared for comparison with copper–chitosan complexes supported on inorganic carriers with a developed surface area (macroporous amorphous silica gel and mesoporous silica of the MCM-41 type with unidimensional channels).

When 1.8 wt % of the chitosan complex was supported onto the macroporous silica gel with initial surface area 330 m<sup>2</sup>/g, the sample containing 0.12 wt % Cu was obtained with specific surface area 210 m<sup>2</sup>/g. The



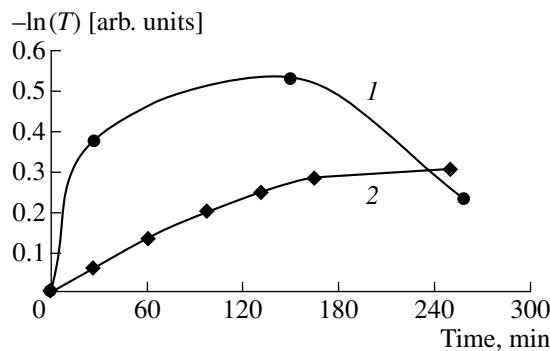
**Fig. 5.** UV-visible spectra of the 9% Cu/chitosan sample: (1) initial sample, (2) after hydrothermal treatment for 70 min.

data of scanning electron microscopy show that islands of the polymer film cover the inorganic support with a thin layer.<sup>1</sup> The ESR spectra of Cu(II) with a well resolved HFS correspond to the total amount of copper introduced in the sample and are supportive of the conclusion that this sample is identical to the bulk chitosan samples in terms of the localization and properties of the Cu(II) sites. Another catalyst (6.3 wt % of chitosan modified with glutaric aldehyde, 0.43 wt % Cu, specific surface area about 500 m<sup>2</sup>/g) was prepared by supporting the chitosan complex on the surface of the mesoporous MCM-41 carrier with diameter of channels ~4 nm and initial specific surface area 1040 m<sup>2</sup>/g.

The following copper-containing catalysts were compared in the catalytic tests: (1) free Cu(II) ions in an aqueous solution of CuCl<sub>2</sub>, (2) the homogeneous copper–chitosan complex, (3) the heterogeneous copper–chitosan complex (globules), and (4) the complexes of copper with chitosan on the surface of high-porosity carriers (silica gel, MCM-41).

When the homogeneous systems (1) and (2) were tested in oxidation of hydroquinone by oxygen in air, no oxidation products were found in the reaction mixture. The kinetic curves for the homogeneous systems presented in Fig. 6 seem to indicate that the copper

<sup>1</sup> The pictures of the surface of the samples with a magnification of 100–5000 were obtained using a JEOL JSM-5300 LV scanning electron microscope.

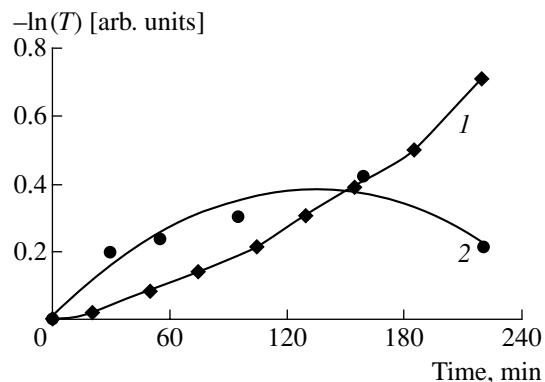


**Fig. 6.** Kinetics of hydroquinone conversion measured in  $\ln T$  (transmittance) units at 20°C in aqueous homogeneous solutions of (1)  $\text{CuCl}_2$  and (2) copper-chitosan complex.

complex is blocked by the quinone formed. Thus, the intermediate complex turns out to be quite stable under the chosen conditions and the catalytic activity of the homogeneous systems is very low.

The conversion of dihydroxybenzene isomers into the corresponding quinones is observed in the presence of the heterogeneous copper-chitosan complexes prepared by the adsorption and precipitation methods. The kinetics of hydroquinone oxidation is shown in Fig. 7. The initial reaction rate appears to be significantly higher for the sample prepared by the adsorption method (Fig. 7), but a substantial decrease of the reaction rate is observed for this catalyst with the progressing reaction. It follows from the ESR data that the distribution of  $\text{Cu}^{2+}$  ions in the interior of the globules prepared by impregnation is not uniform, and the  $\text{Cu}^{2+}$  sites are located preferentially in the layers near the surface of the globules. It is the higher concentration of the accessible surface  $\text{Cu}^{2+}$  ions that may be responsible for the higher initial activity of the catalyst prepared by the adsorption method, while the contribution of the active sites located in the interior of the globules of the precipitated samples is less significant. However, the high concentration of the accessible  $\text{Cu}^{2+}$  ions may cause the further decrease of the reaction rate of the catalysts prepared by the adsorption method. According to the literature data [23], the quinone products may form stable molecular complexes with amino groups of chitosan. It is plausible that the blocking effect is less pronounced for diluted and uniformly distributed sites in the matrix of the precipitated catalyst.

Comparative kinetic curves are shown in Fig. 8 for the precipitated sample and complexes supported on  $\text{SiO}_2$  and MCM-41. The reaction rate for pure silica is negligible. It is seen from the figure that the activity of the catalyst supported on the surface of the macroporous silica gel (specific surface area, 210  $\text{m}^2/\text{g}$ ) is significantly higher than the activity of the bulk glob-

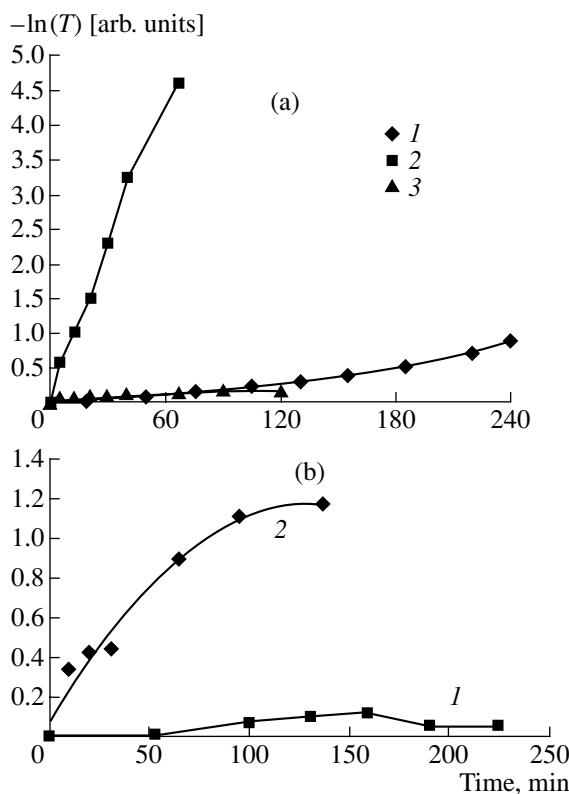


**Fig. 7.** Kinetics of hydroquinone conversion at 20°C on the heterogeneous 6.5% Cu/chitosan complex: (1) coprecipitated sample, (2) catalyst prepared by adsorption.

ules. While comparing these two systems, one should also take into account that the same loading of the silica-supported sample (1.8 wt % of Cu/chitosan on  $\text{SiO}_2$ ) contains 55 times less copper-chitosan complexes (i.e., 55 times less copper). Hence, the activity of the copper sites in a thin film of the polymer supported onto the inert macroporous  $\text{SiO}_2$  carrier and accessible to the substrates exceeds the activity of the active centers in the bulk catalyst at least by two orders of magnitude.

On the other hand, the activity of the systems supported onto the mesoporous MCM-41 carrier turned out to be rather low (Fig. 8a). This result can be easily explained by the peculiarities of the structure of MCM-41. The developed surface area of this mesoporous support is related to the existence of unidimensional nonintersecting channels with diameters of about 4 nm. Chitosan supported onto MCM-41 by impregnation and cross-linking may block the entrances to the channels, especially in the samples swollen in water. In this case the access of the substrate molecules in the channels is limited and the wet samples contain very few accessible active sites. At the same time, in BET measurements of the specific surface area after drying the samples in a vacuum, molecules of nitrogen can enter the channels, and, as a result, the high value of the specific surface area ( $\sim 500 \text{ m}^2/\text{g}$ ) can be obtained.

Thus, the examples of the copper complexes distinctly show the advantages of the systems based on chitosan complexes supported onto inorganic carriers with a developed specific surface area and a macroporous structure. Such an approach based on supporting thin chitosan films on the accessible surface seems to be most efficient for the synthesis of immobilized catalysts with extremely low content of noble or transition metals.



**Fig. 8.** Kinetics of oxidation of (a) hydroquinone and (b) catechol at 20°C on heterogeneous 6.5% Cu/chitosan catalysts: (1) bulk globules, (2) Cu/chitosan/SiO<sub>2</sub>, (3) Cu/chitosan/MCM-41.

## CONCLUSIONS

1. Heterogenized copper–chitosan complexes are active catalysts of liquid-phase oxidation of *o*- and *p*-dihydroxybenzenes, unlike homogeneous systems in which the formation of strong copper-hydroquinone complexes exerts an inhibiting effect on the yield of quinones.

2. Heterogenized copper–chitosan complexes supported onto the surface of macroporous silica gel (KSK, specific surface area 210 m<sup>2</sup>/g) exhibit a significantly higher activity in the oxidation of dihydroxybenzenes. In contrast, the use of the mesoporous MCM-41 carrier was shown to be inefficient, most likely as a result of blocking of the unidimensional channels (diameter, ~4 nm) by the polymer. The preparation of the catalysts with thin-film chitosan coating on the accessible surface opens up new horizons in the synthesis of immobilized chitosan catalysts with a low content of noble metals.

3. ESR data indicate that the matrix of the heterogenized chitosan is capable of stabilizing isolated Cu<sup>2+</sup> ions in a coordinatively unsaturated state. The estimate of the concentration of copper by ESR shows that all copper ions introduced in low-percentage samples (≤1.5 wt % Cu) are detectable by ESR, and the symmetry of the isolated Cu<sup>2+</sup> ions in chitosan is close to

square-planar coordination. Redox transformations of the active centers in the course of catalytic tests or prolonged hydrothermal treatment do not lead to leaching of copper to the liquid phase, and reoxidation of the catalyst by hydrogen peroxide results in complete restoration of the Cu(II) ESR signal.

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