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 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 H$_2$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.

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 CuCl$_2$·2H$_2$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/NH$_2$, was 0.64). The stirring rate of 500 rpm was maintained for 4 h until com-
completion 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 CuCl₂ 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 homogenous 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 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 CuCl₂. 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 SiO₂ (KSK).** A weighed amount (1 g) of amorphous SiO₂ (KSK, particle size, 0.25–1 mm, surface area 330 m²/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 silica 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 SiO₂ with unidimensional channels, diameter of channels, ~4 nm, surface area 1040 m²/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 cm⁻¹ at a resolution of 8 cm⁻¹ and Matte- son Galaxy Series FTIR 5000 spectrometer in the range of 4000–600 cm⁻¹ at a resolution of 4 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.