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Heterogenized redox catalysts on the basis of the chitosan matrix 1. Copper complexes

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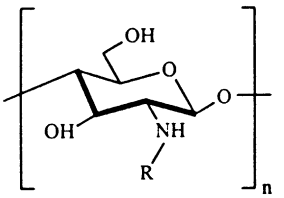
Abstract

Series of heterogenized copper complexes are prepared by either coprecipitation or adsorption of Cu(II) on the bulk chitosan and composite supports (egg-shell type chitosan/SiO_2 and chitosan/MCM-41systems). The morphology and properties of the catalysts are studied by FTIR, UV-Vis, SEM, and ESR methods, and the activity of the redox sites immobilized by the chitosan matrix is tested in oxidation of *o*- and *p*-dihydroxybenzenes in water. The estimate of the copper concentration derived from the ESR data shows that essentially all Cu(II) ions introduced in low-loaded samples ($\leq$1.5 wt.% Cu) are ESR-visible, with the symmetry of isolated Cu^{2+}-sites in chitosan approximating the square-planar coordination. Redox transformations of the active sites in the course of catalytic tests or prolonged boiling in water are not accompanied by copper leaching from the chitosan matrix, and the catalyst reoxidation by H_2O_2 leads to quantitative restoration of the Cu(II)-ESR signal. Thus, the matrix of chitosan is able to stabilize and retain isolated Cu^{2+} ions in highly coordinatively unsaturated state. In contrast with a homogeneous copper–chitosan system demonstrating copper–hydroquinone complexation that suppresses dramatically the yield of the oxidation products, the heterogenized samples are active and stable catalysts in the process of quinone formation. The binary composite system, with a thin film of low-loaded Cu–chitosan supported on macroporous SiO_2, demonstrates significantly higher activity in oxidation of hydroquinone, as compared with the bulk Cu/chitosan sample. This approach to catalyst design opens up a promising way for synthesis of the supported chitosan catalysts with a very low content of noble metals.

Keywords: Chitosan; Cu(II) immobilization; Heterogenized redox catalysts; Cu/chitosan/silica catalysts; Hydroquinone oxidation; FTIR; ESR

1. Introduction

Chitosan, i.e. *N*-deacetylated chitin (poly(1–4)*N*-acetyl-β-D-glucosamine), is a



biodegradable polysaccharide containing different functional groups. It is well known that this polymer demonstrates the unique adsorption ability towards many metal cations and atoms of Periodic Table.

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Thus, this system being capable of strongly binding different ions attracts now growing attention in view of its utilization for removal of cations of heavy metals from diluted aqueous solutions [1–5]. Some data about physical properties of cations entrapped by the chitosan are also available [6–9]. On the other hand, the systems prepared by immobilization of cations by the chitosan matrix can be considered as ecologically friendly catalysts. However, surprisingly, only a few publications focused on application of on chitosan-supported metal complexes in heterogeneous catalytic processes are available in the open literature [10–12]. At the same time, transition metal ions and complexes immobilized on the polymer supports attract increasing attention due to combination of the advantages of homogeneous and heterogeneous catalysts. It is important, from our point of view, that hydrophilic chitosan-supported catalysts could be useful for oxidation processes of fine organic synthesis, such as oxidation of terminal olefins, catechols and catecholamines in water.

The aim of this study is the preparation of diverse chitosan-supported catalysts and the detailed study of the morphology and properties of the catalysts, as well as catalytic testing of the redox sites immobilized by the chitosan matrix in model oxidation processes, such as hydroquinone and olefin oxidation. The first part of our work is devoted to the study of heterogenized copper-containing catalysts on the basis of the chitosan matrix.

2. Experimental

2.1. Materials

As received chitosan powder (made in Korea from crab shells, molecular weight 100,000–150,000) was used without further purification. The deacetylation degree of amino groups was 70%, the moisture content in the chitosan powder was 3 wt.%. Glutaric dialdehyde (chemically pure grade; ca. 25 vol.% in water) was used as a crosslinking agent. SPAN® 60 (sorbitan monostearate) used as emulgator and $CuCl_2 \cdot 2H_2O$ salt were purchased from Fluka AG (Switzerland) as analytical grade reagents. HCl and NaOH were also of analytical grade purity.

2.2. Catalyst preparation

2.2.1. Homogeneous copper–chitosan complex

The calculated amount of $CuCl_2$ 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 blue clear solution. For the FTIR spectroscopic study the homogeneous copper–chitosan solution was deposited on quartz plates and air-dried for 48 h.

2.2.2. Coprecipitation method

The blue clear solution of the homogeneous copper–chitosan complex (0.5–9 wt.% of Cu) was prepared as described above. Then the solution obtained was added drop-wise to a glass beaker with a 0.05 M NaOH solution, with immediate coagulation of drops into spherical globules. Spherical particles formed (diameter, 2/3 mm) were filtered off after 10 min and repeatedly washed by distilled water until neutral pH. After this procedure, globules of the copper–chitosan complex were filtered off and air-dried at room temperature during 48 h.

2.2.3. Adsorption method

A 1.5 wt.% solution of chitosan was added drop-wise to a glass beaker with 0.05 M NaOH solution, with immediate formation of spherical globules of pure chitosan. Particles were filtered off after 10 min, repeatedly washed by distilled water until neutral pH, filtered again, and air-dried at room temperature during 48 h. The weighed amount of copper chloride (calculated assuming quantitative absorption of Cu^{2+}) was dissolved in 20 ml of distilled water and stirred with 1.0 g of dried chitosan particles for 20 min. Then the particles were removed by filtration, washed with distilled water and air-dried for 24 h.

2.2.4. Immobilization of the copper–chitosan complex on the surface of porous silica gel

One gram of amorphous SiO_2 (aerosil; fraction 0.25–1 mm; $S_{BET} = 330\,m^2/g$; water absorption capacity 1.2 ml/g) was impregnated with 1.2 ml of a solution of the homogeneous copper–chitosan complex prepared as mentioned above. Then complex-loaded silica was placed in a 0.05 M solution of NaOH for 15 min, filtered off and repeatedly washed by distilled water until neutral pH. The particles obtained were

dried at room temperature in air for 24 h and then in a vacuum for 10 h.

2.2.5. Immobilization of the copper–chitosan complex on the surface of mesoporous MCM-41

One gram of MCM-41 [pure SiO_2 with one-dimensional channel structure (channel diameter ~4 nm, $S_{BET} \cong 1040\,m^2/g$); water absorption capacity ~4.6 ml/g] was impregnated with 4.6 ml of a 1.5 wt.% solution of chitosan. Then chitosan-loaded MCM-41 was treated with 1.5 ml of 25 vol.% glutaric dialdehide for 3 h, repeatedly washed by distilled water to remove the excess of glutaric dialdehide, and filtered off. The particles obtained were dried at room temperature in air for 48 h and then in a vacuum for 24 h. The weighed amount of copper chloride (calculated assuming quantitative absorption of Cu^{2+} on chitosan) was dissolved in 20 ml of distilled water and stirred with dried chitosan-loaded MCM-41 particles for 30 min. Then the particles were removed by filtration, washed with distilled water, air-dried for 24 h and then in a vacuum for 24 h.

2.2.6. Copper complex with chitosan modified by glutaric dialdehyde

The necessary amount (60 cm^3) of the homogeneous copper–chitosan complex solution in water was added to 60 cm^3 of hexane containing 5 wt.% of SPAN® 60, and the mixture formed was stirred at 60 °C at 3000 rpm to form a water-in-oil emulsion. Then the stirring speed was slowed down to 500 rpm, and 13 ml of a 25 vol.% aqueous solution of glutaric dialdehyde (crosslinking ratio GA/–NH_2 = 0.64 mol/mol) was added drop-wise into the emulsion. The stirring speed was kept at 500 rpm for 4 h during the entire crosslinking process. The product was filtered off and washed several times first by distilled water at 80 °C and then by hexane at 60 °C to remove SPAN® 60 from the complex. The sample obtained was dried at room temperature in air for 48 h.

2.3. Catalytic testing

Catalysts containing 6.5 wt.% Cu were tested at 20 °C in oxidation of isomeric *o*- and *p*-dihydroxybenzenes into corresponding quinones by air. The catalyst loading together with the aliquot of the aqueous solution of dihydroxybenzene (catalyst/substrate molar ratio = 0.1) were placed in the open glass reactor and stirred with a magnetic stirrer. Probes of the reaction mixture were taken periodically for the analysis. The UV-Vis technique (Specord M40) was used to control the reaction proceeding by monitoring the UV absorption by quinones. The absorption bands at 390 and 428 nm were observed for *o*-benzoquinone (pyrocatechol) and *p*-benzoquinone (hydroquinone), respectively. Concentrations of quinones were plotted in arbitrary units, optical density ln(*T*), being proportional to the amount of the compound formed.

2.4. IR-spectroscopic and UV-Vis studies

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 Matteson Galaxy Series FTIR 5000 spectrometer in the range of 4000–600 cm^{-1} at a resolution of 4 cm^{-1} in two modes. (1) Dry globules of chitosan samples were crushed and ground in a mortar by pestle, then the fine powder was mixed with KBr, pressed into a thin pellet, and placed in the sample holder of the Nicolet spectrometer. The OMNIC program was used for the treatment of the spectra. (2) Globules of the sample were ground with a drop of perfluorinated oil in an agate mortar, and the IR spectrum of the mull was recorded between NaCl plates [13]. Then the same specimen was used for UV-Vis spectra recording in the 250–800 nm range (1 nm resolution) in the absorbance mode using a Perkin-Elmer UV/Vis Lambda 18 spectrometer. The use of oil permits to reduce drastically light scattering, which is too strong for dry powders, especially in the UV region [13]. The UV-Vis spectrum of pure chitosan was recorded and subtracted from the spectra of Cu-containing samples as the baseline to discriminate the absorbance by copper sites only. FTIR spectra of the material dispersed in perfluorinated oil (baseline correction, oil spectrum subtraction) were manipulated using the WIN-FIRST software. Strong absorbance peaks due to perfluorinated oil were observed in the 1300–1100 cm^{-1} region, but do not interfere with measurements in the 4000–2000 cm^{-1} region, where the bands of (–OH, –NH, –CH) groups were revealed.

2.5. SEM study

SEM pictures of the sample surface were obtained using a scanning electron microscope JSM-5300LV JEOL. The surface before imaging was decorated by a thin gold layer using JFC-1100E device.

2.6. ESR measurements

ESR spectra were taken in the X-band ($\lambda \cong 3.2$ cm) at 20 and −196 °C using a Bruker ESP300 spectrometer equipped with a 4104OR cavity and a quartz Dewar.[1] The ESR signals were registered at a microwave power of 6.35 mW and modulation amplitude of 2.0 G in the field range of 2000–4000 G (5 scans with a sweep time of 42 s) or 100–4600 G (2 scans with a sweep time of 84 s). The Bruker ESP300E software and the special Bruker program WIN-EPR (version 901201) were used for data processing (baseline correction, double integration). DPPH and frozen water solutions of $Cu(NO_3)_2$ were used as standards for g-factor calculation and quantitative Cu^{2+} ESR analysis.

Globules of catalysts were placed in quartz ampoules to fill the identical volume (3.5 mm diameter × 15 mm height), weighed, evacuated for ∼10 min to 0.03 Torr at 20 °C, and sealed off. ESR spectra were registered at 20 °C and normalized for the differences in the sample weight. Then the ampoules were open to air and ESR measurements were repeated. After that, the globules were impregnated with distilled water and swelled overnight. Then the ampoules were cooled down in liquid nitrogen, and ESR spectra were recorded at −196 °C. These spectra were taken for comparison with those of frozen $Cu(NO_3)_2$ solutions for calculation of the "ESR-visible" fraction of Cu^{2+} in our samples [14,15]. For the sake of accuracy, series of samples were measured consecutively, with ampoules placed in the same position inside the ESR resonator.

3. Results and discussion

FTIR spectra of pure chitosan and the 1.5% Cu/chitosan sample prepared by precipitation are compared in Fig. 1a and b. The spectrum shown in Fig. 1a is pretty close to that reported in the paper [16] devoted to chitin and chitosan characterization by FTIR. As one can see, Cu(II) bonding causes a noticeable change in the shape of the broad absorption line at 3700–1700 cm^{-1} typical of different types of (–OH, –NH) vibrations in polymers. Complexation of Cu(II) ions by the chitosan matrix results in substantial redistribution of vibration frequencies in the above-mentioned region, with a shift to lower wavenumbers. Thus, even for the low-loaded samples, the interaction [Cu^{2+}-polymer matrix] is strong enough to disturb (–OH, –NH) bonds in chitosan. For the sample with 9 wt.% of Cu, this effect is stronger, but quantitation in this case is impossible. It is important also to note that the spectrum of 1.5% Cu/chitosan prepared by impregnation of wet chitosan globules with a Cu(II) solution is identical to the spectrum of the precipitated sample (Fig. 1b). Therefore, complexation of Cu(II) ions with chitosan globules results in ion bonding similar to Cu^{2+}-polymer bonding in the

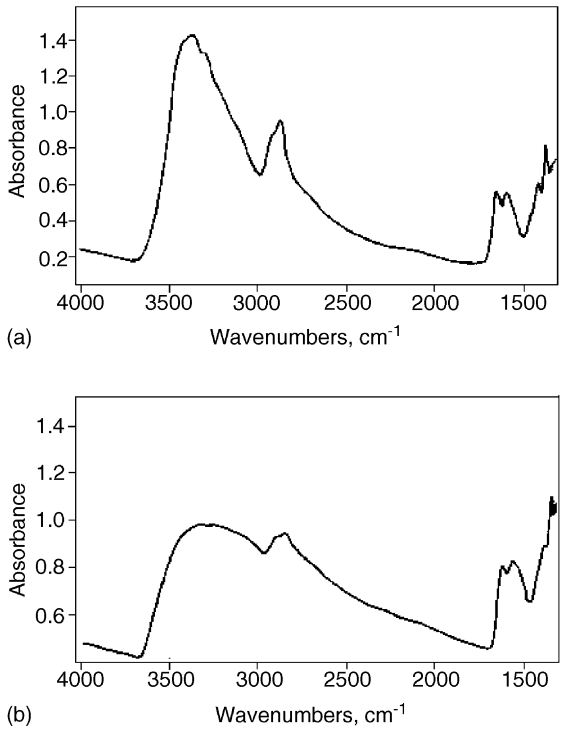


Fig. 1. FTIR spectra, taken at 20 °C for the (OH–, NH–, CH–) vibrations region, of heterogenized chitosan (a) and 1.5% Cu/chitosan (b) samples.

[1] A.V. Kucherov thanks Ford Scientific Labs. (Dearborn, Michigan, USA) for permission to use the spectrometer.

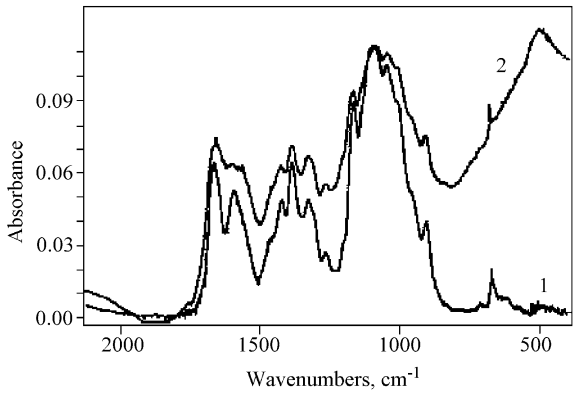


Fig. 2. FTIR spectra, taken at 20 °C for the valence vibrations region, of pure chitosan (1) and 3% Cu/chitosan (2) samples.

uniform sample precipitated from the homogeneous solution.

The spectra of two samples taken in the range 400–2000 cm^{-1} are presented in Fig. 2. Copper introduction into chitosan results in the appearance of a strong band at ~470 cm^{-1}, which could be ascribed to stretching vibrations of Cu^{2+}–N bonds [17]. For the dried homogeneous Cu-complex, this band is observed at 466 cm^{-1}. The frequency values could be indicative of the chelate copper complex, for example the one calculated by the DFT method ($\nu = 472\ cm^{-1}$) in [18]. In the spectrum of the used catalyst, a shoulder at ~590 cm^{-1} appears, which can be attributed to complexation of NH_2-groups with monovalent Cu^{+} ions [17].

FTIR spectra of pure chitosan and the sample 0.5%Cu/chitosan crosslinked with glutaric aldehyde are shown in Fig. 3a and b. Crosslinking itself results in some broadening of the (–OH, –NH) vibration bands (Fig. 3a versus Fig. 1a) but the presence of copper causes a further measurable broadening of these bands (Fig. 3). In contrast to light-blue 0.5% Cu/chitosan, the sample prepared by treatment of 0.5% Cu/chitosan with glutaric aldehyde is dark-brown, i.e. substantial copper reduction upon preparation can be anticipated. In spite of this, complexation of copper with the polymer matrix is strong enough to cause a substantial redistribution of the (–OH, –NH) vibration frequencies.

Summarizing the FTIR data, we can conclude that copper immobilization by chitosan causes the formation of rather strong complexes. This conclusion

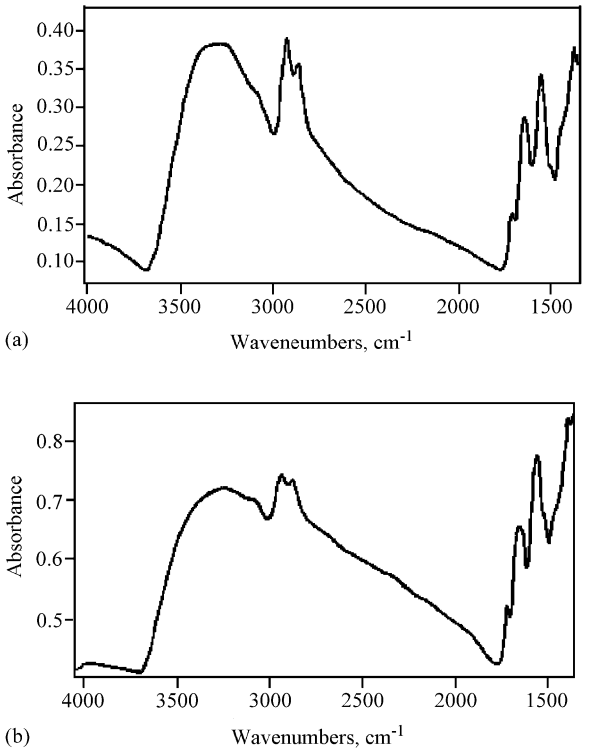


Fig. 3. FTIR spectra, taken at 20 °C for the (OH–, NH–, CH–) vibrations region, of chitosan crosslinked with glutaric aldehyde (a) and the same support containing 0.5% of copper ions (b).

agrees with the known data about the ability of chitosan to absorb copper irreversibly from diluted aqueous solutions [3–5]. However, in studying Cu/chitosan system as the heterogeneous catalytic system, two important questions arise: (1) are the Cu^{2+} active sites stable enough against decomposition and leaching upon catalysis? and (2) are there any peculiarities of redox properties of copper sites immobilized by the chitosan matrix?

The copper loss upon catalytic testing seems to be negligible because the analysis of the liquid phase shows no measurable presence of copper ions in aqueous solutions after catalysis. However, a detailed quantitative ESR study permits to understand much better the peculiarities of Cu^{2+} properties and distribution in the system under investigation.

Fig. 4 shows the Cu(II) ESR spectra of four Cu/chitosan samples. The signal from precipitated 0.5% Cu/chitosan (Fig. 4a) is typical of a well magnetically separated Cu(II) ions. The parameters of

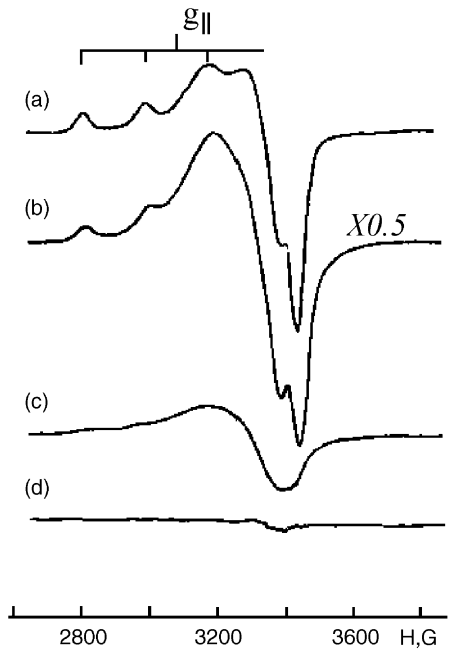


Fig. 4. ESR spectra, taken at 20 °C, for different fresh, dried Cu/chitosan samples: (a) precipitated 0.5% Cu/chitosan; (b) precipitated 1.5% Cu/chitosan; (c) "absorption made" 0.5% Cu/chitosan; (d) 0.5% Cu on chitosan crosslinked with glutaric aldehyde.

hyperfine splitting (hfs) ($g_{||} = 2.24$, $A_{||} = 179$ G; $g_{\perp} = 2.045$) point to the local crystal field of a low symmetry being close to the square-planar coordination [15]. ESR spectra with very similar hfs parameters were reported earlier, and the same tetragonal symmetry was supposed [3,8,19–21]. When the sample was allowed to stay overnight in distilled water a substantial swelling of the spherical globules of Cu/chitosan was observed, with a 2–2.5-fold increase in the particle diameter. At the same time, no significant changes of the ESR signal shape or intensity were noticed. Thus, H_2O molecules penetrating inside polymer are not coordinated as additional ligands to the Cu(II) sites. Quantitation of Cu(II) by comparison with a standard frozen $Cu(NO_3)_2$ solution [14,15] gives a value of 5 ± 0.5 mg of Cu^{2+} per 1 g of chitosan, i.e. virtually all the copper ions in the precipitated low-loaded sample are ESR-visible and originally stabilized as isolated cations in the Cu^{2+} valence state. The ESR signal of the 1.5% Cu/chitosan sample with a higher concentration of copper is shown in Fig. 4b. The hfs in this signal is still rather well resolved, and the absolute intensity of the spectrum (Fig. 4b) corresponds to the presence of 14 ± 1.4 mg of Cu^{2+} in 1 g of the polymer. Again, virtually all the copper sites in the precipitated sample with 1.5 wt.% Cu contribute to the ESR signal from magnetically separated Cu(II) ions. Even for the precipitated sample with a maximum copper loading of 9 wt.%, the ESR signal intensity corresponds to ~2/3 of the copper ions introduced, but in this case, the hfs is not resolved due to a considerable interaction between paramagnetic Cu(II) ions in this concentrated solid solution.

The ESR signal for the 0.5% Cu/chitosan sample prepared by impregnation of solid chitosan (Fig. 4c) demonstrates a considerably less resolved hfs, as compared with the corresponding precipitated sample (Fig. 4a). However, the integral signal intensity corresponds to ~4 mg of Cu^{2+} per 1 g of the polymer (80% of copper is ESR-visible). It looks like the distribution of Cu^{2+} ions in the interior of the impregnated chitosan globules is not uniform, but even Cu^{2+} species concentrated in the near-surface layers are diluted and do not form clusters with Cu–O–Cu bonding.

A very weak Cu(II) ESR signal for the sample 0.5% Cu/chitosan crosslinked with glutaric aldehyde (Fig. 4d) confirms that the main part of the starting Cu(II) ions is reduced upon the treatment. This result being considered together with the FTIR data (Fig. 3) gives the evidence that complexation of copper with the chitosan (–OH, –NH) groups is strong enough even for the Cu^{+} (or Cu^{0}) valence state.

A special series of ESR measurements was initiated by the study of copper loss upon catalytic testing. As was mentioned above, copper washing out by the liquid phase was below the detection limit. At the same time, catalytic testing or boiling in water is accompanied by a substantial change of the sample color. Thus, dynamics of the Cu(II) ESR signal transformations caused by Cu/chitosan treatment in different conditions was studied.

Fig. 5 shows four Cu(II) ESR spectra taken at different steps of the precipitated 0.5% Cu/chitosan sample treatment in distilled water. The corresponding changes in the integral signal intensity (percentage of copper in the Cu^{2+} valence state) are shown in Fig. 6. After every treatment step, the sample charge was dried by evacuation at 20 °C before ESR measurements. Boiling of the sample for first 10 min causes a loss of ~3/4 of the starting Cu^{2+} ESR signal (Fig. 5b),

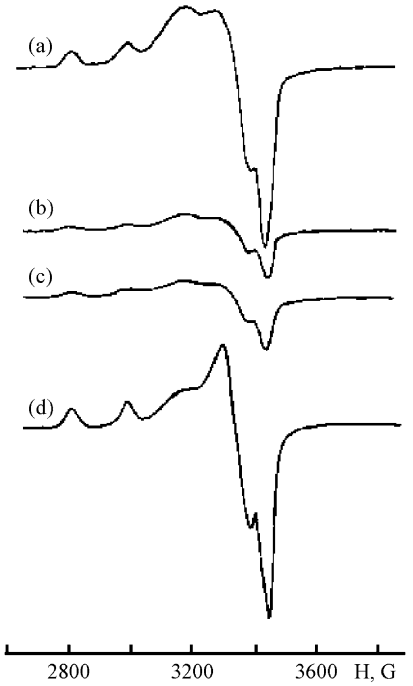


Fig. 5. Changes of ESR spectra, taken at 20 °C, caused by different steps of treatment of 0.5% Cu/chitosan sample (a) fresh precipitated 0.5% Cu/chitosan; (b) after boiling in distilled water for 10 min; (c) after boiling in distilled water for 60 min; (d) after reoxidation by 1% aqueous H_2O_2 solution for 5 min at 20 °C.

and further boiling does not lead to substantial changes of the ESR spectrum (Fig. 5c). However, subsequent treatment of the sample at room temperature with a 1% solution of H_2O_2 for 5 min causes a dramatic enhancement of the ESR signal intensity, as shown in Fig. 5d. The buildup of this signal, with the same hfs and the original integral intensity (Fig. 6), demonstrates clearly a quantitative restoration of the Cu(II)-valence state for all copper ions in the sample.

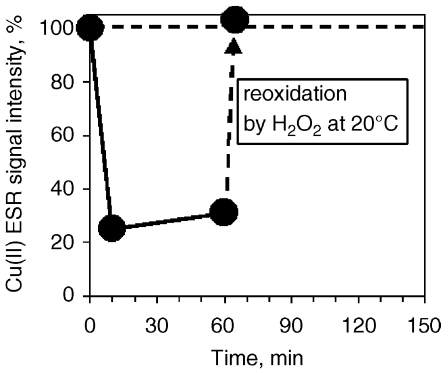


Fig. 6. Changes of the integral intensity of Cu(II) ESR spectra caused by different steps of treatment of 0.5% Cu/chitosan sample (see Fig. 5).

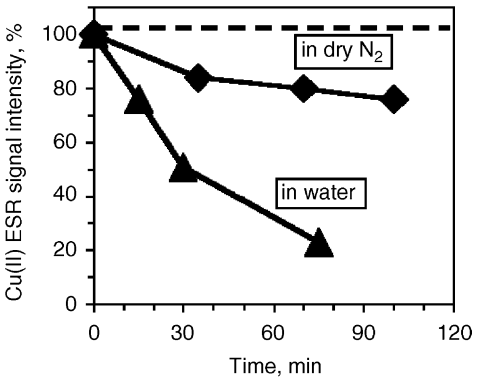


Fig. 7. Changes of the integral intensity of Cu(II) ESR spectra caused by stepwise heating of 9% Cu/chitosan sample at 100 °C: (1) swelled globules in liquid water; (2) dry globules in atmosphere of N_2.

The similar approach was repeated for the sample with a maximum copper content of 9 wt.%. The sample charge was placed into a 5 cm^3 flask containing 4 cm^3 of water, closed hermetically and placed into a thermostat at 101 °C for a given time. After cooling to room temperature, the sample was filtered off, placed into an ESR ampoule, and dried by evacuation at room temperature. Again, a drastic loss of the Cu(II) ESR signal intensity accompanied the sample heating in water (Fig. 7, curve 1), and the ESR-visible Cu(II) ions regained the intensity after the subsequent reoxidation by H_2O_2. Thus, heating of the Cu/chitosan system in distilled water leads to the reduction of the main part of Cu(II) ions by the polymer matrix, but these reduced sites are retained by chitosan and can be quantitatively reoxidized. Color changes accompanying redox transformations of Cu/chitosan upon heating in water are illustrated by UV-Vis spectra (Fig. 8).

If the organic support is able to reduce Cu^{2+} sites upon heating of the chitosan being swelled in water, the question arises about the role of water in this process. So, the experiment was repeated with the dry 9% Cu/chitosan sample heated in a nitrogen atmosphere. The sample charge was placed into a 5 cm^3 flask, purged with dry N_2, closed hermetically, and placed

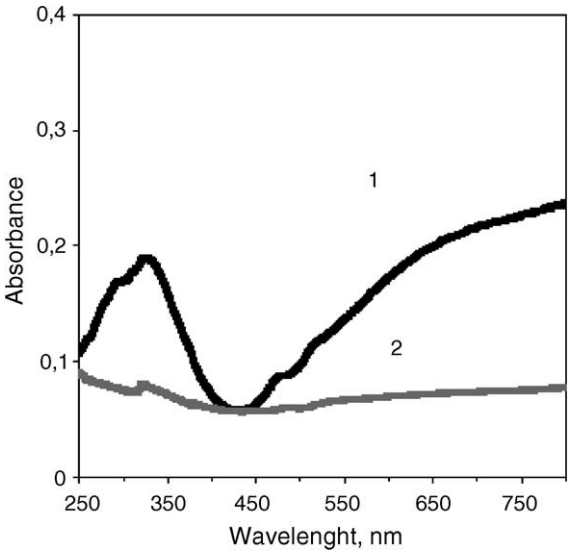


Fig. 8. UV-Vis spectra of fresh 9% Cu/chitosan sample (1) and the same sample heated with water for 75 min (2).

into a thermostat at 101 °C for a given time. Surprisingly, the same thermal treatment in dry conditions (i.e. with much more dense and rigid polymer matrix) causes a substantially weaker reduction of Cu(II) sites of chitosan (Fig. 7, curve 2). Even a smaller effect was found upon Cu/chitosan heating at 80 °C in liquid benzene. It looks like swelling in water (with a 2–2.5-fold increase of the size of globules) provides flexibility of the polymer matrix and facilitates considerably the interaction between Cu(II) sites and reactive groups of chitosan. Thus, water seems to be a very good reaction medium for the system under study. Moreover, the quantitative reoxidation of the copper sites in the core of swelled chitosan particles by a diluted solution of hydrogen peroxide also shows that the permeability of swelled polymer is high enough.

As was mentioned above, catalytic testing caused a substantial change of the samples. A loss of 30–40% of the Cu(II) ESR signal intensity is observed for the samples taken after catalysis. Thus, the dynamic equilibrium $Cu^{2+} \leftrightarrow Cu^{+}$ in working catalyst is shifted substantially to the reduced state, i.e. the reoxidation step in the reaction conditions is not fast. In addition to the Cu(II) ESR signal, a new narrow line appears, with $g \cong 2.005$ and $\Delta H \cong 6$ G, in the ESR spectra of the used Cu/chitosan and [Cu/chitosan]/SiO_2. The presence of a strong ESR signal from Cu^{2+} ions disturbs considerably the baseline of the narrow signal and hinders the interpretation. From one side, a narrow symmetric singlet at $g \cong 2.002$ could be indicative of the quinone cation-radical formation. However, in more detail study of this part of the spectrum the main line at $g \cong 2.005$ looks slightly asymmetric, and two weak shoulders can be identified, at $g \cong 2.010$ and 2.000. In turn, the specific triplet with the parameters obtained could point to the stabilization of paramagnetic $(O_2)^-$ species on catalytic sites [22]. Now, without additional data, it is impossible to single out the interpretation.

However, the problem of the accessibility of active sites is of major importance from the viewpoint of catalytic application of the samples prepared. It is highly probable that the contribution of the main part of sites localized in the interior o the bulk globules of polymer with diameter of 2–3 mm is rather small. So, the egg-shell systems, with a film of polymer covering an inert inorganic support (macroporous amorphous silica gel or mesoporous tubular MCM-41 material), were prepared for comparison with bulk globules of Cu/chitosan. The surface area of 210 m^2/g was found for the catalyst with ~0.12 wt.% Cu, containing 1.8 wt.% of [Cu/chitosan] supported on amorphous silica with wide pores and starting S_{BET} = 330 m^2/g. SEM images of this sample confirm that islands of the thin film of polymer cover the inorganic support (Fig. 9). Cu(II) ESR spectra with well resolved hfs correspond to all the copper introduced and demonstrate that the localization and properties of Cu(II) sites in this sample are identical to those in bulk chitosan samples. As to the sample with 6.3 wt.% of [Cu/chitosan] (or ~0.43 wt.% Cu) supported on MCM-41 (with channels of ~4 nm diameter and starting S_{BET} = 1040 m^2/g), the catalyst with the surface area of ~500 m^2/g was obtained.

In catalytic comparative tests, a series of copper samples was studied: (1) free Cu^{2+} ions in aqueous $CuCl_2$ solution; (2) homogeneous Cu/chitosan complexes; (3) heterogeneous bulk Cu/chitosan globules; and (4) heterogeneous egg-shell catalysts Cu/chitosan/SiO_2 and Cu/chitosan/MCM-41.

As to homogeneous systems (1) and (2), no free oxidation product was detected in the reaction mixture upon hydroquinone oxidation with O_2. The kinetics curves shown in Fig. 10 for the homogeneous systems can be indicative of the formation/accumulation of the

copper/hydroquinone complex only. Thus, under reaction conditions chosen, intermediate complexes are stable, and the catalytic activity of homogeneous systems is negligible.

Transformation of isomeric dihydroxybenzenes into corresponding quinones can be detected in the reaction mixture in the presence of heterogeneous bulk Cu/chitosan catalysts prepared by either precipitation or absorption. The kinetics of hydroquinone oxidation is shown on Fig. 11. The initial rate of the reaction seems to be significantly higher for the sample prepared by copper absorption (Fig. 11) but after some

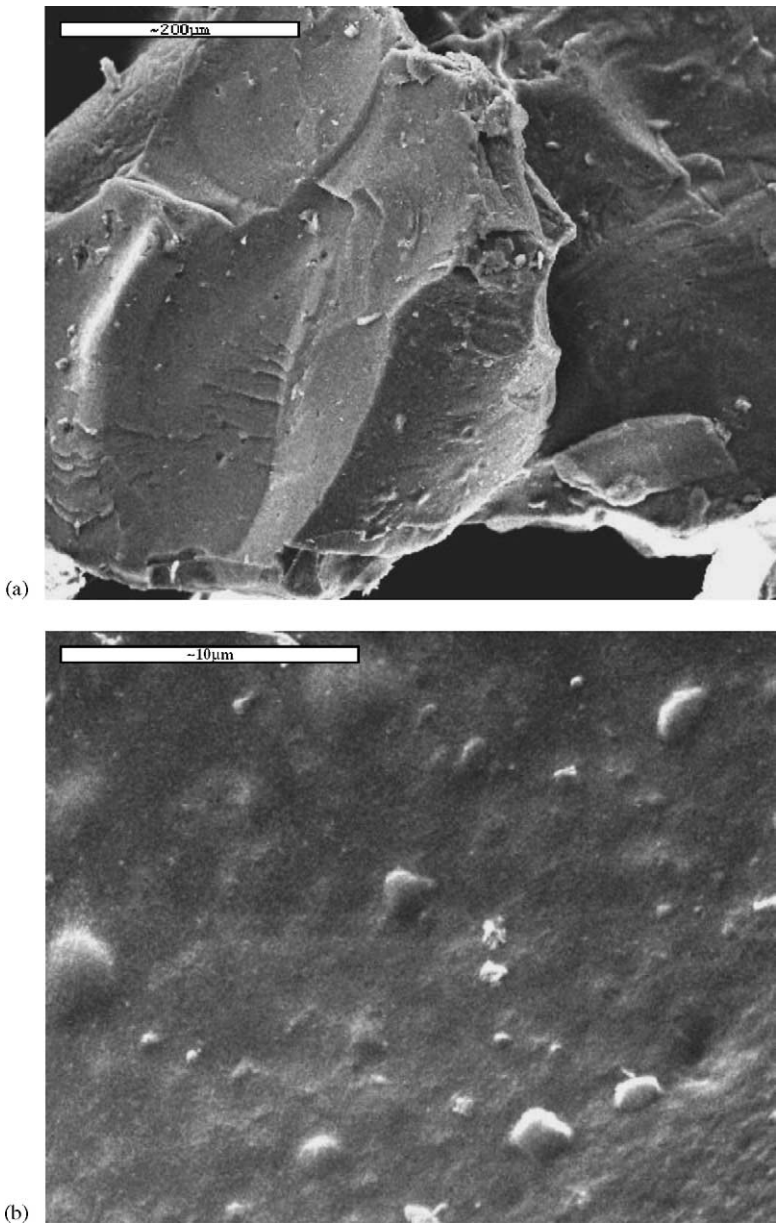
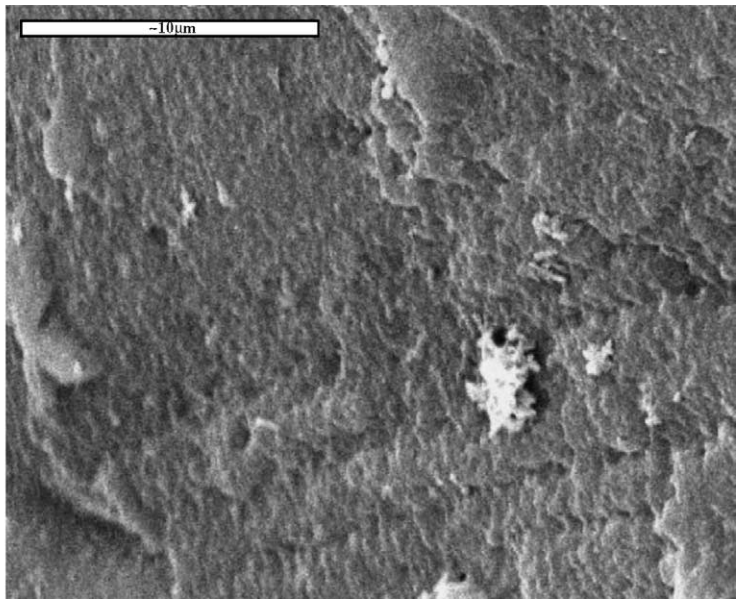


Fig. 9. SEM images of the egg-shell sample 1.8% [6.5%Cu/chitosan]/SiO_2: (a) SiO_2 particle covered by chitosan; (b) SiO_2 surface covered by the chitosan film; (c) free SiO_2 surface.



(c)

Fig. 9. (*Continued*).

period of time the retardation of the process becomes substantial for this catalyst. It was shown by ESR data that the distribution of Cu^{2+} ions inside the impregnated chitosan globules is not uniform, and Cu^{2+} species are concentrated in the near-surface layers of globules. So, a higher concentration of accessible Cu-sites can be responsible for the enhanced initial activity of the "absorption-type" sample, especially if the contribution of the internal sites inside the globules of precipitated samples is small enough. However, the same higher density of accessible Cu^{2+} sites could be responsible, in our opinion, for the subsequent reaction retardation on the "absorption-type" catalyst. It seems that both the product and an intermediate quinhydrone (formed at the initial step of the oxidation) create the stable molecular complex with amino- groups of heterogeneous Cu/chitosan, and the effect is considerably less pronounced for more

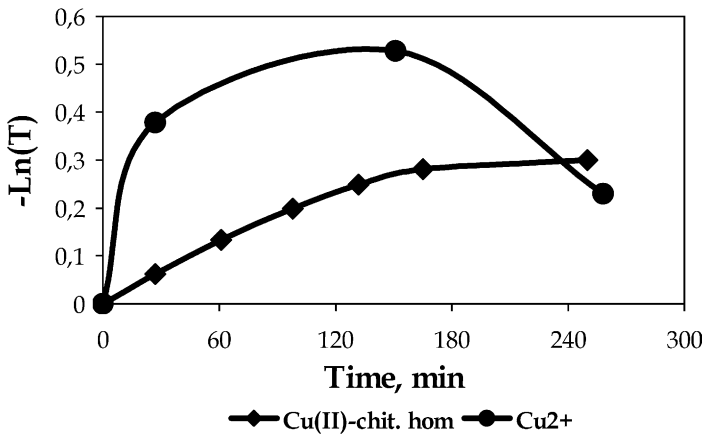


Fig. 10. Kinetics of hydroquinone transformation, at 20 °C, in homogeneous aqueous solutions of $CuCl_2$ (1) and Cu–chitosan complex (2). "*T*": transmittance.

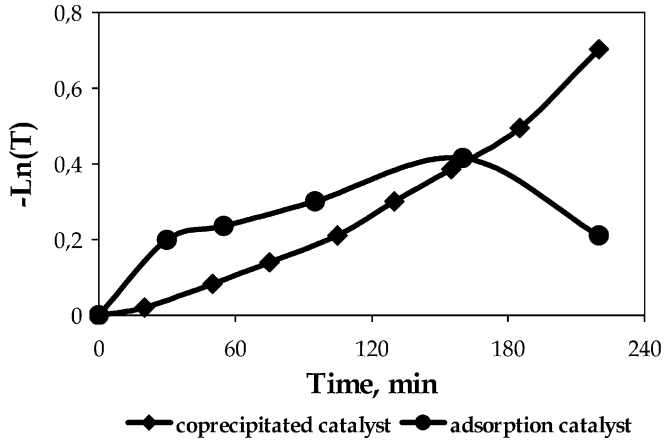


Fig. 11. Kinetics of hydroquinone oxidation, at 20 °C, on heterogeneous Cu-chitosan catalysts: (1) precipitated 6.5% Cu/chitosan; (2) "absorption made" 6.5% Cu/chitosan. "*T*" transmittance.

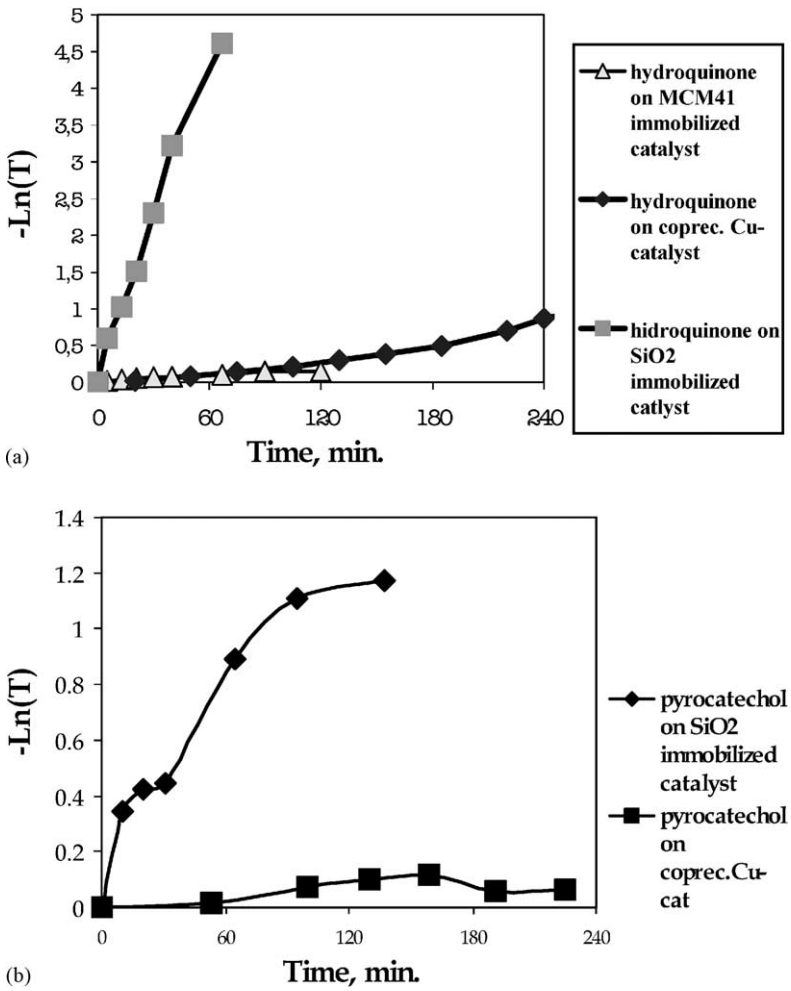


Fig. 12. Kinetics of oxidation, at 20 °C, of hydroquinone (a) and catechol (b) on heterogeneous 6.5% Cu/chitosan catalysts: (1) bulk globules; (2) Cu/chitosan/SiO_2; (3) Cu/chitosan/MCM-41. "*T*": transmittance.

diluted and uniformly distributed sites in the matrix of the precipitated catalyst.

Fig. 12a and b presents comparative kinetics data for the bulk precipitated catalyst and supported [Cu/chitosan]/SiO_2 or [Cu/chitosan]/MCM-41 samples. The rate of the catalytic reaction was negligible on pure silica. As one can see, the activity of the charge of the egg-shell catalyst supported on macroporous amorphous silica, with a surface area of 210 m^2/g, exceeds considerably the activity of the bulk globules. Moreover, in comparison of the two systems it is necessary to take into account that the same charge of the bi-component catalyst (1.8%[Cu/chtosan]/SiO_2) contains ∼55 times less of the Cu/chitosan component (i.e. 55 times less Cu). So, the *specific* activity of copper sites in a thin film of the active component stabilized by the inert disperse macroporous SiO_2 and accessible for reagents exceeds the activity of sites in bulk chitosan by two orders of magnitude, at least.

On the other hand, the activity of the supported system [Cu/chitosan]/MCM-41 seems to be negligible (Fig. 12a). This result can be, however, easily explained by peculiarities of the MCM-41 morphology. High surface of this mesoporous silica material is provided by the internal system of one-dimensional non-crossing channels with diameter of ∼4 nm. Chitosan species supported upon impregnation/crosslinking can easily block the channel entrances, especially when swelled with water. If so, penetration of reagents inside channels is restricted, and the wet sample contains negligible amount of the *accessible* active sites. At the same time, N_2 molecules can penetrate inside the sample dried in vacuum, and BET measurement shows an impressive internal surface area of ∼500 m^2/g.

Thus, by taking copper as an example, we demonstrate the advantages of the design of macroporous egg-shell systems containing chitosan on inorganic supports. It opens a way for future synthesis of the supported chitosan catalysts with a very low content of the active noble or transition metals.

4. Conclusions

1. *Heterogenized copper–chitosan samples are active and stable catalysts for liquid-phase oxidation of o- and p-dihydroxybenzenes*, in contrast to homogeneous systems demonstrating copper–hydroquinone complexation with a negligible yield of quinones. Intermediate quinhydrone formed at the initial stage of oxidation seems to yield a stable molecular complex with amino-groups of heterogenized Cu–chitosan.
2. The bicomponent egg-*shell system* (S_{BET} = 210 m^2/g), *with a thin film of low-loaded Cu–chitosan supported on macroporous silica gel, exhibits significantly higher activity in oxidation of hydroquinones*. Use of the mesoporous MCM-41 is not effective due to strong blocking of the one-dimensional channel system (diameter ∼4 nm) by the polymer. The design of macroporous shell systems opens up perspectives for synthesis of the supported chitosan catalysts with a very low content of the active component, and such systems can be most valuable for the effective use of noble metals.
3. ESR data give a direct evidence that *the matrix of heterogenized chitosan is able to stabilize and retain isolated Cu^{2+} ions in highly unsaturated coordinative state*. The estimate of the copper concentration derived from the ESR data shows that essentially all Cu(II) ions introduced by precipitation in low-loaded samples (≤1.5 wt.% Cu) are ESR-visible, with the symmetry of isolated Cu^{2+} sites in chitosan approaching the square-planar coordination. *Redox transformations of the active sites upon catalysis* or prolonged boiling in water *are not accompanied by copper leaching* from the chitosan matrix, and the catalyst reoxidation by H_2O_2 leads to quantitative restoration of the Cu(II) ESR signal.

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