Macromol. Symp. **2003**, *204,* 175—189

Comparative Study of Cu(II) Catalytic Sites Immobilized onto Different Polymeric Supports

A. Kucherov, E. Finashina, N. Kramareva, V. Rogacheva,*[1] *A. Zezin,*[1]
E. Said-Galiyev,[2] *L. Kustov*
Zelinsky Institute of Organic Chemistry RAS, Leninsky prosp., 47, Moscow 119991, Russia
E-mail: finesta@mail.ru, lab14@ioc.ac.ru
[1] Department of Chemistry, Moscow State University, Leninskie Gory, Moscow 119992, Russia
E-mail: VBR@jenebee.msu.su
[2] Nesmeyanov Institute of Organomet. Compounds RAS, Vavilova Str., 28, Moscow 117813, Russia
E-mail: emest@pms.ineos.as.ru

Summary: The catalysts with copper(II) ions stabilized onto different polymeric matrixes are prepared on either bulk (Cu/chitosan, Cu/polyethyleneimine-polyacrylic acid (PPA), and Cu-diiminate-impregnated polystyrene, polyarylate, or polymethylmethacrylate) or composite supports (egg-shell type Cu/chitosan/SiO_2 and Cu/PPA/SiO_2). The morphology of the samples and peculiarities of Cu(II) cationic sites are studied by SEM and ESR methods, and the catalyst activities are compared in oxidation of *o*- and *p*-dihydroxybenzenes by air in water. The catalytic activity of Cu(II) centers is governed by the coordination of isolated copper ions: for the most active catalysts, i.e., Cu/chitosan and Cu/PPA, the symmetry of isolated Cu^{2+}-sites approximates a coordinatively unsaturated square-planar structure. At the same time, accessibility of active sites to water differs for different polymers, so the contribution of hydrophilicity to the reaction pattern cannot be excluded. Redox transformations of the active sites in the course of catalytic tests do not cause copper leaching from the polymer matrix. The binary composite systems with a film of low-loaded hydrofilic Cu-polymer supported on macroporous SiO_2 demonstrate substantially higher activity in oxidation of hydroquinone and 3,4-dihydroxyphenylalanine, as compared with the bulk Cu/polymer samples. In turn, the specific activity of Cu/chitosan/SiO_2 exceeds significantly that of Cu/PPA/SiO_2 due to stabilization of a thinner and more uniform film of chitosan at the surface of silica.

Keywords: catalysis; Cu(II) immobilization; ESR; metal-polymer complexes; structure-property relations

Introduction

Immobilization of ions and complexes of metals on the surface of different polymeric supports opens up the way for designing catalysts combining the advantages of homogeneous and heterogeneous systems, i.e., possessing high selectivity and activity under mild conditions, easy

DOI: 10.1002/masy.200351415

handling, and reasonably high thermal stability [1]. The use of different synthetic and natural polymer matrices for specific stabilization of active sites permits to combine a wide range of properties that should meet modern industrial needs. Cellulose and its structural polysaccharide analogs, such as chitin and chitosan, demonstrate a set of important properties (biodegradability, lack of toxicity, hydrophilicity and compatibility with living matter) making these polymers very attractive as supports for catalytic processes in water.

Some data about physical properties of different cations entrapped by chitosan are available in the recent literature [2-4], including copper-chitosan complexes [5-7]. A few publications focused on application of chitosan-supported metal complexes in heterogeneous catalytic processes are also available [8-10]. In our previous work [11,12] we studied in detail the peculiarities of the structure and properties of copper/chitosan complexes. It was demonstrated that the heterogenized Cu/chitosan and especially egg-shell Cu/chitosan/SiO_2 were effective catalysts in the process of oxidation of isomeric hydroquinones in water [11,12]. However, natural crab-shell chitosan, with its unique adsorption ability toward diverse metal cations and atoms of Periodic Table, is a quite complex biopolymer. Questions arise about standardization of this natural support, as well as about regularity of catalytic sites immobilized in this complex matrix. Therefore, synthetic chitosan-like analogs, with a regular structure and similar assortment of functional groups, can be regarded as an alternative to the natural support.

The aim of this study is the preparation of diverse polymer-supported Cu catalysts and the study of the morphology and properties of the catalysts, as well as comparative catalytic testing of the copper redox sites immobilized onto different polymeric matrices in the model reaction of oxidation of dihydroxybenzenes and 3,4-dihydroxyphenylalanine (DOPA). Thus, structure-properties relationship is under investigation when redox sites in the Cu/chitosan system are compared with centers stabilized by synthetic polymers of different structure.

Experimental

Catalyst Preparation

Cu/chitosan Complexes

Details of Cu/chitosan preparation are given in [11]. At first, a homogeneous 1% wt. Cu/chitosan complex was prepared by dissolution of the calculated amount of $CuCl_2$ in a 1.5% solution of chitosan in 0.1 M HCl at room temperature, and the mixture was stirred until the formation of a blue clear solution. Then a film of polymer was prepared by submersion of the glass wafer covered by a film of the homogeneous Cu/chitosan complex into 0.5 M solution of NaOH for 2 h. The film formed was washed by distilled water until neutral pH and air-dried at room temperature during 48 h. The wet heterogenized film of Cu/chitosan can be preserved intact in distilled water for months.

Immobilization of the Copper-chitosan Complex on the Surface of Macroporous Silica Gel "Co-precipitation" Method ([Cu-chitosan]/SiO_2 Complex)

One gram of amorphous SiO_2 (KSS; fraction 0.25 – 0.5 mm; $S_{BET} = 450$ m^2/g; water absorption capacity 1.8 ml/g) was impregnated with 1.8 ml of a solution of the homogeneous copper-chitosan complex prepared as mentioned above. Then complex-loaded silica was placed in a 0.5 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.

"Absorption" Method (Cu/[chitosan-SiO_2] Complex)

The silica charge (see above) was impregnated with a homogeneous solution of 1.5% wt. of chitosan in water. Then chitosan-loaded silica was placed in a 0.5 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, and immersed in an aqueous solution of $CuCl_2$ containing the calculated copper amount corresponding to 1% wt. Cu/chitosan ratio. Quantitative absorption of Cu ions from the solution was confirmed by photocolorimetry. The catalyst obtained was washed by distilled water and dried at room temperature.

Ternary Polyelectrolyte Complex Cu/polyethyleneimine-polyacrylic Acid (PPA)

Films of interpolyelectrolyte complex of polyacrylic acid and branched polyethyleneimine were prepared according to [13] by pouring equimolar water-ammonia solutions of the two components onto a polyethylene wafer. The film obtained was stabilized by heating at 170°C for 20 min. Then ternary Cu/PPA samples were obtained by immersion of the film for 3-4 h in an aqueous solution of $CuSO_4$ containing the calculated amount of copper corresponding to the 1% or 27% wt. Cu/PPA ratios.

Immobilization of the Copper-PPA Complex on the Surface of Macroporous Silica Gel

"Co-precipitation" Method ([Cu-PPA]/SiO_2 Complex)

The charge of amorphous SiO_2 (see *2.1.2*) was placed for 2-3 h in a 0.21 N water solution of the 1%Cu/PPA at room temperature and pH = 8.5. Complex-loaded silica was dried in air at room temperature and then at 50°C.

"Absorption" Method (Cu/[PPA-SiO_2] Complex)

The silica charge was kept in a small volume of the equimolar water-ammonia mixed solution of polyacrylic acid and polyethyleneimine (3.7% wt. PPA/SiO_2 ratio), dried at room temperature, and heated at 170°C for 15 min. The egg-shell support obtained was immersed for 3-4 h in a water solution of $CuSO_4$ containing the calculated copper amount corresponding to the 1% wt. Cu/PPA ratio. Blue particles of the sample were filtered off and dried at room temperature and then at 50°C.

Cu-diiminate Impregnated into Polymethylmethacrylate(PMMA), Polystyrene (PS), or Polyarylate (PAr) Matrices

The starting diiminate copper complex, Cu-bis-(1,1,1,3,5,5,5-heptafluoro-4-iminopent-2-ene-2-aminate) (Cu(II)-HFDI), was synthesized according to [14].

PMMA and PS polymers in the form of granules were purchased from Aldrich. The films, with a thickness of 30 ± 2 μm, were prepared by pouring chloroform solutions of the two polymers on cellophane wafers. The polyarylate film (a polyester of bis-phenol A and tere-isophthalic acid), with a thickness of 39 ± 2 μm, was received from Plastpolymer, Russia.

To insert the copper complex into the polymers, pieces of polymer films (20-30 mm in size) were treated with the powder of Cu(II)-HFDI at a high pressure in supercritical CO_2 [14]. Conditions of treatment and copper content in the samples are listed in Table 1.

Table 1. Conditions of insertion of Cu(II)-HFDI into polymers by treatment in supercritical CO_2 and copper concentration in the samples obtained.

Polymer	Temperature, °C	Processing time, h	CO_2 pressure, MPa	Cu content, % wt.
PAr	45	1.35	9.0	0.154
PS	45	1.6	9.0	0.379
PMMA	45	1.6	9.0	2.31

SEM Study

SEM pictures of the samples (magnification from 50 to 5000) were obtained using a scanning electron microscope JSM-5300LV JEOL. The surface before imaging was decorated by a thin gold layer using a JFC-1100E device.

ESR Measurements

ESR spectra were taken in the X-band ($\lambda \cong 3.2$ cm) at 20°C and -196°C using an ESR spectrometer equipped with a 4104OR cavity and a quartz Dewar. The ESR signals were registered at the lack of saturation in the field range of 2500 - 3500 G or 100 - 4000 G. The special Bruker program WIN-EPR (version 901201) was used for data processing (baseline correction, double integration). DPPH was used as a standard for g-factor calculation.

Pieces of catalysts were placed in glass ampoules to fill the identical volume (3 mm diameter x 10 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 samples were impregnated with distilled water and swelled overnight. Then the ampoules were cooled in liquid nitrogen, and ESR spectra were recorded at -196°C. For the sake of accuracy, series of samples were measured consecutively, with ampoules placed in the same position inside the ESR resonator.

Catalytic Testing

Oxidation of *o*- and *p*-dihydroxybenzenes into Quinones

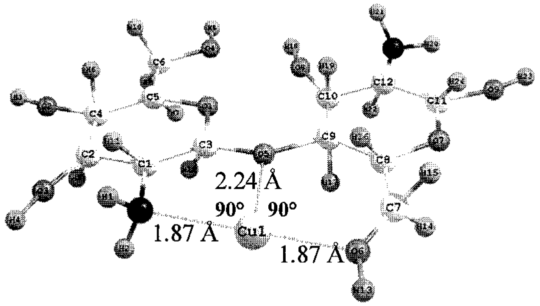
Catalysts (1%Cu/chitosan; 1%Cu/PPA; 0.15%Cu/PAr; 0.38%Cu/PS; 2.3%Cu/PMMA) were tested at 20°C in oxidation of isomeric *o*- and *p*-dihydroxybenzenes by air into corresponding quinones in water. The catalyst loading together with the aliquot of the aqueous solution of dihydroxybenzene (catalyst/substrate 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 monitor the reaction by the UV absorption attributed to quinones. The absorption bands at 390 nm and 428 nm were observed for *o*-benzoquinone (catechol) 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.

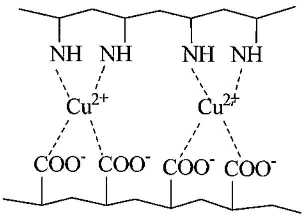
Oxidation of 3,4-Dihydroxyphenylalanine (DOPA)

Egg-shell catalysts (3.5%[1%Cu-chitosan]/SiO_2; 3.7%[1%Cu-PPA]/SiO_2) were tested at 20°C in oxidation of DOPA by O_2 into corresponding *o*-quinone in water. The catalyst loading together with the aliquot of the aqueous solution of DOPA (catalyst/substrate molar ratio = 0.02) were placed in the closed glass reactor under O_2 flow (120 cm^3/min) 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 by monitoring the UV absorption by product (the absorption band at 475 nm). Again, concentrations of quinone formed were plotted in arbitrary units, optical density ln(T), being proportional to the amount of the compound.

Results and Discussion

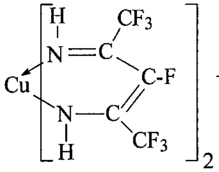
The structure of copper-polymer complexes chosen for comparison with copper/chitosan complexes [15] studied earlier in detail [11,12] are given below.

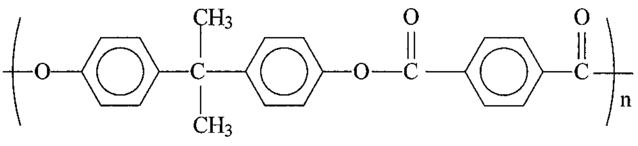




The ternary polyelectrolyte complex Cu/polyethyleneimine-polyacrylic acid (PPA) can be regarded as a synthetic analog of chitosan, with a similar ligand environment of the copper ion in the polymer matrix. Similar to chitosan, PPA is capable of binding copper in significant concentrations (up to 27% wt.), forms thin films easily, and this polymer is hydrophilic.

Cu^{2+}-diiminate complexes in polymethylmethacrylate (PMMA), polystyrene (PS), and polyarylate (PAr) can also be prepared in the form of thin films but differ in both the Cu-site structure and affinity of the polymeric supports to water.





Polyarilat (PAr)

Figure 1 shows the kinetics of hydroquinone oxidation on wet and dried films of 1%Cu/chitosan and 1%Cu/PPA. Direct comparison of the two catalysts with the same copper concentration demonstrates that the reaction rates for two wet polymeric samples coincide surprisingly well (Fig. 1, circles). Thus, the *intrinsic* catalytic activity of copper sites in the two water-swelled, low-dense polymer matrices seems to be identical.

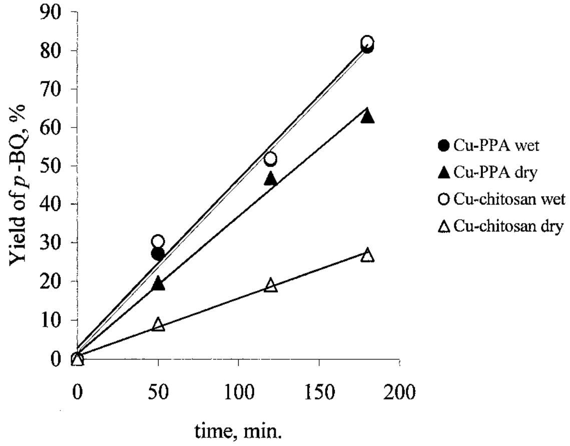


Fig. 1. Kinetics of hydroquinone oxidation on wet and dried films of 1%Cu/chitosan and 1%Cu/PPA.

When pre-dried films are used as catalysts, a noticeable difference in activities is observed (Fig. 1, triangles). This discrepancy can be related to differences in the swelling process for two pre-dried matrices. As to the total amount of water retained by wet polymers, the weight loss upon drying of two wet films (20°C, 48 h) comes to 86.7% and 92.4% for Cu/PPA and Cu/chitosan, respectively. So, the dried chitosan film seems to be more dense and it absorbs water more slowly. As a result, the discrepancy observed (Fig. 1) can point to different accessibility of active sites in pre-dried films. The copper loss upon catalytic testing is negligible, because the analysis of the liquid phases shows no measurable presence of copper ions in aqueous solutions after catalysis.

Figure 2 shows the Cu(II) ESR spectra of two Cu/PPA samples. For the sample with the high copper content (27% wt.) the signal without hyperfine splitting (*hfs*) is observed (Fig. 2,a; dotted line). This spectrum demonstrates a considerable magnetic interaction between closely arranged Cu(II) ions in a heavy-loaded matrix. Another signal, with well resolved *hfs,* is seen for the low-loaded 1%Cu/PPA (Fig. 2, b) and it is typical of a well magnetically separated Cu(II) ions. The shape of this signal is identical to that obtained earlier for low-loaded Cu/chitosan [11,12]. The parameters of *hfs* ($g_{\parallel} = 2.24$, $A_{\parallel} = 179$ G; $g_{\perp} = 2.045$) point to the local crystal field of a low symmetry being close to the square-planar coordination [16]. ESR spectra with very similar *hfs* parameters were reported earlier, and the same tetragonal symmetry was supposed [5,17,18]. Catalytic testing causes a loss of ~25% of the Cu(II) ESR signal intensity, as observed for the sample taken after catalysis (Fig. 2,c). Thus, the dynamic equilibrium $Cu^{2+} \leftrightarrow Cu^{+}$ in working catalyst is shifted noticeably to the reduced state, i.e., the reoxidation step in the reaction conditions is not fast.

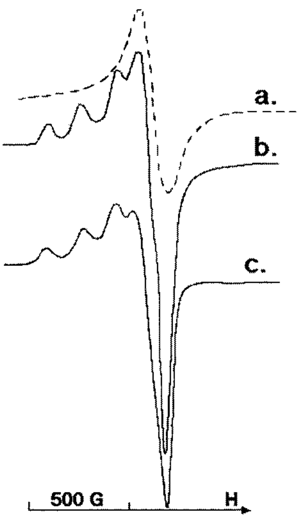


Fig. 2. ESR spectra, taken at 20°C, of fresh 27%Cu/PPA (a), fresh 1%Cu/PPA (b), and 1%Cu/PPA after catalytic testing (c).

Thus, in accordance with our expectations, the PPA matrix provides irreversible immobilization of isolated Cu(II) ions (for low-loaded samples) with a coordinatively unsaturated square-planar symmetry identical to that observed in chitosan.

Catalytic testing of Cu/PS, Cu/PAr and Cu/PMMA films in oxidation of dihydroxybenzenes shows the lack of activity for all three samples. On closer examination of this result, account must be taken of a low Cu content in Cu/PS and Cu/PAr samples, and especially of hydrophobicity of polystyrenic and polyarylic matrices hindering effective interaction of reagents with catalytic sites and their diffusion from the water solution. In smaller extent this explanation can be applied to the 2.3%wt. Cu/polymethylmethacrylate sample possessing higher affinity to water. To clarify this point, the model pattern ~0.5%[Cu-diiminate]/chitosan was prepared and tested. In contrast to Cu/chitosan, the catalytic activity of [Cu-diiminate]/chitosan was negligible in spite of hydrophilicity of the matrix. So, the question arises about the peculiarities of the structure of the active Cu site itself.

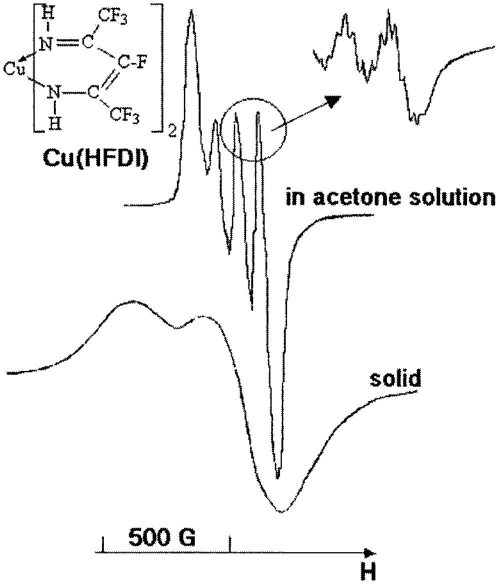


Fig. 3. ESR spectra of the starting Cu(II)-HFDI taken at –196°C.

ESR spectra of solid and dissolved Cu(II)-HFDI, taken at –196°C, are given in Fig. 3, and spectra of Cu(II)-HFDI inserted in different polymers are presented in Fig. 4. A broad asymmetric signal from the solid complex (Fig. 3) is typical of strongly interacting Cu(II) ions and gives no information about the local crystal field of Cu(II) sites. However, dissolution of the complex in acetone permits to prepare a diluted system with negligible magnetic interaction between ions separated by solvent molecules. This frozen diluted system is characterized by the presence of both *hfs* and additional super-*hfs* in the ESR spectrum (Fig. 3). Parameters of *hfs,* with A = 85 G, point that Cu(II) sites in the diiminate complex are located in a distorted bi-pyramidal environment. Well resolved super-*hfs* provides a direct evidence of interaction of the Cu(II)-site with nitrogen atoms of HFDI-ligands being located in the first coordination sphere of the copper ion.

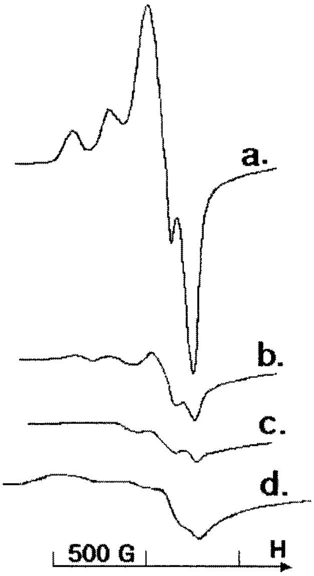


Fig. 4. ESR spectra taken at -196°C of Cu(II)-HFDI inserted in different polymers: (a) 2.3% Cu(II)-HFDI-PMMA; (b) 0.38% Cu(II)-HFDI-Par; (c) 0.15% Cu(II)-HFDI-PS; (d) Cu(II)-HFDI-chitosan.

Spectra of Cu(II)-HFDI inserted in different polymers (Fig. 4), being compared with the signal of the diluted frozen Cu(II)-HFDI solution (Fig. 3), demonstrate the preservation of the starting local structure for the Cu-diiminate complexes inserted in all polymers studied. So, no relocation of copper from Cu(II)-HFDI species to sites in polymer itself occurs, and intact isolated Cu(II)-HFDI sites are retained even in chitosan (Fig. 4, d). These species, with Cu^{2+} strongly bonded by diiminate ligands and having a low degree of coordinative unsaturation, demonstrate a negligible catalytic activity as distinct to Cu(II)-chitosan. Thus, the low symmetry of coordination of the Cu(II)-site seems to play the decisive role in catalytic oxidation on polymer-immobilized copper catalysts. The same strong dependence between the *intrinsic* activity of the isolated Cu(II)-site and the degree of coordinative unsaturation of the ion was demonstrated earlier for Cu/zeolite catalysts [19-21].

Egg-shell Catalysts

It was demonstrated in our previous work [11,12] that the binary egg-shell system, with a thin film of low-loaded Cu-chitosan supported onto macroporous SiO_2, exhibited significantly higher activity in oxidation of dihydroxybenzenes, as compared with the bulk Cu/chitosan sample. This approach to catalyst design is used now to prepare samples for comparative study, with chitosan or PPA layers supported on another sample of macroporous silica gel. Oxidation of both hydroquinone and DOPA is studied.

Both composite systems, with a film of low-loaded Cu-polymer supported onto macroporous SiO_2, demonstrate significantly higher activity in oxidation of hydroquinone, as compared with corresponding bulk samples. At the same time, a pronounced difference in catalytic activities of two egg-shell systems, with two different polymers, is observed. Dependencies obtained for the two reactions are very similar, and we can use the data for DOPA oxidation (Fig. 5) to illustrate the relationship observed. No noticeable influence of the sample preparation mode (co-precipitation or absorption) is seen (Fig. 5) demonstrating that variation of the copper introduction method is of a minor importance in the case of silica-supported polymer films. ESR spectra for all the samples are identical in shape and point to the same square-planar coordination of isolated Cu^{2+} ions in composite systems (Fig. 6). Surprisingly, the reaction rate for Cu/chitosan/SiO_2 exceeds that for Cu/PPA/SiO_2 at least by a factor of 4 (Fig. 5). Taking into account that two <u>bulk</u> catalysts demonstrate identical activities (Fig. 1), one can assume that the difference in activities of the egg-shell samples, with the same structure of active sites, can only be related to peculiarities of the morphology of these two systems. Therefore, the structure and morphology of Cu/chitosan/SiO_2 and Cu/PPA/SiO_2 are compared in detail by using SEM. SEM pictures of the two systems, taken at different magnifications, are presented in Fig. 7 and listed in Table 2.

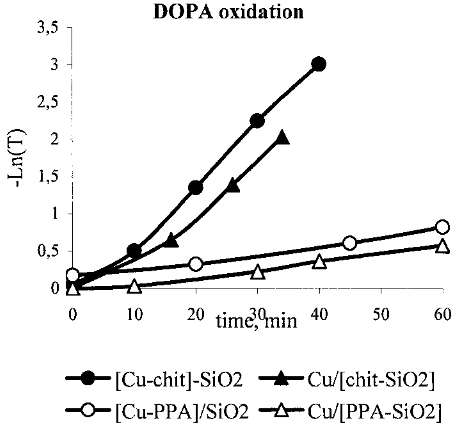
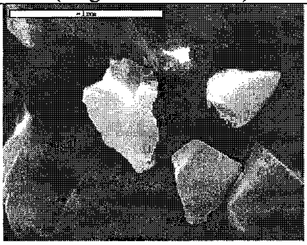
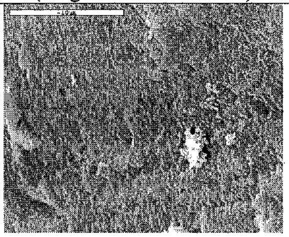
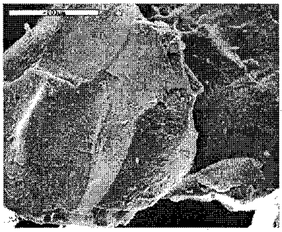
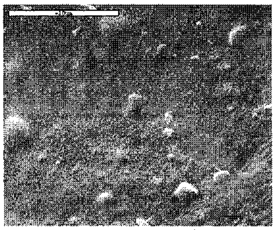
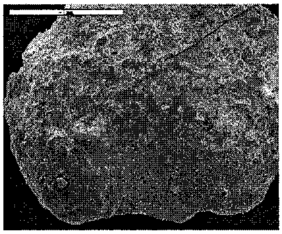
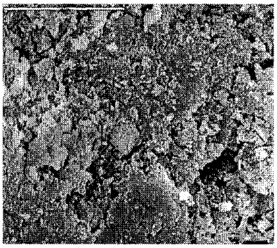
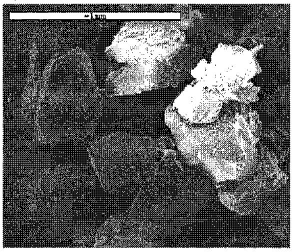


Fig. 5. Kinetics of DOPA oxidation on egg-shell samples of 1%Cu/chitosan/SiO_2 and 1%Cu/PPA/SiO_2.

The picture for Cu/chitosan/SiO_2 taken at magnification x5000 demonstrates the formation of a thin, continuous film without cracks (Table 2). It looks that adhesion is high, the chitosan layer is uniformly spreaded out on the silica and fills micropores at the surface. Really, BET evaluation of the total surface area shows the reduction of the specific surface area from starting 450 down to ~270 m^2/g. Two Cu/PPA/SiO_2 samples retain a larger part of the surface upon polymer fixation (310-320 m^2/g). What is more important, macro- and micro-images of the Cu/PPA/SiO_2 look quite different (Table 2). Films of supported PPA look damaged and fragmentated, with multiple breaks and islands (Fig. 7). Fragments of the PPA film are thicker, as compared with chitosan (Table 2). Thus, the higher catalytic activity of Cu/chitosan/SiO_2 can be explained by the formation of a much more uniform, thin, continuous film of Cu/chitosan providing substantially more effective use of the Cu active sites, as compared with thick, three-dimensional islands of Cu/PPA on the same silica.

Table 2. SEM pictures of silica gel and egg-shell system catalysts.

Sample	General view of particles (magnification x 50)	Surface of the particles (magnification x 5000)
SiO_2 particle size 0.2-0.4 mm $S_{BET} = 450\ m^2/g$		
[Cu-chit]/SiO_2 $S_{BET} = 272\ m^2/g$		
Cu-[PPA-SiO_2] $S_{BET} = 328\ m^2/g$		
[Cu-PPA]-SiO_2 $S_{BET} = 308\ m^2/g$		

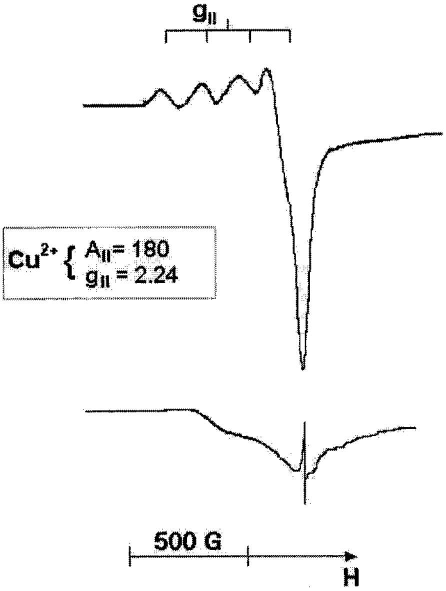


Fig. 6. ESR spectra, taken at -196°C, of fresh (a) and used (b) 1%Cu/PPA/SiO_2.

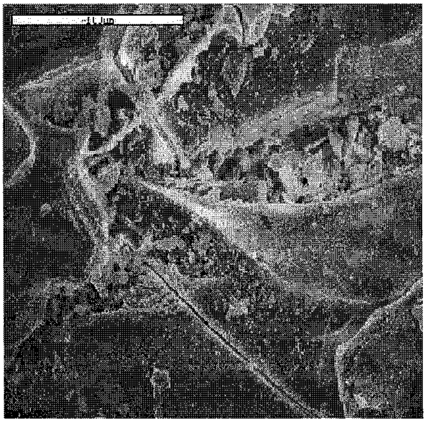


Fig. 7. SEM picture of the surface of Cu/[PPA-SiO2], magnification x1000.

Conclusions

1. Comparative study of several polymer-supported copper catalysts shows that the intrinsic catalytic activity of isolated Cu(II) centers in water-phase oxidation is related to the coordination of copper ions. For the most active catalysts, i.e., Cu/chitosan and Cu/PPA, the symmetry of isolated Cu^{2+}-sites approximates a square-planar coordination. At the same time, some influence of hydrophilicity of the polymer cannot be excluded. Redox transformations of the active sites upon catalytic testing are not accompanied by copper leaching from the polymer matrices.
2. The egg-shell Cu/chitosan/SiO_2 and Cu/PPA/SiO_2, with a film of low-loaded hydrophilic Cu-polymer supported onto macroporous silica, demonstrate a substantially higher activity in oxidation of hydroquinone and DOPA, as compared with corresponding bulk Cu/polymers. In turn, the specific activity of Cu/chitosan/SiO_2 exceeds significantly that of Cu/PPA/SiO_2 due to stabilization of a thin, uniform film of chitosan at the surface of silica. PPA forms damaged, thick island with less accessible Cu-sites on the same silica support.

[1] A. Choplin, F. Quignard, *Coord. Chem. Rev.*, **1998**, *178-180*, 1679.
[2] M. Ruiz, A. M. Sastre, E. Guibal, *React. Func. Polym.*, **2000**, *45*, 155.
[3] K. Yoshizuka, Zh. Lou, K. Inoue, *React. Func. Polym.*, **2000**, *44*, 47.
[4] E. Guibal, N. Von Offenberg Sweeney, M. C. Zikan, T. Vincent, J. M. Tobin, *Int. J. Biomol. Macromol.* **2001**, *28*, 401.
[5] E. Chiessi, M. Branca, A. Palleschi, B. Pispisa, *Inorg. Chem.*, **1995**, *34*, 2600.
[6] W. S. Wan Ngah, C. S. Endud, R. Mayanar, *React. Func. Polym.*, **2002**, *50*, 181.
[7] M. Rhazi, J. Desbrieres, A. Tolaimate, M. Rinaudo, P. Vottero, A. Alagui, *Polymer*, **2002**, *43*, 1267.
[8] Huaimin Guan and Yuejin Tong, *Huaxue Wuli Xuebao*, **1997**, *10*, 174.
[9] Huaimin Guan, *Fujian Shifan Daxue Xuebao, Ziran Kexueban*, **1996**, *12*, 75.
[10] G. Paradossi, E. Chiessi, F. Cavalieri, D. Moscone, and V. Crescenzi, *Polym. Gels Networks*, **1997**, *5*, 525.
[11] A. V. Kucherov, N. V. Kramareva, E. D. Finashina, A. E. Koklin, and L. M. Kustov, *J. Mol. Catal.*, **2003**, *198*, 377.
[12] N. V.Kramareva, E. D. Finashina, A.V. Kucherov, and L.M. Kustov, *Kinetika i Kataliz*, **2003**, in press.
[13] N. M. Kobanov, A. I. Kokorin, V. B. Rogacheva, and A. B. Zezin, *Vysokomolekuliarnye soedinenia (Rus)* **1979**, *XXI*, 209.
[14] E. Said-Galiyev, L. Nikitin, R. Vinokur, M. Gallyamov, M. Kurykin, O. Petrova, B. Lokshin, I. Volkov, A. Khokhlov, K. Schaumburg, *Ind. Eng. Chem. Res.*, **2000**, *39*, 4891.
[15] N. C. Braier, R. A. Jishi, *J. Molecular Structure*, **2000**, *499*, 51.
[16] A. A. Slinkin, A. V. Kucherov, *Catal. Today*, **1997**, *36*, 485.
[17] Y.-C. Su, H.-M. Guan, C. X. Cheng, *Huaxue Xuebao*, **1999**, 57, 596.
[18] E. Chiessi, G. Paradossi, M. Venanzi, B. Pispisa, *J. Inorg. Biochem.*, **1992**, *46*, 109.
[19] A. V. Kucherov, T. N. Kucherova, A. A. Slinkin, *Catal. Letters*, **1991**, *10*, 289.
[20] A. V. Kucherov, C. P. Hubbard, M. Shelef, *J. Catal.*, **1995**, *157*, 603.
[21] A. V. Kucherov, C. P. Hubbard, T. N. Kucherova, M. Shelef, In: Progress in Zeolite and Microporous Materials (H. Chon, S.-K. Ihm, Y.S. Uh Eds.), *Studies in Surf. Sci. and Catal.*, **1997**, *105B*, 1469.