

Oxidation of L-cysteine in oxygen-saturated aqueous solution in the presence of Cu(II)-containing adjusted polymers

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Abstract

The influence of synthesis conditions of adjusted sorbents based on polyethylenepolyamine on catalytic properties of their Cu(II)-containing samples has been studied. It was shown that adjustment of sorbents leads to a significant increase in activity of Cu(II)-containing catalysts on their base. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic properties of cross-linked polymers adjusted toward Cu(II)-ions sorption have been investigated. Earlier we have developed a principle of preparation of complexing polymers based on use of memory of polymer composition [1,2]. The principle consists in conformational prearrangement of macromolecules of non-crosslinked complexing polymers to a position favorable for complexing metal and catalyzed substrate, followed by fixation of conformations optimum for the complex formation by means of intermolecular cross-linking. Such adjusted metal-containing catalysts show higher

catalytic activity in the reactions of organic compounds oxidation than their non-adjusted analogues [3].

The influence of adjustment of a Cu(II)-containing catalyst based on cross-linked polyethylenamine (PEPA) on its catalytic activity in the reaction of L-cysteine oxidation with molecular oxygen :



where RSH-L-cysteine, RS – SR-cystine, has been studied using ESR spectroscopy.

2. Experimental

The sorbents AN-31 and AN-31a A Cu, synthesized based on PEPA and epichlorohydrin-ammonia oligomer (ECHA), and distinguished by the PEPA:oligomer molar ratio, are objects

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of the present investigation. The index 'a' indicates that a sorbent has been subjected to the process of adjustment, and the index 'A' is the amount of Cu(II)-ions incorporated into a sorbent during adjustment (in mmol/g PEPA). The metal ions were removed from the obtained adjusted sorbents by 1M HCl treatment. Sorption of Cu(II) was conducted on the samples with the initial protonation degree of amino groups $\alpha = 0.4$ under static conditions. pH values of the initial $\text{CuCl}_2 \times 3\text{H}_2\text{O}$ solutions were equal to 4. The Cu(II)-ions content in a sorbent phase was determined from the decrease in their concentration in solution by compleximetric titration with EDTA. ESR spectra of Cu(II) were recorded on the computerized spectrometer PS 100.X (Belarus) at X-band frequencies at room temperature.

Catalytic experiments were conducted in aqueous solutions at 313 K in a static system containing a glass reactor with two divisions positioned inside a thermostat. Two divisions in the reactor allow to prevent mixing individual components of reaction solution up to finishing all preparatory operations [4]. The reactor was fitted to a high-speed rocker. When the rocker was switched on, intensive stirring of reaction solution took place and experiment was started. The initial solution had pH 7.8. The system was washed with oxygen and connected to the oxygen burette. When the high-speed rocker was switched on, the measurement of oxygen absorption was conducted.

The liquid-phase oxidation dehydration is a convenient model reaction for the study of the processes of sulfur-containing compounds oxidation with oxygen, as dimer-cystine is the only product of the similar oxidation.

Since the initial reaction rate v_0 can not be measured directly due to an autocatalytic induction period, it has to be extrapolated from measurements obtained after this period. For this extrapolation, the simplifying assumption of a pseudo-first-order reaction is stated [5,6]

$$c_t = c_0 \exp(-kt) \quad (1)$$

where c_0 and c_t are the initial and temporal oxygen concentrations respectively, and k is the reaction constant. The first derivative of Eq. (1)

$$v_t = \partial c_t / \partial t = -c_t k \exp(-kt) \quad (2)$$

is used for the extrapolation at the end of the induction period, yielding the desired initial reaction rate v_0 .

The temporal oxygen consumptions measured by the oxygen burette are converted into consumed oxygen concentrations in the oxygen-saturated solution

$$c_t = (n_{\text{O}_2, \text{max}} - n_{\text{O}_2, t}) / V_R \quad (3)$$

based on the totally consumed, $n_{\text{O}_2, \text{max}}$, and temporal mole of oxygen, $n_{\text{O}_2, t}$, as measured in the burette, and the volume of the reaction solution V_R .

The non-catalytic autoxidation ($v_{0, \text{cat}}$), evaluated separately and yielding $v_{0, \text{O}} = 7.88 \times 10^{-4} \text{ M} \times \text{min}^{-1}$ ($\text{M} - 1$ mole of $\text{O}_2 / 1$ liter of reaction solution) ($c_{0, \text{L-cysteine}} = 0.689 \text{ mol/l}$), was subtracted from the catalyzed overall conversion. The result is defined as 'effective initial rate'

$$v_{0, \text{eff}} \equiv v_0 - v_{0, \text{non-cat}} \quad (4)$$

For calculation of v_0 -values no less than four experiments were conducted. The 'specific initial rates', $v_{0, \text{sp}}$, were calculated by putting $v_{0, \text{eff}}$ to mmol of Cu(II)-ions containing in reaction solution. The obtained coefficient of variation was less than 10%.

3. Results and discussion

The initial portions of the curves on the plots of $^{10}\log c$ vs. $^{10}\log t$ (Fig. 1) are straight lines. This fact indicates the initial reaction rate can be calculated by Eq. (1). A slight deviation of the curves from straight line in subsequent, in our opinion, is caused by the partial passage of

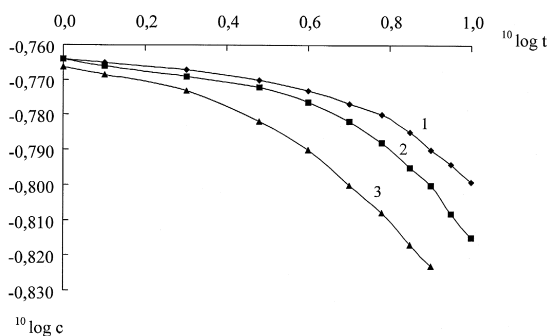


Fig. 1. Plots of $^{10}\log c$ vs. $^{10}\log t$ for oxidation of L-cysteine in the presence of the non-adjusted (1) and adjusted (2,3) Cu(II) complexes with polymer of PEPA and ECHA. Concentration of Cu(II), mmol/l: 1–4.34; 2–4.34; 3–5.25.

Cu(II)-ions into reaction solution as evidenced by the change in ESR spectra intensity of Cu(II) in a phase of the studied samples after catalysis. It is seen from Fig. 1 that the adjusted toward Cu(II) samples of a catalyst show higher catalytic activity than non-adjusted ones with the same Cu(II)-ions content. With an increase in molar proportion of Cu(II) in the reactor output of the reaction increases also. The results of $v_{0, \text{eff}}$ - and $v_{0, \text{sp}}$ -calculations are presented in Table 1. An ESR spectrum of Cu(II) in a phase of the studied samples, as a rule, is a superposition of anisotropic and isotropic signals. Anisotropic signal is well resolved in parallel orientation to magnetic field. It is caused by Cu(II)-ions situated in crystal fields of D_{4h} symmetry and belongs to individual Cu(II) com-

plexes located inside small micropores of a sorbent far from each other. Isotropic signal represents a wide and almost symmetric line that is appeared in an ESR spectrum as a result of exchange interaction between rather closely spaced Cu(II) complexes (~ 0.8 nm). In all cases g -factor of symmetric line, g_0 , is equal to the average g -value, \bar{g} , $\bar{g} = (g_{\parallel} + 2g_{\perp})/3$. Therefore, it is caused by the Cu(II) complexes of the same structure that anisotropic signal, but located inside large micropores that contain a significant amount of amino groups. These complexes are called magnetic clusters. The ratio, l , between Cu(II)-ions giving anisotropic and isotropic signals in the studied samples are presented in Table 1. A difference between Cu(II)-content in a sorbent phase (chemical analysis data) and amount of the Cu(II)-ions giving an ESR spectrum has been found. A portion of Cu(II)-ions does not give ESR spectra. This effect is well known [7] and, as an example, is characteristic of the condensed Cu(II) hydroxide. The formation of Cu(II) hydroxide as an individual phase inside the studied samples granules at significant degrees of saturating with Cu(II)-ions has been proved by Dr. Zagorodni's experiments on Cu(II)-ions sorption under dynamic conditions (unpublished data).

It was found that in a phase of the non-adjusted sample AN-31, the square-planar complex of Cu(II) with four amine groups from two ethylenediamine cycles is formed. It is charac-

Table 1

Oxidation of L-cysteine in the presence of the non-adjusted and adjusted PEPA based Cu(II) complexes

n — PEPA:ECHA mass ratio; m — weight of a sorbent; ν — H_2O :L-cysteine: ($\text{Cu}^{2+} \times 10^3$) molar ratio; l — ratio between amount of Cu(II) complexes giving anisotropic and isotropic ESR spectra, respectively.

Sample no.	Sorbent	n	m (g)	ν	$v_{0, \text{eff}}$, ($\text{M} \times \text{min}^{-1}$)	$v_{0, \text{sp}}$, ($\text{M} \times (\text{mmol}$ $\text{Cu(II)} \times \text{min})^{-1}$)	l
1	AN-31a 2Cu	1:1.5	0.05	55.6:1:0	0	0	—
2	AN-31	1:1	0.05	55.6:1:0.043	0.0013	0.030	0.2/0.8
3	AN-31a 2Cu	1:1.5	0.095	55.6:1:0.043	0.0033	0.077	0.15/0.85
4	AN-31a 3Cu	1:1.5	0.04	55.6:1:0.023	0.0028	0.122	0.2/0.8
5	AN-31a 3Cu	1:1.5	0.04	55.6:1:0.043	0.0022	0.051	0/1
6	AN-31a 3Cu	1:1.5	0.05	55.6:1:0.055	0.0042	0.076	0/1

terized by the following ESR parameters : $g_{||} = 2.205 \pm 0.005$; $A_{||} = 17.8 \pm 0.3$ mT. In the case of the adjusted samples the formation of a complex of Cu(II) with four amine groups was detected too. But it is a slightly distorted square-planar complex where four nitrogen atoms are located in the same polymeric chain next to each other and united by means of ethylene bridges. The deviations from square-planar structure of the above mentioned complex appeared in this case lead to a decrease in parallel hyperfine coupling constant, $A_{||}$. The ESR parameters of Cu(II)-complexes in the adjusted samples are: $g_{||} = 2.202 \pm 0.005$; $A_{||} = 16.0 \pm 0.3$ mT.

The analysis of the data presented in Table 1 indicates the influence of adjustment of samples on their catalytic activity. With approximately the same ratio l (samples 2, 3, 4) adjustment leads to an increase in the 'specific initial rate' of oxygen consumption, $\nu_{0,sp}$, by 2.5 and 4 times respectively. The catalytic data are in good accordance with the results of ESR investigations [7] and indicate an increase in degree of adjustment of the studied samples with the increase in an amount of Cu(II)-ions incorporated into them during adjustment (in mmol/g PEPA). It was found earlier [7] that the samples prepared at the following ratios between PEPA and ECHA can be considered successful: 1:1, 1:1.3 and 1:1.5. The other samples (ratios 1:2, 1:2.5 and 1:3) did not show a significant degree of adjustment. Therefore, the catalytic activity of only the samples with PEPA:ECHA ratio = 1:1 and 1:1.5 was studied. With an increase in the ECHA portion cross-linking degree of the samples increases, which shows itself as a decrease in their swelling. It can be assumed that accessibility of Cu(II)-ions inside a solid phase to substrate will decrease too, therefore a higher catalytic activity of the samples with PEPA:oligomer = 1:1 ratio should be expected. In this connection, the low value of $\nu_{0,sp}$ for the sample 2 is explained exclusively by structure of ethylenediamine complex in its phase. Hence, the higher catalytic activity of the adjusted sam-

ples as compared to their 'non-adjusted' analogues can be caused by the above mentioned features of Cu(II) complexes structure and changes in reology of cross-linked polyelectrolytes connected with features of synthesis of these sorbents.

The amounts of Cu(II)-ions in a sorbent phase both giving (N_s) and not giving ESR spectra (N_{ns}) were determined in the studied samples by ESR method with using paramagnetic centers concentration standard. These data are necessary for explanation of the results of the catalytic experiments ($\nu_{0,sp}$) on the samples 4, 5, 6. It was found that N_s -(in mmol Cu(II)/g sorbent) and N_{ns} -(in mmol Cu(II)/g sorbent) values for these samples are equal to: sample 4 — 0.252 and 0.325; sample 5 — 0.337 and 0.867; sample 6 — 0.638 and 0.892, respectively. A correlation of these data with $\nu_{0,sp}$ -values allows to conclude that the adjusted samples containing individual Cu(II)-complexes (sample 4) show the highest catalytic activity (Table 1). Copper magnetic clusters are intermediate in catalytic activity between individual Cu(II) complexes and copper ions not giving ESR spectra. This conclusion results from a comparison of the samples 5 and 6 in which an amount of the copper not giving ESR spectra is almost equal, whereas an amount of magnetic Cu(II) clusters increases approximately of 89% in the sample 6. To such increase of magnetic clusters amount there corresponds an increase in $\nu_{0,sp}$ only of 49%. Perhaps, it is caused by a restricted accessibility of a part of Cu(II)-ions contained in magnetic clusters to the substrate and their exclusion from catalysis.

4. Conclusion

The results obtained show that the special prearrangement of active centers of macromolecule-metal complexes leads to an essential increase in activity of the catalysts prepared on their base.

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