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The catalytic oxidation of hydroquinone: influence of surface properties of polymeric catalysts with aminoguanidyl ligand on catalytic properties

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Abstract

The heterogenized catalysts were prepared by aminolysis of nitrile groups in acrylonitrile, vinyl acetate and divinylbenzene terpolymer using aminoguanidine bicarbonate and by a subsequent complexation reaction with copper(II) nitrate. To study the catalytic activity of these catalysts, the model oxidation reaction of hydroquinone to *p*-benzoquinone by hydrogen peroxide was carried out. Under optimal conditions only the main product, i.e. *p*-benzoquinone (yield 95%) was obtained after 60 min. The existence of free, i.e. uncomplexed groups in active center environment is necessary to use the Cu(II)–resin complexes as oxidation catalysts. The optimal ratio of uncomplexed aminoguanidyl groups to carboxyl group concentration was about 0.6 for the Cu(II) ion loading in the range of 0.26–0.41 mmol/g and 0.7 for the Cu(II) loading in the range of 0.16–0.26 mmol/g.

Keywords: Copper(II); Aminoguanidyl ligand; Hydroquinone oxidation; Supported catalysts

1. Introduction

Many polymer–metal complexes have been found to exhibit high catalytic activity in comparison with the low molecular weight analogs [1,2]. The catalytic applications of the copper complexes with chelating resins as the hydroquinone oxidation catalysts have been described for many years [2]. The influence of catalyst structure on catalytic ability are very interesting part. In the most cases in the presence of Cu(II)–resins systems the hydroquinone oxidation leads to *p*-benzoquinone with yield below 60% [1–6]. The structures of ligands and resins influence catalytic activity and stability [3–6]. For example, the acrylic resin with hydrazide ligands, containing immobilized Cu(II) ions displayed the highest catalytic activity (60%), which did not decrease even after repeated use of the catalysts [5].

Also, it is important to consider the effect of functional group distribution in the polymer catalysts as well as their composition on their catalytic activity [2,4–6]. The kind and concentration of functional groups is very important for the sorption (when the carriers are used as chelating resins) and for the kinetic and catalytic investigations (when the metal–resin systems are used as the catalysts for selected reaction).

The oxidation of hydroquinone (H_2Q) to *p*-benzoquinone (Q) by means of hydrogen peroxide was chosen as model reaction to test the catalytic behavior of Cu(II) complexes with aminoguanidyl and carboxyl groups immobilized on polymer support. The influence of the free (i.e. uncomplexed) aminoguanidyl and carboxyl group concentration on the catalytic activity of Cu(II)–resin complexes was presented.

2. Experimental

The copolymers of acrylonitrile, vinyl acetate and divinylbenzene (A) were prepared by suspension polymerization. More details on the preparation of this copolymer can be found elsewhere [7]. The copolymer was obtained from the monomer mixture included 10 wt.% DVB and diluted with 2-ethylhexanol and cyclohexanol (1:9). The nitrile groups concentration in A was 11.53 mmol/g.

To prepare the resins (A–X), the aminolysis of nitrile groups by aminoguanidine bicarbonate was carried out. The modification conditions were described earlier [8] and presented in Table 1. The water regain, *W* (g/g), was determined

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Table 1
The characteristics of the ion exchangers with aminoguanidyl groups and the catalysts based on them

Ion exchanger	Aminolysis time (h)	Diluents during aminolysis	W (g/g)	Z_{NH_2} (mmol/g)	Z_{COOH} (mmol/g)	Z_C (mmol/g)	Z_{NH_2}/Z_{COOH} (mmol/mmol)	Catalysts	$Z_C/C_{Cu(II)}$	Z_{Ck} (mmol/g)	S (mmol/g)
A-1	10	Dioxan	2.2	1.38	2.63	4.01	0.52	KA-11	10.0	2.90	0.26
A-2	10	Dioxan	1.96	0.95	3.89	4.84	0.24	KA-21	10.0	4.20	0.16
								KA-22	5.0	4.50	0.34
A-3	24	Dioxan/water	1.83	0.32	2.06	2.38	0.13	KA-31	5.0	0.99	0.35
								KA-32	0.9	1.15	0.31
A-4	25	*n*-Butanol/water	2.61	2.05	3.02	5.07	0.67	KA-41	5.0	3.43	0.41
A-5	20	*n*-Butanol/water	1.82	1.86	2.45	2.74	0.76	KA-51	10.0	2.00	0.19
								KA-52	5.0	1.30	0.36
								KA-53	2.0	1.36	0.35
A-6	24	Dioxan	2.38	2.68	2.86	5.07	0.94	KA-61	10.0	4.01	0.26
								KA-62	2.5	3.15	0.48
A-7	24	Dioxan/water	2.12	0.20	3.064	3.26	0.09	KA-71	5.0	1.71	0.39
								KA-72	4.0	2.47	0.20

Z_{NH_2}: the aminoguanidyl group concentration. Z_{COOH}: the carboxyl group concentration. Z_{NH_2}/Z_{COOH}: ratio of the aminoguanidyl groups to carboxyl groups before Cu(II) sorption. Z_C, Z_{Ck}: total aminoguanidyl and carboxyl group concentration before and after sorption, respectively. S: the Cu(II) sorption (the Cu(II) ion loading).

by centrifugation and calculated according to Ref. [7]. Concentration of amine and carboxyl groups (Z_{NH_2} and Z_{COOH}, respectively) was determined by Colella–Siggia method [8,9].

The resin with carboxyl groups (A-0) was prepared by basic hydrolysis of A. However, the resins with blocked carboxyl groups were obtained by modification of A-8 and A-7 by means of bromofenacyl bromide (BF), fenacyl bromide (F) or methanol (C). These modifications led to A-6BF, A-6F and A-5C, respectively. The synthesis was performed according to [10].

2.1. Catalyst preparation (KA–XY)

Sorption of Cu(II) was performed by the batch method from $Cu(NO_3)_2 \cdot 3H_2O$ solution (1×10^{-2} or 5×10^{-3} mol/dm^3) in acetate buffer at pH 5 to obtain the catalyst with Cu(II) active centers (Fig. 1a). The concentration of Cu(II) ion in the solution after sorption was determined by atomic absorption spectrophotometry AAS (Perkin Elmer).

Every catalyst was encoded by “KA–XY” symbol. “A” stands for polymer support–poly(acrylonitrile-co-vinyl acetate-co-divinylbenzene). The resins after modification are encoded by A–X, where X is a kind of resin. Y allows to distinguish the catalysts, which were prepared from the same resin but were characterized by different Cu(II) ion loading.

2.2. Oxidation of hydroquinone (H_2Q)

Hydrogen peroxide solution (5.6×10^{-2} mol/dm^3, pH 5) and hydroquinone (H_2Q) solution (4×10^{-3} mol/dm^3) was added to swollen catalyst in a polyethylene flask. Entire mixture was shaken for 60 min at 35 °C. The Cu(II) to H_2Q ratio was 1:10. The concentration of unreacted hydroquinone (H_2Q) and *p*-benzoquinone (Q) was determined by UV/Vis spectrophotometry using JASCO 570c UV/Vis spectrophotometer. The characteristic bands were at $\lambda = 289.0$ nm for H_2Q and 246.5 nm for Q. The initial rate of reaction after 10 min of oxidation reaction (called catalytic activity of catalyst), the oxidation degree of H_2Q (L_{H_2Q}) and yield of Q (Y_Q) after 60 min of oxidation reaction were calculated from following equations: $v_0 = \Delta[Q]/t$, $L_{H_2Q} = (\Delta[H_2Q]/[H_2Q]_0) \times 100\%$ and $Y_Q = ([Q]/[H_2Q]_0) \times 100\%$, respectively. The selectivity (D) was defined as the ratio of main product concentration [Q] to the reacted substrate concentration $\Delta[H_2Q]$.

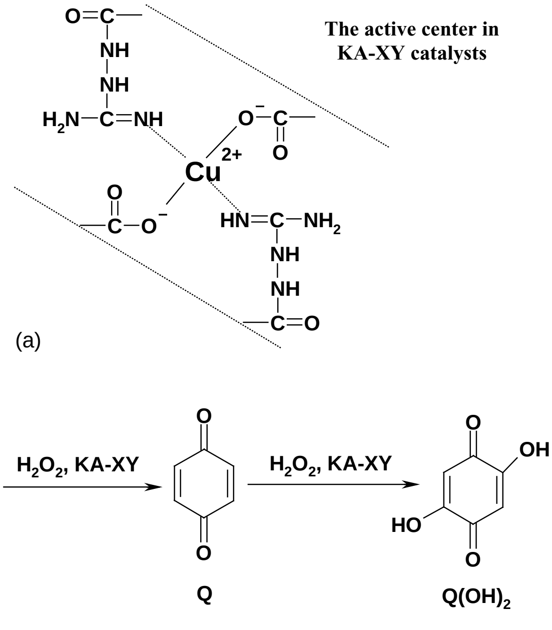

Fig. 1. (a) The structure of active centers (N_2O_2 type) in catalysts KA–XY; (b) the oxidation reaction of hydroquinone (H_2Q) to *p*-benzoquinone (Q) by means of hydrogen peroxide. The main product is Q but in the unfavorable conditions the 2,5-dihydroxy-*p*-benzoquinone forms as the by-product.

3. Results and discussion

3.1. Synthesis and characteristic of resins with aminoguanidyl and carboxyl groups

The resins with aminoguanidyl groups were prepared by aminolysis of nitrile groups of terpolymer A and served as a solid support for immobilization of Cu(II) ions. It was found that during aminolysis the nitrile groups were converted to N-substitute amides and carboxyl groups [12]. The resins A–X were characterized by a high hydrophilicity due to the presence of carboxyl and hydroxyl groups (hydrolysis of ester groups in VA). The increase of water regain (Table 1) indicates the higher hydrophilicity of obtained resins in comparison to terpolymer A ($W = 1.8$ g/g). The concentration of aminoguanidyl and carboxyl groups depends on aminolysis conditions, e.g. reaction time and kind of diluents (Table 1).

To prepare the resin with carboxyl groups only or with aminoguanidyl groups only, the basic hydrolysis of A and the blocked reaction of carboxyl groups of A-6 and A-5 resin were carried out. The A-0 resin, which contains the carboxyl groups only, was obtained as the result of hydrolysis of A resin (Table 2).

However, the resins with blocked carboxyl groups (A-6BF, A-6F and A-5C) were prepared in the reaction between A-6 and bromofenacyl bromide BF (or fenacyl bromide F) as well as in the esterification of carboxyl groups of A-5 by means of methanol (C). The blocked reaction of carboxyl groups in A-6 using BF or F was accompanied with mer molecular weight increase (Table 2). It was supposed that the reaction of both bromides proceeded with carboxyl groups as well as with the aminoguanidyl groups. Additionally, the hydrolysis of nitrile groups of A-6 (unreacted during aminolysis) was continued. As the result of these modifications, the resins (A-6BF and A-6F) with lower aminoguanidyl group and higher carboxyl group concentrations than those in A-6 were obtained. Given that all carboxyl groups in A-6 reacted with BF or F, the theoretical nitrogen content (Z_N) was calculated ($Z_N = Z_N^{A\text{-}6}/(1 + \Delta m)$), where Δm noted the mass difference between A-6 and A-6BF(F) caused by the formation of bromofenacyl (fenacyl) groups. In both cases, Z_N was similar to this for A-6 (the $Z_N^{A\text{-}6}$ was 12.1 mmol/g). For this reason it can be suggested that during the blocked reaction the crosslinking reaction proceeded, which caused the aminoguanidyl group concentration to decrease.

The different situation was observed, when the esterification of carboxyl groups of A-5 was performed. The A-5C resin was obtained as the product of esterification (Table 2). The aminoguanidyl and carboxyl group concentration was not determined because the ester groups hydrolyze in aqueous solution. The insignificant increase of Z_{COOH} (about 0.3 mmol/g) was observed. However, Z_N was practically the same as in A-5.

In order to determine the sorption ability of amphoteric resins, sorption of Cu(II) ions (S—the Cu(II) loading) was measured from Cu(II) solutions at pH 5.0. The Cu(II) ion loading was in the range of 0.16–1.43 mmol/g. It is known that Cu(II) ions can be complexed by both aminoguanidyl and carboxyl groups of the resins [8]. Under studied sorption conditions the N_2O_2 type complexes (Fig. 1a) were formed as confirmed in earlier research [8,11]. If Z_{NH_2} was low, the type O_4 or O_3N complexes could be formed, too. This situation was observed for catalyst KA-01 (Table 2) and for catalysts prepared from A-3 or A-7 resin. The structures of ligands and resins influence significantly on catalytic ability of Cu(II)–resin systems.

3.2. Catalytic activity in hydroquinone oxidation

The catalytic properties of Cu(II) ions immobilized on resins were studied in model oxidation reaction of hydroquinone (H_2Q) using hydrogen peroxide in aqueous medium (Fig. 1b). The *p*-benzoquinone (Q) was a main product of H_2Q oxidation. 2,5-Dihydroxy-*p*-benzoquinone ($Q(OH)_2$) appeared only when the reaction was carried out under unfavorable conditions. The parameters of spectra and the catalytic oxidation were previously discussed in detail [11]. Earlier research of H_2Q oxidation showed that the optimal Cu(II) loading for catalysts was in the range 0.35–0.45 mmol/g, the optimal molar H_2Q to Cu(II) ratio was 10:1 and optimal pH was about 5.0 [11].

As it turned out [11], the square planar Cu(II) complexes (Fig. 1a), which involve the two aminoguanidyl groups and two carboxyl groups (N_2O_2 type) showed the highest catalytic activity in hydroquinone oxidation. One of

Table 2
The characteristics of the ion exchangers with carboxyl groups only and with blocked carboxyl groups and the catalysts based on them

Ion exchanger	W (g/g)	Z_{NH_2} (mmol/g)	Z_{COOH} (mmol/g)	Z_C (mmol/g)	Z_X (mmol/g)					Catalysts	S (mmol/g)	L_{H_2Q} (%)	Y_Q (%)	$Y_{Q(OH)_2}$ (%)	D (%)
					C	H	N	Br	O						
A-0	3.50	–	7.86	7.86	–	–	–	–	–	KA-01	0.54	17.4	10.6	6.7	61.0
A-6BF	1.50	0.39	3.29	3.68	47.5	44.8	8.9	1.62	8.21	KA-6BF1	0.41	56.6	50.0	6.3	88.3
A-6F	1.74	0.22	4.47	4.69	50.8	58.9	9.1	–	8.43	KA-6F1	0.42	67.8	61.2	6.6	90.3
A-5C	–	–	–	–	54.0	63.4	11.4	–	8.11	KA-5C1	0.21	50.6	44.0	6.6	87.0
										KA-5C2	0.36	37.3	30.7	6.7	82.3

Catalytic activity in H_2Q oxidation of these systems. Z_X: content of chemical elements; X = C, H, N, O, Cl or Br. L_{H_2Q}: oxidation degree of hydroquinone. Y_Q: yield of *p*-benzoquinone. $Y_{Q(OH)_2}$: yield of 2,5-dihydroxy-*p*-benzoquinone. D: selectivity of *p*-benzoquinone.

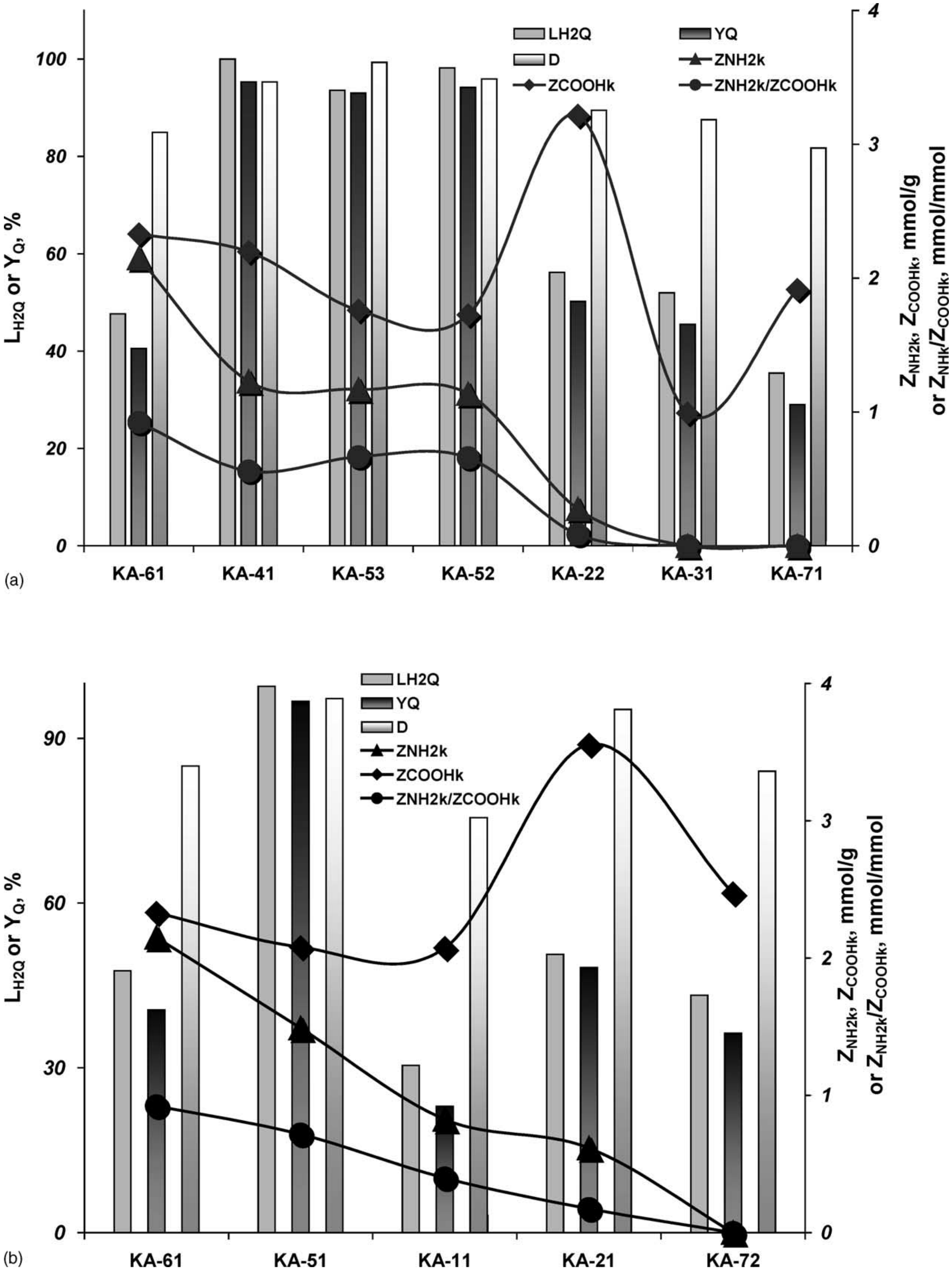

Fig. 2. The influence of free, uncomplexed aminoguanidyl and carboxyl groups and its ratios on the oxidation of H_2Q (L_{H_2Q}) and the yield of Q (Y_Q) for the KA–XY catalysts. The Cu(II) ion loading in the range: (a) 0.26–0.41; (b) 0.16–0.26 mmol/g.

the most important factors, changing the catalytic ability of Cu(II)–resin systems, is the Cu(II) complex stability, which is responsible for catalytic activity and catalyst stability [11,12]. During hydroquinone oxidation by means of hydrogen peroxide in the presence of Cu(II) complexes two processes—reduction Cu(II) → Cu(I) and reoxidation Cu(I) → Cu(II) of active centers—overlap. These processes require the change of complex structure (square planar ↔ tetrahedral) and are responsible for oxidation rate [11,12]. The Cu(II) complex stability, which results from the ligand length, its lability and the Cu(II)–ligand bond energy, correspond with catalysts stability. If the N_2O_2 type complexes were formed during Cu(II) sorption and the Cu(II) loading was not high (0.1–0.4 mmol/g), the catalysts show the highest catalytic stability. In this case the oxidation degree decreased only about 30% after first cycle of oxidation. However, the presence of other type of complexes in catalysts decreased the oxidation degree and initial oxidation rate. The loss of catalyst stability was connected directly with Cu(I) and Cu(II) complex stability and strongly with leaching of Cu(I) or Cu(II) ions from catalysts. These results will be presented in the near future [12].

3.3. *Influence of free, uncomplexed aminoguanidyl and carboxyl group concentration*

One of the very important properties of catalysts, which influence very strongly the catalytic activity of presented systems, will be discussed. This is the free, uncomplexed aminoguanidyl and carboxyl group concentrations (Z_{NH_2k}, $Z_{\mathrm{COOH}k}$) and their ratio ($Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k}$) in catalysts. The term “free groups” means the aminoguanidyl and carboxyl groups after Cu(II) ion sorption, which do not participate in the formation of active center of catalysts. Their importance lies in: the hydrophilic–hydrophobic character of catalysts, the diffusion properties in catalyst beads and isolation of active center.

The catalysts KA–XY were split into two groups differing in the Cu(II) ion loading (Fig. 2). For Cu(II) loading in the range of 0.26–0.41 mmol/g, the highest oxidation degree of H_2Q ($L_{\mathrm{H_2Q}}$) showed the catalysts with the $Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k}$ near to 0.6 (Fig. 2a). The increase of Z_{NH_2k} and $Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k}$ influenced unfavorable $H_2Q \rightarrow Q$ oxidation course. The low $Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k}$ ratio and the significant domination of the carboxyl groups in the catalysts indicated the additional importance of the carboxyl groups in the case of optimal Cu(II) ion loading. Namely, the high Z_{COOH} and the low $Z_{\mathrm{NH_2}}$ in the resins before sorption can cause the formation of the type O_4 complex. It turned out that the Cu(II) complexes, which involve only carboxyl groups, catalyzed the hydroxylation of $Q \rightarrow Q(OH)_2$. The application of catalysts with $Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k} \sim 0$ caused the decrease of selectivity for Q (from 97 to 85%).

In the case of low Cu(II) ion loading ($S = 0.16$–0.26 mmol/g, Fig. 2b), the highest oxidation degree was observed for catalysts with $Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k}$ about 0.7. The high free group concentration (e.g. 3.2 mmol/g for KA-21) caused at first the increase of diffusion limitations (by high $Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k}$) or the increase of concentration of the O_4 type Cu(II) complex and catalyst hydrophilicity (by low $Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k}$). The presence of relatively large aminoguanidyl groups in the active center environment can decrease the H_2Q oxidation degree ($L_{\mathrm{H_2Q}}$), as the result of difficulties in reaching the active center. The decrease of $L_{\mathrm{H_2Q}}$ ensued by significant increase of $Z_{\mathrm{COOH}k}$ (decrease of $Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k}$). It can be suggested that this decrease of $L_{\mathrm{H_2Q}}$ was caused by the increase of catalysts hydrophilicity. Additionally, the low $Z_{\mathrm{NH}_2k}/Z_{\mathrm{COOH}k}$ ratio (close to 0) suggested that the active centers of type O_4 play a important role in H_2Q oxidation, causing the decrease of oxidation degree and catalyst selectivity.

To compare the catalytic activity of KA–XY catalyst with mixed complexes (type N_2O_2) with catalysts containing the type O_4 complexes or the type N_3O and N_4 complexes, the oxidation reaction of H_2Q was carried out in the presence of KA-01, KA-6BF1, KA-6F1, KA-5C1 and KA-5C2 catalysts, respectively (Table 2).

The oxidation reaction in the presence of KA-01 proceeded with decrease of $L_{\mathrm{H_2Q}}$, Y_{Q} and selectivity (about 61% for Q) (Table 2).

The catalysts with blocked carboxyl groups (KA-6BF1, KA-6F1, KA-5C1 and KA-5C2) did not show the good catalytic activity in comparison to catalyst based on resin without blocked carboxyl groups and with the same Cu(II) ion loading (KA-62, KA-52). It should be emphasized that $L_{\mathrm{H_2Q}} \sim 100\%$ and $Y_{\mathrm{Q}} \sim 100\%$ were observed for H_2Q oxidation in the presence of KA-62 and KA-52. The use of KA-6BF1 and KA-6F1 catalysts caused the decrease of the initial oxidation rate (v_0) in comparison with KA-62 ($v_0 = 1.24 \times 10^{-6}$ mol/dm^3 s). In the case of KA-5C2 the initial oxidation rate was kept. However, $L_{\mathrm{H_2Q}}$ and Y_{Q} displayed decrease of initial oxidation rate compared to KA-52.

4. Conclusion

The oxidation of H_2Q by hydrogen peroxide in presence of Cu(II) complexes with aminoguanidyl and carboxyl groups anchored to polymer support leads to Q as the main product. The KA–XY catalysts, in which the square planar, mixed Cu(II) complexes (type N_2O_2) with functional groups of resins forming the catalytic active center, were the most active catalysts. The catalytic activity of these catalysts is dependent on the aminoguanidyl and carboxyl group concentrations and their ratios. The existence of free groups in active center environment is necessary to use these systems as oxidation catalysts. The free groups can change the hydrophobic–hydrophilic character of catalysts and decrease the interaction between the active centers.

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