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Biomimetic Oxidation of Thiol with Oxygen Catalyzed by Octacarboxyphthalocyaninatoiron(III) and -cobalt(II) Fixed on Amorphous Part-Enriched Rayon Staple Fibers^{*1}

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Abstract: In order to discuss the catalysis observed in the odor-removing reaction catalyzed by octacarboxyphthalocyaninatoiron(III) and -cobalt(II) [Fe(III)- and Co(II)-ocpc] fixed on the amorphous part-enriched rayon staple fibers, the oxidation of 2-mercaptoethanol (RSH) using these fibers was studied in an aqueous solution containing molecular oxygen at pH 7.0 and at 25 °C. The catalytic activities of metallophthalocyanines were determined by the measurement of the oxygen consumption during the reaction with a Warburg respirometer. The kinetics of the enzyme-like reaction was characterized in terms of a bisubstrate Michaelis-Menten's rate law. The rate constants of the rate-determining steps (turnover numbers) of 7.3 and 23.8 min⁻¹ were obtained with the Fe(III)- and Co(II)-ocpc-fiber catalysts, respectively, and were lower than those of the unfixed metal complexes alone in solution. However, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values were approximately the same as those of the complexes alone suggesting that the oxidation mainly proceeded on the surface of the fibers. The catalysts fixed on the rayon staple fibers were more stable against radical species in the reaction solution than the unfixed catalysts, and could be repeatedly utilized as a catalyst for the aerobic oxidation of RSH.

1. Introduction

Metallophthalocyanines attract our interest strongly because of their structural similarity to the active center of naturally occurring haemenzymes[1]. We have studied on a series of functional metallophthalocyanines and their polymers as models for *catalase* [2-5], *peroxidase* [6], *oxidase* [7, 8]. Quite recently, we have found that octacarboxyphthalocyaninatoiron(III) and -cobalt(II) [Fe(III)- and Co(II)-ocpc's] are remarkably effective catalysts for the biomimetic oxidation of thiol compounds with molecular oxygen [9, 10]. In the application of these compounds to odor-removing goods, the catalyst carrier which has adequate properties for the biomimetic

oxidation must be used.

Hydroxyl groups in the regenerated cellulose fibers are useful to fix the functional molecules with carboxyl groups on those and to form a hydrophilic domain for the reaction field with the negatively charged substrates. They are therefore useful as a supporting material for the application of Fe(III)- and Co(II)-ocpc catalysts to the biomimetic odor-removing fibers. The amorphous part-enriched rayon staple fibers having 14% of crystallinity have been discovered by Daiwabo Co. Ltd. (Osaka, Japan) [11]. The amounts of adsorption of metal-ocpc (M-ocpc) on this rayon staple fibers were over hundred times of those on the regular rayon fibers. In the former the M-ocpc molecules homogeneously penetrated into the rayon staple fibers [11].

The foul odorants arising from spoiled garbage or sewage contain sulfur compounds such as mercaptan and

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hydrogen sulfide. It had been found that the Fe(III)-ocpc and Co(II)-ocpc fixed on the amorphous part-enriched rayon staple fibers could effectively reduce the amounts of these compounds with bad odors in air. From this fact, we have developed a new type of odor-removing fiber which removes odors through the enzyme-like reaction in contrast to activated charcoal which removes odors through the absorption of the odor-producing compounds.

In this paper, in order to compare the catalytic properties of the odor-removing reaction of the M-ocpc's fixed to the fibers with those of unfixed M-ocpc's, the aerobic oxidation of 2-mercaptoethanol catalyzed by Fe(III)-ocpc and Co(II)-ocpc fixed on the amorphous part-enriched rayon staple fibers has been investigated.

2. Experimental

2.1 Materials

Amorphous part-enriched rayon staple fibers developed by Daiwabo Co., Ltd. (Osaka, Japan) were used. Fe(III)- and Co(II)-ocpc 's were synthesized and purified as described in an earlier article [2]. 2-Mercaptoethanol and the other reagents were of analytical grade and were used without further purification. The fixing of M-ocpc on the rayon staple fibers was carried out as follows: 30 g of the fibers was added to 150 mL of the aqueous mixture containing 0.98 mmol/L M-ocpc (0.1 N KOH), and kept at 20 °C for 24 h with shaking. The treated fibers were added to 150 mL of 0.1 mol/L aqueous acetic acid, rinsed with an enough amount of pure water, and dried at 60 °C. The amounts of adsorbed Fe(III)- and Co(II)-ocpc on the rayon staple fibers were of 4.58 and 2.40 wt-%, respectively.

2.2 Aerobic Oxidation of 2-Mercaptoethanol Catalyzed by M-ocpc's on the Rayon Staple Fibers

The rayon staple fibers containing M-ocpc's were cut into snippets, about 2 mm long, and used as heterogeneous catalysts in the following reaction. The reaction rates of oxidation of 2-mercaptoethanol in the presence of these catalysts were measured by determining the oxygen consumption in the reaction mixture with a Mitamura-Riken Warburg Respirometer. All experiments were conducted at 25 ± 0.1 °C with a shaking speed of 136 r.p.m. "Standard solution" (5 mL) contains the catalysts in 10^{-7} mol/L, 2-mercaptoethanol (RSH) in the initial concentration $[\text{RSH}]_0$ of 0.256 mol/L, and oxygen

Fig. 1 Oxidation of 2-mercaptoethanol (RSH) catalyzed by Fe(III)- and Co(II)-ocpc fixed on the rayon staple fiber: $[\text{M-ocpc}]_0 = 1.0 \times 10^{-7}$ mol/L, $[\text{RSH}]_0 = 0.253$ mol/L, $[\text{O}_2]_0 = 2.38 \times 10^{-4}$ mol/L, pH = 7.0, Temp. = 25.0 °C; ($\circ$), Fe(III)-ocpc fixed on the rayon fiber; (Δ), Co(II)-ocpc fixed on the rayon fiber; ($\bullet$), Fe(III)- and Co(II)-ocpc ; ($\square$), rayon staple fiber alone.

in the initial concentration $[\text{O}_2]_0$ of 2.38×10^{-3} mol/L. The concentrations of the catalyst, RSH and O_2 were varied for the measurement.

The catalytic reaction was started by the addition of an RSH solution into a catalyst solution. Before the addition, the pH of these solutions was adjusted with 0.1 M KOH or HCl. The exact concentration of RSH in the stock solution was determined by the reaction with an I_2 solution, followed by the titration of excess I_2 with a $\text{Na}_2\text{S}_2\text{O}_3$ standard solution. The exact concentrations of catalysts in the stock solutions were determined by metal analysis with an atomic absorption spectrophotometer. The initial reaction velocity, $V_0 = -d[\text{O}_2]/dt$ (in mol/L/min) was calculated from the slope of the curve of the oxygen consumption for the oxidation of 2-mercaptoethanol at $t=0$. The concentration of oxidized 2-mercaptoethanol was calculated from the amount of consumed oxygen during the reaction.

3. Results and Discussion

Fig. 1 shows rate curves of the oxygen consumption

for the aerobic oxidation of 2-mercaptoethanol catalyzed by octacarboxyphthalocyaninatoiron (III) and -cobalt (II) [Fe(III)- and Co(II)-ocpc's] fixed on the amorphous part-enriched rayon staple fibers in an aqueous solution at pH 7.0 and at 25 °C, in comparison with that by the original fibers alone. The oxidation proceeded in the cases of Fe(III)- and Co(II)-ocpc's on the fibers. But no reaction occurred in the case of the original fibers alone. The rate of oxygen consumption catalyzed by Co(II)-ocpc on the fibers was higher than that by the Fe(III)-ocpc on the fibers.

We already reported that the mechanism for the aerobic oxidation of 2-mercaptoethanol catalyzed by polycarboxyphthalocyaninatoiron (III) and -cobalt (II)(M-pc) in an aqueous solution at pH 7.0 could be written by the following equations[9, 10];

where RSH is 2-mercaptoethanol, $K_{\text{RSH}}^{\text{H}}$ is the dissociation constant of RSH, and k_1 , k_2 , k_3 , k_4 , and k_5 are rate constants in each process of the reactions. The rate of the oxidation of 2-mercaptoethanol can be shown in Eqs. (8) and (9) by using the method of King and Altman [12]

$$\frac{1}{V_0} = \frac{1}{V_{\text{max}}} + \frac{K_A}{V_{\text{max}}} \cdot \frac{1}{[\text{O}_2]_0} \quad (8)$$

where $[\text{RSH}]_0$ is excess

$$\frac{1}{V_0} = \frac{1}{V_{\text{max}}} + \frac{K_B'}{V_{\text{max}}} \cdot \frac{1}{[\text{RSH}]_0} \quad (9)$$

where $[\text{O}_2]_0$ is excess

where V_0 is the initial reaction velocity (in mol/L/min), $[\text{O}_2]_0$ and $[\text{RSH}]_0$ are the initial concentrations of O_2 and RSH in the reaction solution, respectively, $V_{\text{max}} = k_5[\text{M-pc}]_0$

Fig. 2 $1/[\text{RSH}]_0 \cdot 1/V_0$ relationship for the oxidation of 2-mercaptoethanol (RSH) by M-ocpc fixed on the rayon staple fiber: $[\text{M-ocpc}]_0 = 1.0 \times 10^{-7} \text{ mol/L}$, $[\text{RSH}]_0 = 0.012 \sim 0.253 \text{ mol/L}$, $[\text{O}_2]_0 = 2.38 \times 10^{-4} \text{ mol/L}$, pH = 7.0, Temp. = 25.0 °C; (○), Fe(III)-ocpc fixed on the rayon fiber; (△), Co(II)-ocpc fixed on the rayon fiber.

Fig. 3 $1/[\text{O}_2]_0 \cdot 1/V_0$ relationship for the oxidation of 2-mercaptoethanol (RSH) by M-ocpc fixed on the rayon staple fiber: $[\text{M-ocpc}]_0 = 1.0 \times 10^{-7} \text{ mol/L}$, $[\text{RSH}]_0 = 0.253 \text{ mol/L}$, $[\text{O}_2]_0 = 2.38 \times 10^{-4} \sim 5.73 \times 10^{-3} \text{ mol/L}$, pH = 7.0, Temp. = 25.0 °C; (○), Fe(III)-ocpc fixed on the rayon fiber; (△), Co(II)-ocpc fixed on the rayon fiber.

$\text{pc}]_0$ ($[\text{M-pc}]_0$ is the initial concentration of M-pc), $K_A = (k_4 + k_5)/k_3$ and $K_B' = K_B[\text{H}^+]/K_{\text{RSH}}^{\text{H}}$ ($K_B = k_5/k_1$).

According to Eq.(9), $1/V_0$ values obtained from several rate curves were plots against $1/[\text{RSH}]_0$ at constant $[\text{O}_2]_0$ in Fig. 2. Fig. 3 shows a plot of $1/V_0$ against $1/[\text{O}_2]_0$ at constant $[\text{RSH}]_0$ according to Eq. (8). The linear relation-

Table 1 Kinetic Parameters for the Aerobic Oxidation of 2-Mercaptoethanol Catalyzed by Octacarboxyphthalocyaninometal fixed on Amorphous Part-Enriched Rayon Staple Fibers in Aqueous solution at pH 7.0 and 25.0 °C^{a)}

Catalyst	$V_{\max}$ $\text{mol L}^{-1} \text{ min}^{-1}$	K_B' mol L^{-1}	k_5 min^{-1}	$\Delta H^\ddagger$ kcal mol^{-1}	$\Delta S^\ddagger$ $\text{cal mol}^{-1} \text{ K}^{-1}$
Fe(III)-ocpc rayon ^{b)}	1.09×10^{-4}	5.17×10^{-2}	7.3	7.0	-39.6
Co(II)-ocpc rayon ^{b)}	6.20×10^{-4}	5.16×10^{-2}	23.8	5.4	-42.1
Fe(III)-ocpc ^{c)}	7.20×10^{-5}	2.47×10^{-3}	720.0	7.1	-29.7
Co(II)-ocpc ^{c)}	8.40×10^{-5}	5.05×10^{-3}	840.0	4.6	-37.9

^{a)} $[\text{RSH}]_0 = 7.13 \times 10^{-3} \sim 2.85 \times 10^{-1} \text{ mol L}^{-1}$. ^{b)} $[\text{M-ocpc}]_0 = 2.61 \times 10^{-5} \text{ mol L}^{-1}$. ^{c)} $[\text{M-ocpc}]_0 = 1.00 \times 10^{-7} \text{ mol L}^{-1}$.

ship between $1/V_0$ and $1/[\text{Substrates}]_0$ shown in these figures strongly supports the proposed mechanism given by Eqs. (1) to (7). Therefore, Fe(III)- and Co(II)-ocpc's fixed on the rayon staple fibers perform the oxidation of 2-mercaptoethanol using molecular oxygen in an aqueous solution at pH 7.0 following the enzyme-like kinetics. This type of mechanism has been originally suggested by Theorell and Chance [13].

Kinetic parameters for the oxidation of 2-mercaptoethanol with molecular oxygen catalyzed by Fe(III)- and Co(II)-ocpc's on the fibers are listed in Table 1 in comparison with the unfixed M-ocpc's as water-soluble catalysts [9]. In the M-ocpc-fiber catalysts, the values of the rate constant of k_5 in the rate-determining step given by Eq. (4) are about 1/30 to 1/100 of those of the unfixed catalysts. On the other hand, the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for Fe(III)- and Co(II)-ocpc's on the fibers are approximately the same as those in the cases of the unfixed complexes alone. These lower activities by Fe(III)- and Co(II)-ocpc's on the fibers are not attributable to a lowering of the essential catalytic activity of M-ocpc's because no change was observed in the spin state of each active metal ion in M-ocpc's by ESR measurements. We reported recently the catalase-like reactivity for decomposition of hydrogen peroxide (H_2O_2) catalyzed by Fe(III)-ocpc fixed on the amorphous part-enriched rayon staple fiber in an aqueous solution at pH 7.0 and 25 °C [5], where the fixed catalyst on the fibers for the decomposition of H_2O_2 in heterogeneous systems was more active than the unfixed Fe(III)-ocpc in solution. We also reported that Fe(III)-ocpc fixed on the rayon staple fibers contained the distorted rhombic-coordinated iron(III) ion in the high spin state, which is one of the requirements for appearance of the catalytic activity. This shows that

Fig. 4 Effect of repetition of reaction on catalytic activities of M-ocpc fixed on the rayon staple fibers for the oxidation of 2-mercaptoethanol (RSH): $[\text{M-ocpc}]_0 = 1.0 \times 10^{-7} \text{ mol/L}$, $[\text{RSH}]_0 = 0.244 \text{ mol/L}$, $[\text{O}_2]_0 = 2.38 \times 10^{-4} \text{ mol/L}$, pH = 7.0, Temp. = 25.0 °C; (○), (●), (◐), Fe(III)-ocpc fixed on the rayon fiber; (△), (▲), (◑), Co(II)-ocpc fixed on the rayon fiber; (○) and (△), the 1st run; (●) and (▲), the 2nd run; (◐) and (◑), the 3rd run.

the essential catalytic activities of M-ocpc's were kept even in the fibres. These results suggest that the oxidation mainly proceeded on the surface of the fibers but it was hard to occur inside the fibers. The substrates with relatively large sizes can not easily access the active sites of the M-ocpc molecules inside the fibers.

The reaction solutions were greenish blue at the beginning of the reaction and turned to pale yellow or colorless *via* green during the first 120 min. The unfixed metallophthalocyanine catalysts in an aqueous solution

were usually unstable to the radical species generated in the course of radical reactions [9]. We reported that immobilized 2, 9, 16, 23-tetracarboxyphthalocyaninatoiron(III) on a polymer matrix became very stable, and can be repeatedly utilized[3]. Fig. 4 shows rate curves for the repeated runs of the aerobic oxidation of 2-mercaptoethanol catalyzed by Co(II)-ocpc fixed on the amorphous part-enriched rayon staple fibers in an aqueous solution at pH 7.0 and at 25 °C. The reaction was repeated three times. It was observed for the Co(II)-ocpc-fiber catalyst that the activity of the third run was about 76% of that of the first one. These observations show that the Co(II)-ocpc catalyst on the fibers had the higher activity and the longer lifetime for the catalytic oxidation of 2-mercaptoethanol than the Fe(III)-ocpc catalyst.

In summary, we have found that the Co(II)-ocpc catalyst fixed on the fiber acts in the mechanism same as that for the unfixed Co(II)-ocpc catalyst and has the longer lifetime than that of the unfixed one. In addition, the amorphous part-enriched rayon staple fiber is one of the adequate materials as a carrier of the catalyst for the aerobic oxidation of 2-mercaptoethanol in an aqueous solution at pH 7.

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