

Functional metallomacrocycles and their polymers: 34. Kinetics and mechanism of the biomimetic decomposition of hydrogen peroxide catalysed by heterogeneous octacarboxyphthalocyaninato iron(III) supported on amorphous enriched rayon staple fibres

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Catalase-like decomposition of hydrogen peroxide with the octacarboxy-phthalocyaninatoiron(III) (Fe(III)-oapc) supported on amorphous enriched rayon staple fibre (degree of crystallinity = 14%) was studied in aqueous solution at pH 7.0 and 25°C. The Fe(III)-oapc supported on the rayon staple fibre is remarkably effective as an immobilized catalyst for decomposition of hydrogen peroxide. The reaction rate was analysed in terms of Michaelis–Menten kinetics, which suggests that the catalysed decomposition of hydrogen peroxide proceeds via the formation of an activated complex. Iron atom distribution of the rayon staple fibre indicated that Fe(III)-oapc existed on the fibre homogeneously. Electronic and e.s.r. spectra of the fibre suggests monomeric Fe(III)-oapc with a distorted rhombic coordinating high spin iron(III) ion. Fe(III)-oapc is considered to be immobilized by hydrogen bonding between carboxylic groups on Fe(III)-oapc and hydroxy groups of cellulose, and a weak coordination bonding of iron with hydroxy groups on cellulose. The immobilization of Fe-oapc to the rayon staple fibre extends its catalytic lifetime and makes the catalyst molecule the monomeric active state. Copyright © 1996 Elsevier Science Ltd.

(Keywords: catalase-like decomposition; hydrogen peroxide; octacarboxy-phthalocyaninatoiron (III); rayon staple fibre; Michaelis–Menten kinetic)

INTRODUCTION

Phthalocyanine (tetrabenzotetraazaporphyrin) has a same frame structure with porphyrin except that the *meso*-bridge is nitrogen instead of carbon and that four benzene rings are additionally fused¹. However, metallophthalocyanines have attracted considerable interest because of their structural similarity to the active centre of naturally occurring haemproteins². We have hitherto studied the synthesis of functional metallophthalocyanines and their polymers, and their

catalase-like^{3–5}, peroxidase-like⁶, and oxidase-like^{7,8} reaction as enzyme models. In particular, we have recently found that Fe(III)-oapc is a remarkably effective catalyst for the decomposition reaction of hydrogen peroxide in aqueous solution at pH 7.0, compared with hemin, other metallophthalocyanines and iron complexes³. The catalytic decomposition proceeds via the formation of an activated complex from the catalyst and the substrate³. However, dissolved Fe(III)-oapc catalyst was unstable, that is, upon the reaction beginning it turned green and yellow or even colourless after 5 min. We have also reported that immobilized 2,9,16,23-tetracarboxyphthalocyaninatoiron(III) on the

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polymer matrix became very stable because its lifetime extended to about ten-fold in the reaction solution^{4,5}. The oxidation of thiol compounds catalysed by Fe(III)-oapc in the presence of molecular oxygen has been reported⁷. The biomimetic oxidation of thiols which have toxic bad odours is just appropriate to apply to an odour-removing system under mild and friendly conditions. If the fibres for clothing employed as a carrier of the catalyst, Fe(III)-oapc, the removal of hydrogen peroxide which generates from molecular oxygen by the catalytic oxidation against the thiols is a serious problem. The fibres containing the catalyst for odour-removing are also required as a catalytic activity for the decomposition of hydrogen peroxide.

The cellulose fibre is a very fine fibre with a large surface area per volume. They also contain sufficient amounts of reactive groups to combine functional molecules and also hydrophilic hydroxy groups⁹. They are therefore useful as supporting materials for the application to an Fe(III)-oapc catalyst. This paper is concerned with the immobilization of Fe(III)-oapc to amorphous-enriched rayon staple fibre, and kinetics as well as mechanistic studies on the biomimetic H₂O₂ decomposition reaction by Fe(III)-oapc supported on the rayon staple fibre in an aqueous solution.

EXPERIMENTAL

Materials

Amorphous enriched rayon staple fibre (degree of crystallinity = 14%) was supplied by Daiwabo Co., Ltd. (Osaka, Japan). Octacarboxyphthalocyaninatoiron(III) and cobalt(II) (M-oapc, M = Fe(III), Co(II)) were synthesized and purified in our laboratory as described in an earlier article³. All other chemicals were of analytical grade and used without further purification.

Supporting of Fe(III)-oapc on rayon staple fibre

Thirty grams of the fibre were added to 150 ml of the aqueous mixture containing 9.8×10^{-4} M Fe(III)-oapc and 0.1 M KOH, and stirred continuously at several temperatures from $10-60 \pm 0.5^\circ\text{C}$ for 24 h. The fibre thus treated was added to 150 ml of 0.1 M aqueous acetic acid solution, washed with water, and dried at 60.0°C .

Measurement of catalysis

The rayon staple fibres containing Fe(III)-oapc were cut into snippets about 2 mm long. The decomposition rates of hydrogen peroxide by the catalysts were determined by measuring the concentration of oxygen originating in the reaction solution with a Mitamura-Riken Warburg respirometer. All experiments were conducted at $10-60 \pm 0.5^\circ\text{C}$ at a shaking speed of 100 cycles min^{-1} . The catalytic reaction was started by the addition of hydrogen peroxide solution into the catalyst solution in which the ionic strength was kept constant at 0.1 M (KCl) and pH was adjusted to 7.0. pH was measured by using an ORION 701-A pH-meter. The exact concentration of H₂O₂ solution was determined by titration with a KMnO₄ solution. The concentration of all reagents, pH and reaction temperature used in practice are shown in Figures 1-9, and Tables 1 and 2. The initial reaction velocity, $V_0 = -d[\text{H}_2\text{O}_2]/dt$ (in $\text{mol l}^{-1} \text{s}^{-1}$) was taken from the slope of the tangent of the concentration of H₂O₂ decomposed *versus* time curve

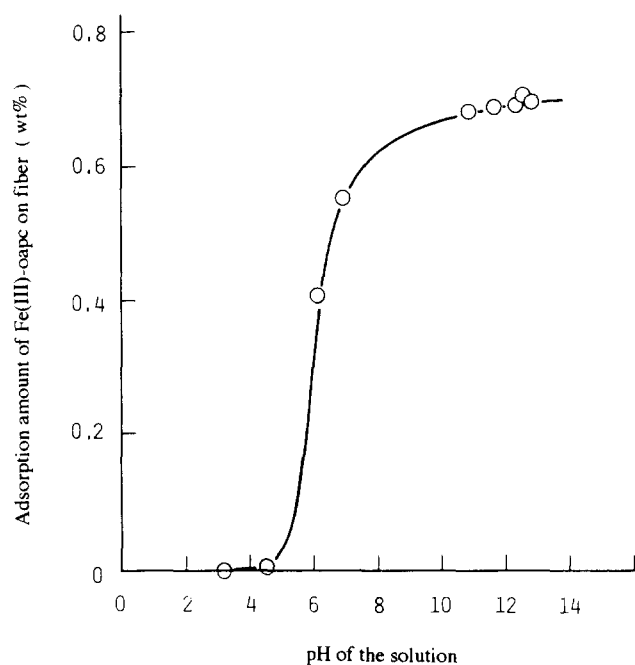


Figure 1 Relationship between pH in Fe(III)-oapc aqueous solutions and adsorption amount of Fe(III)-oapc on rayon fibres. $[\text{Fe(III)-oapc}] = 3.44 \times 10^{-3} \text{ mol l}^{-1}$ at 20.0°C , for 1 h

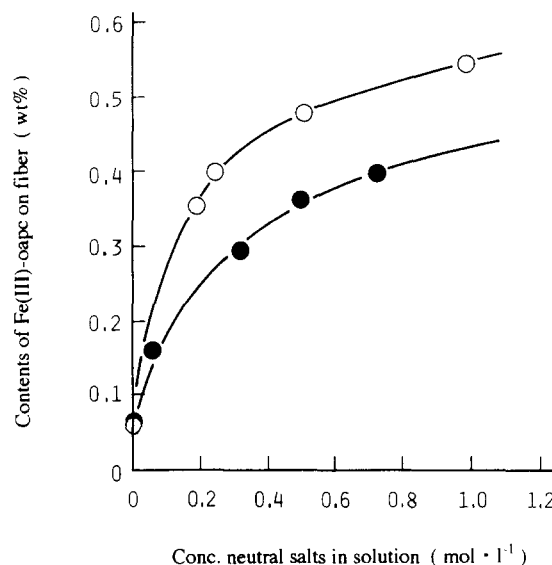


Figure 2 Effect of neutral salts in solution on adsorption of Fe(III)-oapc on rayon fibre. Fibre 30 g/300 ml of aqueous solution. $[\text{Fe(III)-oapc}] = 3.44 \times 10^{-3} \text{ mol l}^{-1}$, pH = 12.2 at 20.0°C , for 1 h. (○) Na₂SO₄; (●) NaCl

at $t = 0$. The concentration of H₂O₂ decomposed was calculated from the concentration of O₂ generated in the reaction solution. This agreed with the concentration determined by titration with KMnO₄ within the range of error.

Apparatus

Adsorbed amounts of Fe(III)-oapc on the fibre were determined from Fe contents by a Hitachi 170-70 Zeeman-effect atomic absorption spectrophotometer. Electronic spectrum of the fibre containing a Fe(III)-oapc was recorded on a Orinpus 21177 microspectrophotometer. The distribution of Fe in the fibre was determined using a Shimadzu EPM 810Q X-ray

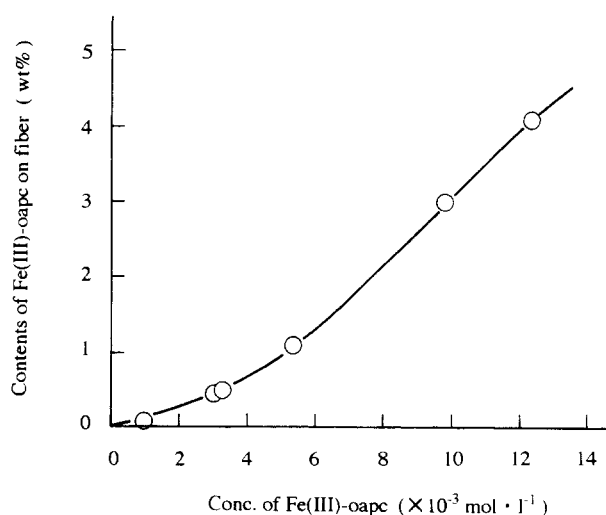


Figure 3 Relationship between concentration of Fe(III)-oapc in aqueous solutions and adsorption amount of Fe(III)-oapc on rayon fibres. Fibre 30 g/300 ml of aqueous solution, pH = 12.2 at 20.0°C, for 1 h

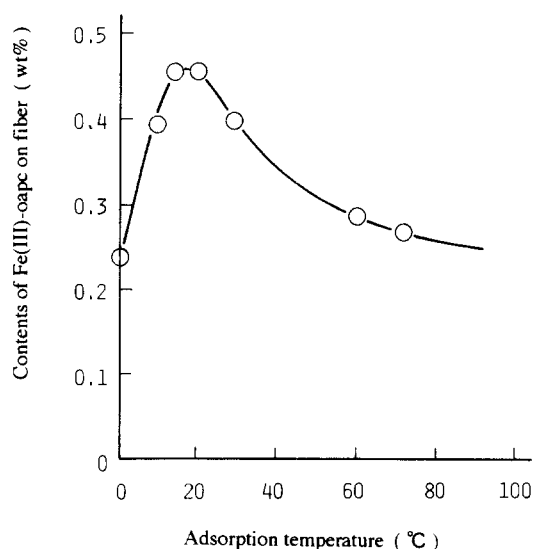


Figure 4 Effect of temperature in solution on adsorption amount of Fe(III)-oapc on rayon fibres. Fibre 30 g/300 ml of aqueous solution, $[\text{Fe(III)-oapc}] = 3.44 \times 10^{-3} \text{ mol l}^{-1}$, pH = 12.2, for 1 h

microanalyzer. E.s.r. spectra were measured with a Varian E-line spectrometer that had 100-kHz field modulation. The operation was X-band (9.196 GHz for 213 K) and the microwave power was 100 mW. The samples were placed in quartz tubes of 4 mm D^{-1} for measurement at 7.5 K with liquid helium and the g -value being calculated by using solid DPPH as the g -marker.

RESULTS AND DISCUSSION

Adsorption of Fe(III)-oapc on amorphous enriched rayon staple fibre

Fe(III)-oapc was soluble in water above pH 7.0. Therefore, the fibre was added to the aqueous solution containing Fe(III)-oapc at above pH 7.0, and stirred continuously for the prescribed time at 20.0°C. The carboxylate groups in the peripheral site of Fe(III)-oapc are dissociated into carboxylate anions, and Fe(III)-oapc is adsorbed in the amorphous enriched

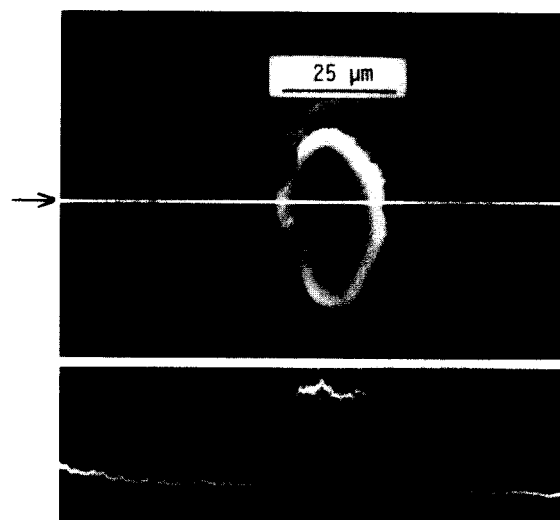


Figure 5 Fe distribution patterns of Fe(III)-oapc adsorbed on the rayon fibres by X-ray microanalyser. Adsorption amount 4.11 wt%. Scanning line: \rightarrow

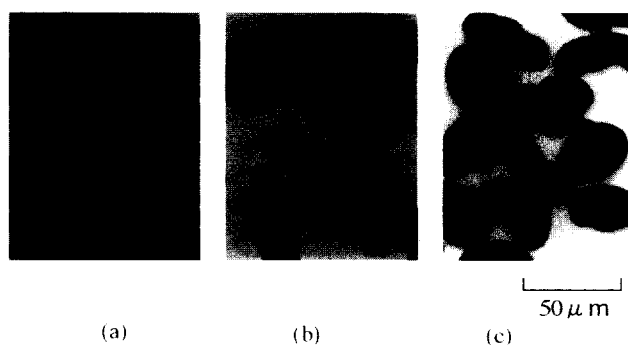


Figure 6 Micrographs of the rayon fibres containing Fe(III)-oapc. Contents of Fe(III)-oapc: (a) 0.06 wt%, (b) 0.46 wt% and (c) 4.11 wt%

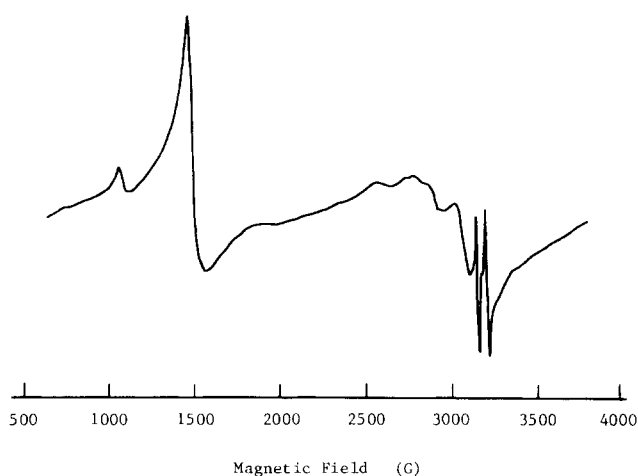


Figure 7 E.s.r. spectra of Fe(III)-oapc adsorbed on the rayon fibre at 7.5 K

rayon staple fibre. Next, the fibre containing an Fe(III)-oapc was treated with aqueous acetic acid solution at pH below 3.0. The potassium ions of $-\text{COOK}$ groups on Fe(III)-oapc in the fibre was replaced with a hydrogen ion, where upon the solubility of Fe(III)-oapc on the fibre in water decreased, and Fe(III)-oapc was fixed in the fibre. *Figure 1* shows the effects of

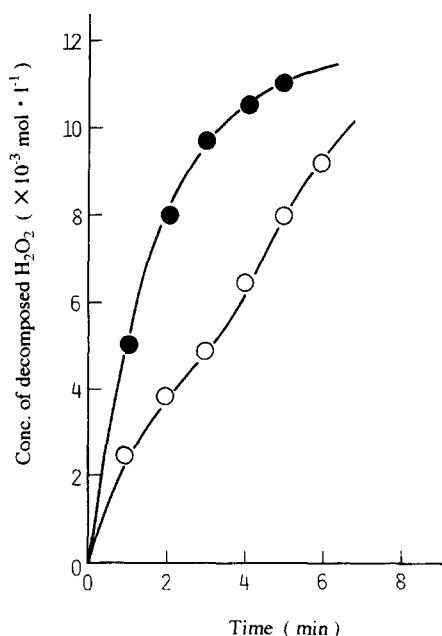


Figure 8 Decomposition of hydrogen peroxide by Fe(III)-oapc adsorbed on rayon fibre. $[\text{Fe(III)-oapc}]_0 = 5.0 \times 10^{-5} \text{ mol l}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 5.0 \times 10^{-2} \text{ mol l}^{-1}$, pH 7.0, 25.0°C. (●) Fe(III)-oapc adsorbed on rayon staple fibre and (○) Fe(III)-oapc dissolved in solution

Table 1 Thermodynamic parameters for the adsorption of Fe(III)-oapc on the amorphous-enriched rayon staple fibre^a

Temp. (K)	$\Delta\mu^0$ (kg kJ mol ⁻¹)	ΔH^0 (kg kJ mol ⁻¹)	ΔS^0 (kg J mol ⁻¹ deg ⁻¹)
273	-1.3	37 ^b	130
283	-2.9		120
293	-4.0		110
303	-3.1	-27 ^c	-98
321	-1.9		-90

^a Degree of crystallinity = 14%

^b From 273 to 293 K

^c From 303 to 321 K

pH in the aqueous solution containing Fe(III)-oapc on the adsorption amounts of Fe(III)-oapc on rayon fibres. Increasing pH above pH 5.0 led to increasing adsorption amounts of Fe(III)-oapc on the fibres. The result suggests that on increasing pH above 5.0, the ionization of the carboxylic groups on Fe(III)-oapc is promoted in the solution, so that the solubility of Fe(III)-oapc increases. From the adsorption experiments in various

Table 2 Kinetic parameters for the decomposition of H₂O₂ catalysed by metallophthalocyanine octacarboxylic acid adsorbed on amorphous-enriched rayon staple fibre at 25.0°C in aqueous solution at pH 7.0

Complexes	V_{max} (mol l ⁻¹ min ⁻¹)	K_m (mol l ⁻¹)	k_3 (min ⁻¹)	ΔE^a (kJ mol ⁻¹)
Fe(III)-oapc rayon ^b	8.9×10^{-3}	4.9×10^{-3}	180	3.9
Co(II)-oapc rayon ^b	3.2×10^{-4}	5.3×10^{-4}	6.3	8.4
Fe(III)-oapc ^c	8.6×10^{-3}	7.1×10^{-3}	170	4.7
Co(II)-oapc ^c			7	
Hemin			6	

^a From 10.0 to 40.0 ± 0.5°C

^b Immobilized catalysts: $[\text{Mt-oapc}]_0 = 5.0 \times 10^{-5} \text{ mol l}^{-1}$

^c Dissolved catalysts: $[\text{Mt-oapc}]_0 = 5.0 \times 10^{-5} \text{ mol l}^{-1}$

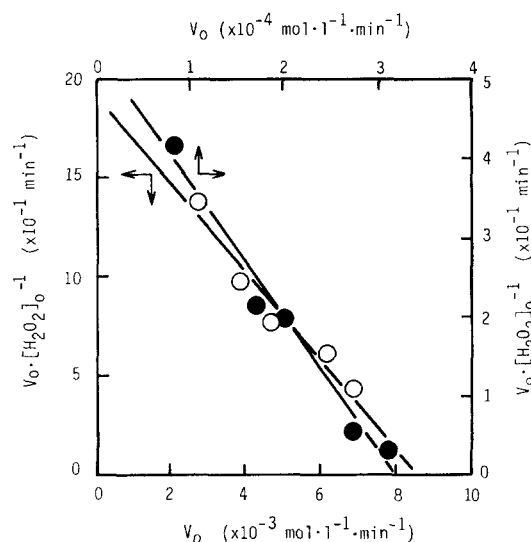


Figure 9 Determination of the reaction parameters by a plot according to the Eadie-Hofstee equation at 25.0 ± 0.5°C at pH 7.0. (○) Fe(III)-oapc adsorbed on rayon staple fibre and (●) Co(II)-oapc adsorbed on rayon staple fibre

concentrations of Fe(III)-oapc aqueous solution, it was found that adsorption amounts of Fe(III)-oapc on amorphous rayon staple fibre were of <10.0 wt%. The adsorption amounts of Fe(III)-oapc on this rayon fibre was much larger than that on regular rayon staple fibres (0.1 wt%). Figure 2 shows the effects of the addition of neutral salts in solution on adsorption of Fe(III)-oapc on the amorphous enriched rayon staple fibres. The adsorption amounts of Fe(III)-oapc on the fibre increased with an increase in the concentration of neutral salts in the solution. The facts suggest that the adsorption amounts of Fe(III)-oapc on the fibre increases with a decrease in the electrostatic repulsion of negatively charged carboxylate ions on Fe(III)-oapc.

Equilibrium adsorption isotherms

The results of adsorption isotherms in which the variation in the concentration of Fe(III)-oapc on the fibre with the concentration of Fe(III)-oapc in solution are shown in Figure 3. This result shows the typical Freundlich equation, yielding a straight line when the data are plotted logarithmically. It may be expressed as

$$[\text{Fe(III)-oapc}]_{\text{in fibre}} = K[\text{Fe(III)-oapc}]_{\text{in solution}}^X \quad (1)$$

where $[\text{Fe(III)-oapc}]_{\text{in fibre}}$ and $[\text{Fe(III)-oapc}]_{\text{in solution}}$ are the concentrations of Fe(III)-oapc in the fibre and in

solution respectively, K is a constant, and X is a fractional power. This fact indicates that the adsorption of Fe(III)-oapc takes place on nonspecific sites in the fibre. The effect of temperature on the adsorption of Fe(III)-oapc on the fibre is shown in Figure 4. The absolute temperature of the adsorption (T), the standard chemical potential ($\Delta\mu^0$), i.e. free energy change in the interaction of Fe(III)-oapc with the rayon staple fibre, and standard heat of adsorption (ΔH^0) are related by

$$\frac{d(\Delta\mu^0/T)}{d(1/T)} = \Delta H^0 \quad (2)$$

From the standard chemical potential and heat of adsorbing, the standard change in entropy (ΔS^0) may be calculated by

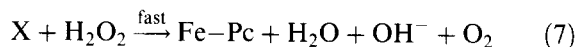
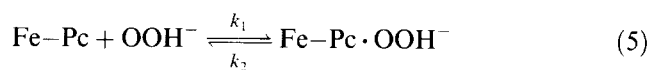
$$-\Delta\mu^0 = \Delta H^0 - T\Delta S^0 \quad (3)$$

where $-\Delta\mu^0 = RT \ln([\text{Fe(III)-oapc}]_{\text{in solution}}/[\text{Fe(III)-oapc}]_{\text{in fibre}})$. The thermodynamic parameters for the adsorption of Fe(III)-oapc on the rayon fibre are listed in Table 1. The difference between the standard chemical potential of Fe(III)-oapc in solution and in fibre phases ($\Delta\mu^0$) is negative in such an experimental temperature range. However, below 20°C it decreases while above 20°C it increases with the rise of temperature. The latter case is lower by a factor of about 1/200 than the general phenominal affinity change ($\Delta\mu^0$) of dyes for the fibres⁹. Below 20°C, the affinity is governed by the factor that positive enthalpy is compensated by an increase in entropy. This result of positive entropy suggests that water molecules in the fibre are substituted for Fe(III)-oapc and released to the bulk solution or that hydrophobic interaction operated in this interaction. Above 20°C, ΔH^0 is about $-6.38 \text{ kcal mol}^{-1}$ which is 1/400-fold the ΔH^0 value for dyeing of direct dyes onto cellulose fibre, e.g. Chrysophenine G has a ΔH^0 value of $-14 \text{ kcal mol}^{-1}$ in the range 60–90°C for several kinds of cellulose fibres⁹. This fact may be due to the hydrogen bonding between carboxylic groups on Fe(III)-oapc and hydroxyl groups of cellulose and to weak coordination bonds of Fe(III) atoms. In this condition, entropy is negative probably because the decrease of the degree of freedom of Fe(III)-oapc exceeds the increase of the degree of freedom of released water molecules. Coordination structure around Fe(III)-oapc in the amorphous enriched rayon staple fibre treated at 25°C was characterized. The amorphous rich rayon staple fibre containing Fe(III)-oapc had a dark green colour. The microscopic photograph of the cross-section of the rayon fibre containing Fe(III)-oapc showed that Fe(III)-oapc is penetrating deeply into the rayon fibre. Figure 5 shows the Fe distribution pattern along the cross-section of the Fe(III)-oapc supported on rayon fibres by X-ray microanalyser. The figure also indicates that Fe atoms exist in the fibre homogeneously. Figure 6 shows the microscopic spectrum of the rayon fibres containing Fe(III)-oapc. As can be seen in the figure, the rayon fibre containing Fe(III)-oapc exhibits an absorption peak around 680 nm. Metallophthalocyanine compounds exhibit absorption peaks around 630 and 670 nm. The species absorbing around 630 nm is a dimer and that absorbing around 670 nm is a monomer¹⁰. Therefore, the Fe(III)-oapc in the rayon fibre are of a monomer structure. For the absorption of Fe(III)-oapc in the

rayon fibre, the dimerization of Fe(III)-oapc may be sterically hindered by the polymer chain. The coordination sphere around Fe(III)-oapc adsorbed on staple rayon fibre was further characterized by e.s.r. spectroscopy at 7.5 K (Figure 7). The g -value of 4.32 is attributed to the distorted rhombic coordinate high spin iron(III) on the phthalocyanine ring, which is similar to catalase and peroxidase^{11–13}. This may indicate that probably one site at the axial position of the Fe(III)-oapc ring is weakly coordinated with the hydroxy group of pyranose in rayon fibre⁹.

Catalase-like activity of Fe(III)- and Co(II)-oapc supported on the amorphous rayon enriched fibre

Figure 8 compares the rate curves of the decomposition of H_2O_2 by Fe(III)-oapc supported on the rayon fibre and free Fe(III)-oapc dissolved in aqueous solution at pH 7.0 and 25°C. In the rayon fibre attached Fe(III)-oapc, the decomposition proceeded smoothly compared with that of free Fe(III)-oapc³. We have already reported that the mechanism for the decomposition reaction of H_2O_2 catalysed by Fe(III)-oapc in aqueous solution at pH 7.0 can be written as³



where $K_{\text{H}_2\text{O}_2}$ is the dissociation constant of H_2O_2 , and k_1 , k_2 as well as k_3 are rate constants in each process for the reaction, respectively. The rate of the decomposition reaction of H_2O_2 can be written as shown in equation (8) assuming that k_3 is the rate constant of the rate-controlling step by using the steady-state Michaelis–Menten method¹⁴

$$V_0 = -\frac{V_{\text{max}}[\text{H}_2\text{O}_2]_0}{K_m + [\text{H}_2\text{O}_2]_0} \quad (8)$$

where V_0 as well as V_{max} are the initial as well as the maximum reaction velocity, K_m is the Michaelis constant, and $[\text{H}_2\text{O}_2]_0$ is the total concentration of H_2O_2 . For the determination of the values of V_{max} and K_m the procedure attributed to Eadie and Hofstee¹⁵ was used and equation (8) was transformed to

$$\frac{V_0}{[\text{H}_2\text{O}_2]_0} = -\frac{1}{K_m} V_0 + \frac{1}{K_m} V_{\text{max}} \quad (9)$$

where $V_{\text{max}} = k_3[\text{Fe(III)-oapc}]_0$ ($[\text{Fe(III)-oapc}]_0$ is the total concentration of Fe(III)-oapc) and $K_m = (k_2 + k_3)/k_1$. The application of the Eadie–Hofstee equation (9) to the case of the immobilized catalyst was attempted. Figure 9 shows plots of $V_0/[\text{H}_2\text{O}_2]_0$ against V_0 for the decomposition reaction of hydrogen peroxide catalysed by Fe(III)- and Co(II)-oapc on the rayon staple fibre at pH 7.0 and 25°C. The linear nature of these plots lends strong support to the proposed mechanism of equations (4)–(7). In other words, the catalysed decomposition of hydrogen peroxide by the immobilized Fe(III)-oapc proceeds via the formation of the same activated

complex (Fe(III)-oapc OOH^-) with the dissolved Fe(III)-oapc system which is inhibited by the presence of imidazole or KCN^3 .

Kinetic parameters for the decomposition reaction of hydrogen peroxide in aqueous solution at pH 7.0 are listed in Table 2. The values of k_3 and K_m for the reaction catalysed by Fe(III)-oapc in the fibre show the same values with free Fe(III)-oapc which is dissolved in reaction solution. This indicates that even in the fibre Fe(III)-oapc catalyses the decomposition reaction in a similar mechanism with the dissolved catalyst.

From the result, Fe(III)-oapc supported on the amorphous enriched rayon staple fibre is found to be a remarkably effective catalyst for the decomposition reaction of hydrogen peroxide, compared with free Fe(III)-oapc catalyst. The microscopic electronic spectrum of Fe(III)-oapc supported on rayon staple fibre exhibited an absorption band around 670 nm, indicating that Fe(III)-oapc is in a monomeric state¹⁰. One of the reasons for the higher activity of Fe(III)-oapc supported on the rayon fibre may be seen in the increasing concentration of monomeric catalyst molecules in the fibre matrix, which is the more active Fe(III)-oapc than the aggregated catalyst³. Moreover, the iron(III) ion in Fe(III)-oapc supported on the rayon staple fibre is in the distorted rhombic coordinate high spin state, revealed by e.s.r. spectrum in which the rhombic signal appears at $g = 4.32$ (Figure 7). It is known that high-spin iron(III)-porphyrin and phthalocyanine with distorted rhombic coordination structure are useful in the decomposition of hydrogen peroxide, which is also similar to catalase or peroxidase¹¹⁻¹³. The iron ion in catalase or peroxidase is coordinated with the four pyrrole nitrogens of protoporphyrin IX and imidazole nitrogen of a histidine residue from the polypeptide chain of the porphyrin defined on the proximal side. The sixth coordination position of iron ion on another side of the porphyrin is coordinated by an hydroxy group at neutral pH. H_2O_2 or HOO^- may be able to coordinate with iron ion at the sixth site by ligand exchange reaction with the hydroxy group. These enzymes act in a higher oxidation state of iron¹⁶.

Fe(III)-oapc dissolved in the reaction mixture containing H_2O_2 or HO_2^- is very unstable. Upon the reaction beginning, it turns green and finally yellow or even colourless after 5 min. It is already known that immobilized iron phthalocyanine on the polymer matrix becomes very stable, and can be repeatedly utilized⁴. It is obvious that the supported Fe(III)-oapc catalyst is much more stable for the peroxide as compared with the free Fe(III)-oapc catalyst. This stabilization may be attributable to immobilization which prevents oxidative destruction by the peroxide of the phthalocyanine ring, because the phthalocyanine ring is surrounded by cellulose chains by forming the hydrogen bonds, and these hardly receive the attack of the peroxide.

CONCLUDING REMARKS

The immobilized Fe(III)-oapc on the rayon staple fibre is an effective catalyst having a long lifetime

for the decomposition of hydrogen peroxide in aqueous solution at room temperature compared with the dissolved Fe(III)-oapc. Amorphous enriched (degree of crystallinity = 14%) rayon staple fibre is particularly desirable in support materials. The adsorption amounts of Fe(III)-oapc on this amorphous enriched rayon staple fibre were much larger than that on regular rayon staple fibre (degree of crystallinity = 40%). Fe(III)-oapc may be supported by the hydrogen bonding between carboxylic groups on Fe(III)-oapc and hydroxy groups of cellulose, and a weak coordination bonding of iron ion with hydroxy groups of cellulose in the fibre. From the microscopic electronic and e.s.r. spectra, Fe(III)-oapc supported on the rayon fibre is in a monomeric state and contains the distorted rhombic coordinating high spin iron(III), which is also similar to catalase and peroxidase. Fe(III)-oapc supported on the rayon staple fibre has a greater distortion than those of catalase and peroxide, and therefore is a remarkably effective immobilized catalyst for the hydrogen peroxide decomposition reaction, as well as a free Fe(III)-oapc catalyst. The reaction proceeds according to the catalase-like mechanism. The removal activity for hydrogen peroxide of Fe(III)-oapc in the fibre for clothing was demonstrated.

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