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Studies on Catalytic Activity of Chelating Resins. I. The Catalytic Activity of Resin–Metal Chelates for the Oxidation of 2,6-Dihydroxyphenylacetic Acid and Hydroquinone

Hiroaki EGAWA,* Takamasa NONAKA, and Noboru KOZAKURA
Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860

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Some crosslinked chelating resins were prepared and the catalytic activity of the resin–metal chelates for the oxidation of 2,6-dihydroxyphenylacetic acid(homogentisic acid) and hydroquinone was investigated. The resin–Cu(II), resin–Au(III), and resin–Ag(I) chelates had a high catalytic activity. Especially resin–Cu(II) chelate had the highest catalytic activity for these oxidation reactions, and its activity did not decrease even after repeated use. The chelating resins having hydrazide or polyethylenepolyamine side chains had a high catalytic activity. In order to have a high catalytic activity, the resin–metal chelates must leave coordination places open for the substrate to coordinate to metal in the chelates. In the oxidation of homogentisic acid, the catalytic activity of gel type resin increased with the increase of crosslinking degree in the range from 0.5% to 7.5%. However, the catalytic activity of the macroreticular chelating reins was scarcely affected by the degree of crosslinking. The oxidation reaction of homogentisic acid showed a kinetic behavior of a typical Michaelis-Menten type.

It is known that Cu(II) ion acts as a catalyst for the oxidation of organic substrates by molecular oxygen.[1,2] Pecht and coworkers reported that the binding of Cu(II) to polyhistidine enhanced the catalytic activity of Cu(II) for the oxidation of homogentisic acid and hydroquinone.[3] However, the catalytic activity of crosslinked chelating resin–metal complexes(resin–metal chelates) for the oxidation of the substrate mentioned above have never been investigated. The use of resin–metal chelates as catalysts have apparently the following advantages:

1) The resin–metal chelates can easily be separated by filtration from the products after use.

2) The resin–metal chelates can be used repeatedly many times. Therefore, if the resin–metal chelates have a high catalytic activity for the various reactions, they will be applicable to an industrial use. Many kinds of the chelating resins having thiol group, hydrazino carbonyl group, and polyethylenepolyamine side chain have been prepared in our laboratory. In this report the oxidation of homogentisic acid and hydroquinone catalyzed by resin–metal chelates was investigated.

Experimental

Preparation of Crosslinked Chelating Resins. Seven chelating ion exchange resins were used for this research. Each resin was prepared as follows, and the estimated structures of functional groups in these chelating ion exchange resins with the abbreviated symbols are shown below.

RST: The macroreticular styrene–divinylbenzene (7 mol%) copolymer beads were prepared by suspension polymerization in the presence of 2,2,4-trimethylpentane (100 vol%). The gel type syrene–divinylbenzene copolymer beads were also prepared by suspension polymerization. Abovementioned styrene–divinylbenzene copolymer beads and commercial macroreticular copolymer beads were chloromethylated with chloromethylether at 0—5 °C. The chloromethylated copolymer beads were treated with triethylenetetramine.[4]

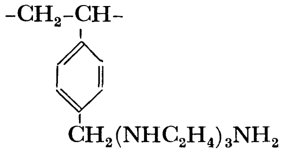
RMH: The macroreticular methyl methacrylate–divinylbenzene copolymer beads (RM) were prepared by suspension polymerization in the presence of 2,2,4-trimethylpentane. The copolymer beads were treated with hydrazine hydrate.[5]

RMT: The macroreticular copolymer beads (RM) were treated with triethylenetetramine.[6]

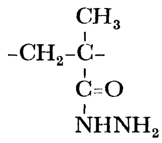
RGT: The macroreticular poly(glycidyl methacrylate) beads (RG) were prepared by suspension polymerization in the presence of 2,2,4-trimethylpentane (50 vol%). The polymer beads were treated with triethylenetetramine.[7]

RGS: The macroreticular polymer beads (RG) were treated with ammonium thiocyanate, and then followed by the reaction with ethanolic potassium hydrogensulfide.[8]

The cationic exchange resin WK-11 and the chelating resin CR-10 were kindly supplied from Mitsubishi Kasei

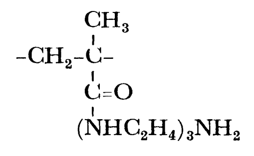


RST



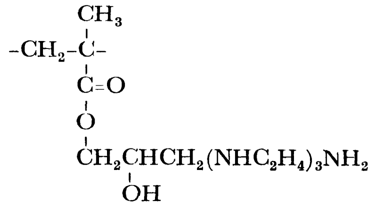
$$\begin{array}{c} CH_3 \\ -CH_2-C- \\ C{=}O \\ NHNH_2 \end{array}$$

RMH



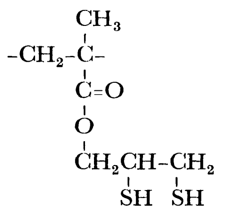
$$\begin{array}{c} CH_3 \\ -CH_2-C- \\ C{=}O \\ (NHC_2H_4)_3NH_2 \end{array}$$

RMT



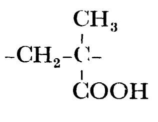
$$\begin{array}{c} CH_3 \\ -CH_2-C- \\ C{=}O \\ O \\ CH_2CHCH_2(NHC_2H_4)_3NH_2 \\ OH \end{array}$$

RGT



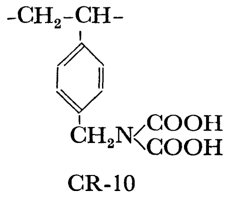
$$\begin{array}{c} CH_3 \\ -CH_2-C- \\ C{=}O \\ O \\ CH_2CH-CH_2 \\ SH\ \ SH \end{array}$$

RGS



$$\begin{array}{c} CH_3 \\ -CH_2-C- \\ COOH \end{array}$$

WK-11



CR-10

TABLE 1. CHARACTERIZATION OF THE MACRORETICULAR CHELATING RESINS USED IN THIS RESEARCH

Resin	Specific surface area m^2 g^{-1}	Pore volume ml g^{-1}	Average pore radius Å	Anion exchange capacity mequiv. g^{-1}	Cu^{2+} adsorbed (mmol/g)
RST-L[a)]	16.1	1.02	700	9.04	2.56
RST-I[a)]	302	0.70	215	4.28	1.35
RST-II[a)]	242	0.49	230	4.21	1.27
RST-III[a)]	94	0.88	680	3.60	0.93
RST-IV	38	0.83	290	6.96	1.69
RMH 3-50[b)]	5.0	0.59	2400	3.83	2.23
RMH 5-50	12.2	0.46	750	3.55	2.32
RMH 10-50	16.9	0.45	530	3.08	1.86
RMT 5-10	0	0	—	5.94	0.35
RMT 5-30	1.0	0.07	395	7.81	1.26
RMT 5-50	4.6	0.28	775	7.15	1.98
RMT 5-90	0.4	1.01	39000	7.36	0.87
RGT	0.7	0.65	10000	7.05	1.99
RGS	0.6	0.52	9400	—	0.78
WK-11	—	—	—	—	1.00
CR-10	—	—	—	—	1.64

a) RST-L, -I, -II, and -III were prepared from commercial copolymer beads. b) The former and latter numbers represent the volume percentage of divinylbenzene in the monomer mixture and the volume percentage of 2,2,4-trimethylpentane to the monomer mixture, respectively.

Kogyo Co. Ltd. The resins used in this research were macroreticular chelating resins except the resins described as gel type resin. The characterization of the resins used in this research is shown in Table 1.

Adsorption of Metal Ion on the Chelating Resins. The chelating resin (0.25 g) was weighed accurately and immersed in 50 cm^3 of an aqueous metal solution at room temperature for 96 h. The amount of metal ion adsorbed on the resins was calculated by chelatometric determination of the metal ion concentration in the supernatant.

Measurement of Anionic Exchange Capacity of Resins. The resin (OH type) (0.5 g) was weighed accurately and immersed in 100 cm^3 of a 0.1 mol dm^{-3} HCl–1 mol dm^{-3} KCl aqueous solution at room temperature for 24 h with occasional shaking. The anionic exchange capacity was determined by titrating the concentration of hydrochloric acid in the supernatant with a 0.1 mol dm^{-3} NaOH solution.

Measurement of the Catalytic Activity. A mixture containing homogentisic acid (or hydroquinone), phosphate buffer solution (pH 7), and resin–metal chelates was placed in a 500 cm^3 three-neck flask and stirred at a revolution rate of 300 rpm at 40 °C (or 50 °C for hydroquinone). The catalytic reactions were carried out under air except the experiments described as under nitrogen. The initial concentrations of homogentisic acid and hydroquinone were controlled to 4×10^{-4} mol dm^{-3}. The rate of their oxidation was measured by the titration with ammonium cerium nitrate or spectrophotometrically at 290 nm.

Results and Discussion

Effect of the Kind of Metal Ion on the Catalytic Activity. The effect of adsorbed metal ions on the catalytic activity was investigated by use of macroreticular chelating resins at 40 °C. The amount of metal added to the reaction system was kept constant (4×10^{-4} g atom). The amounts of the resin–metal chelates added to the reaction system were different in each oxidation reaction, since the amounts of metal ions adsorbed on the resins were different. The oxidation rates of homogentisic acid are shown in Fig. 1, in which the catalytic activity decreased in the following order, RST–Cu(II) > RST–Au(III) > RST–Ag(I) > RST–Hg(II) > RST–Fe(III). RST–Ni(II) and RST–Zn(II) chelates showed scarcely the catalytic activity for the oxidation of homogentisic acid.

In the oxidation of hydroquinone, the catalytic activity decreased in the following order: RST–Au(III) > RST–Ag(I) > RST–Cu(II) > RST–Hg(II).

The RST–metal chelates which showed a high catalytic activity were used repeatedly three times. The results are shown in Fig. 2. The chelates were dried at 50 °C for 12 h after they were once used. Then they were used repeatedly as catalysts. Figure 2 shows that the catalytic activity of RST–Cu(II) chelates did not decrease, even when the chelates were used repeatedly, whereas those of RST–Au(III), RST–Ag(I), and RST–Hg(II) chelates decreased gradually, as the chelates were used repeatedly. Especially, the

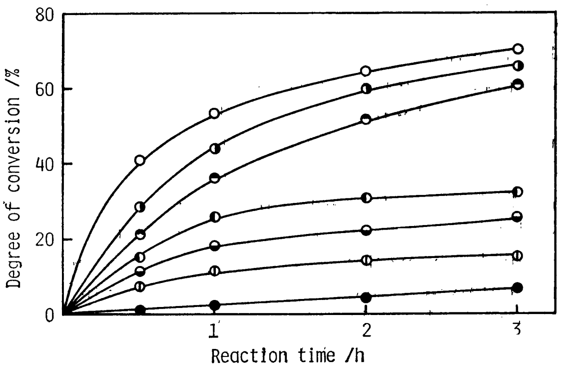


Fig. 1. Effect of the kind of metal ions on the oxidation of homogentisic acid.
Metal content: 4×10^{-4} g atom, catalyst: RST-L–metal chelate. Metal ion; ○: Cu(II), ◑: Au(III), ◓: Ag(I), ◐: Hg(II), ◒: Fe(III), ⦶: adsorption of substrate, ●: autoxidation.

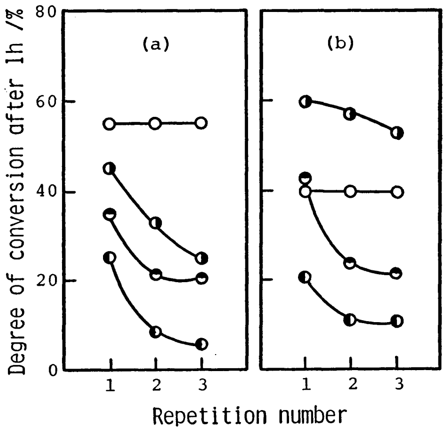


Fig. 2. The catalytic activity of RST–metal chelates for the oxidation of homogentisic acid and hydroquinone after repeated use.
Metal content: 4×10^{-4} g atom, catalyst: RST-L–metal chelate, (a): homogentisic acid, (b): hydroquinone. Metal ion; ○: Cu(II), ◑: Au(III), ◓: Ag(I), ◐: Hg(II).

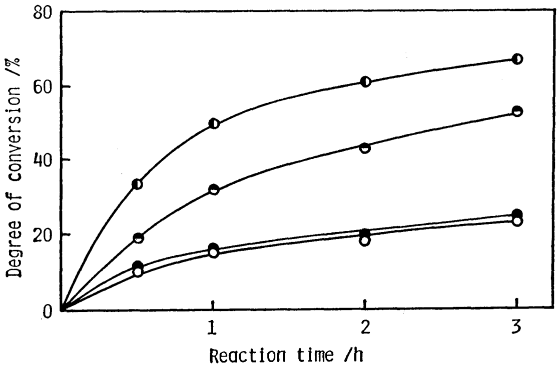


Fig. 3. Effect of the mole ratio of Cu(II) to the ligand on the oxidation of homogentisic acid.
Cu(II) content: 1.25×10^{-4} g atom, catalyst: RST-L–Cu chelate. Cu(II)/N(mole ratio); ◐: 0.28; ◓: 0.22, ●: 0.11, ○: 0.06.

extent of the decrease of the catalytic activity of RST–Ag(I) and RST–Hg(II) chelates is larger than that of RST–Au(III) chelate. During the oxidation reaction Ag(I) and Hg(II) were eluted from the chelates into the reaction solution.

Copper(II), gold(III), and mercury(II) in the resin–metal chelates which showed high catalytic activities have the coordination number of 4, while the coordination number of 2 in the reduced states. This change of the coordination number is responsible for the catalytic activity. The fact that Cu(I) forms a stable complex as well as Cu(II) is probably the reason why the catalytic activity of RST–Cu(II) chelate did not decrease, when the chelate was used repeatedly. The reason of a high catalytic activity of the RST–Ag(I) chelate is not clear yet.

Effect of the Mole Ratio of Cu(II) Adsorbed to the Ligand in Resins(Cu(II)/N) on the Catalytic Activity. Figure 3 shows the oxidation rate of homogentisic acid catalyzed by the RST–Cu(II) chelates with various Cu(II)/N ratios. The catalytic activity increased with an increase in the Cu(II)/N ratios in the resin–metal chelates. These results suggest that, in order to have a high catalytic activity, the resin–metal chelates must leave coordination places open for the substrate to coordinate to the metal. The same results were also observed for RMT–Cu(II) and RGT–Cu(II) chelates. These results agree with those obtained by Sigel,[9] and Hatano *et al.*[10]

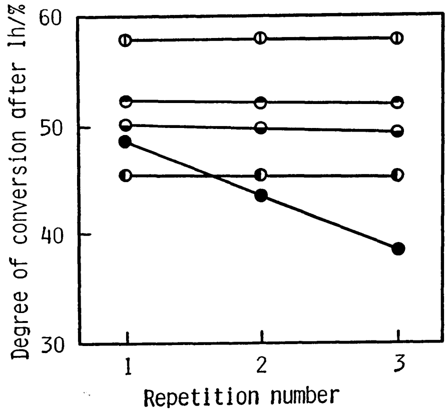


Fig. 4. The catalytic activity of various resin–Cu(II) chelates for the oxidation of homogentisic acid after repeated use.

	⦶	◓	◒	●	◐
Resin	RMH 5-50	RST-I	WK-11	RGS	CR-10
Cu(II) content / 10^{-4} g atom	3.0	3.0	3.0	1.0	4.0

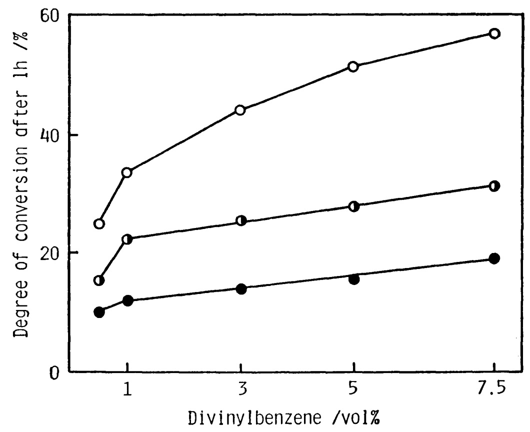


Fig. 5. Effect of the degree of crosslinking of the resins on the oxidation of homogentisic acid(I).
Cu(II) content: 2×10^{-4} g atom, catalyst: RST(gel type)–Cu(II) chelate. Repetition number; ○: 1, ◑: 2, ●: 3.

Effect of the Kind of Chelating Resins on the Catalytic Activity. The catalytic activity of various resin–Cu(II) chelates for the oxidation of homogentisic acid was investigated. The amounts of Cu(II) added into the reaction system are listed below Fig. 4 which revealed the highest catalytic activity of RMH–Cu(II) chelate. These resin–Cu(II) chelates were used three times. The catalytic activities of RMH–Cu(II), RST–Cu(II), WK-11–Cu(II), and CR-10–Cu(II)chelates scarcely decreased, whereas that of RGS–Cu(II) chelate decreased gradually, as these chelates were used repeatedly. The decrease of catalytic activity of RGS–Cu(II) chelate is ascribed to the elution of Cu(II) ion from the resin–metal chelate during the oxidation reaction.

Effect of the Degree of Crosslinking of Chelating Resins on the Catalytic Activity. Firstly, the effect of the degree of crosslinking of resins on the oxidation of homogentisic acid was investigated by use of gel type resins with different degrees of crosslinking. Figure 5 shows that the catalytic activity of gel type resin–Cu(II) chelates increased with an increase in the degree of crosslinking in the range from 0.5% to 7.5%, and the catalytic activity decreased gradually, as the resin–Cu(II) chelates were used repeatedly. The anion exchange capacity and the adsorption capacity for Cu(II) ion of these resins are listed in Table 2, which shows that both these capacities decreased with an increase of the crosslinking degree, and the decrease of the adsorption capacity is larger than that of the anion exchange capacity. The adsorption capacity of highly crosslinked resins for metal ions seems to be limited by steric hindrance. From the results mentioned above, the catalytic activity increase with an increase of crosslinking degree of resins is ascribed to the fact that metals in the higher crosslinked resin–metal chelates have a larger number of coordination places for substrate than those in the lower crosslinked resin–metal chelates. Figure 6 shows the oxidation rate of homogentisic acid catalyzed by RMH–Cu(II) chelates with different degrees of crosslinking. In this case, the catalytic activity did not decrease with an increase in the degree of crosslinking, and the catalytic activity did not decrease after repeated use. The decrease of the catalytic activity of gel type resin–Cu(II) chelates is ascribed to the elution of Cu(II) ion from the chelates to the reaction system during the oxidation reaction. The results suggest that the macroreticular chelating resins are suitable as catalysts for the oxidation reaction.

Table 2. Anion exchange capacity of gel type resins and the amount of Cu(II) adsorbed with the resins

Crosslinking of gel type resins (DVB$^{a)}$%)	Anion exchange capacity mequiv. g-resin^{-1}	Cu(II) adsorbed (mmol/g-resin)
0.5	7.85	1.71
1.0	7.70	1.59
3.0	6.81	0.82
5.0	6.34	0.48
7.5	5.81	0.10

a) Divinylbenzene (volume percent) in the monomer mixture.

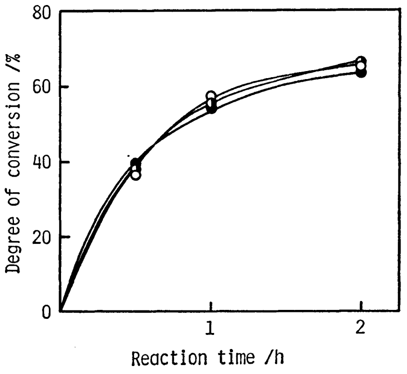


Fig. 6. Effect of the degree of crosslinking of the resins on the oxidation of homogentisic acid (II).
Cu(II) content: 4×10^{-4} g atom, catalyst: RMH–Cu(II) chelate. Resin; ◑: RMH 3-50, ○: RMH 5-50, ●: RMH 10-50 (See Table 1).

The Effect of the Porosity of Macroreticular Chelating Resins on the Catalytic Activity. The catalytic activity of resin–Cu(II) chelates for the oxidation of homogentisic acid was investigated by use of the macroreticular chelating resin(RMT) with different porosities. The results are shown in Fig. 7. RMT with different porosities were prepared by the amination of macroreticular copolymer beads which were polymerized by varying the amount of 2,2,4-trimethylpentane in the suspension polymerization. The chelating resin prepared by use of 2,2,4-trimethylpentane (50 vol% on monomer) had the specific surface area of 4.6 m^2/g, the pore volume of 0.28 cm^3 and the average pore radius of 775 Å (Table 1), and this resin had the maximum adsorption capacity for Cu(II) ion (Fig. 7). These results suggest that the resin which was prepared under the conditions mentioned above had the most suitable pore structures for the adsorption of Cu(II) ion. The catalytic activity of this resin did not decrease, when the resin was used repeatedly. However, the catalytic activity of all other resins decreased gradually after repeated use. The reason is also ascribed to the elution of Cu(II) adsorbed because of the instability of these resin–Cu(II) chelates. Figure 8 shows the oxidation rate of homogentisic acid catalyzed by RST–Cu(II) chelates. These RST have different porosities, especially, specific surface areas (Table 1). The catalytic activity increased

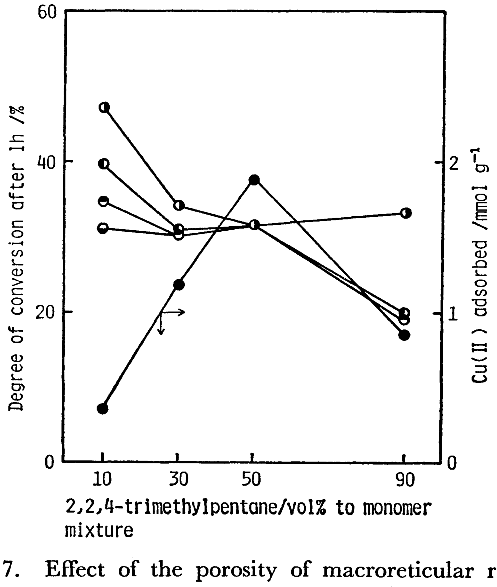


Fig. 7. Effect of the porosity of macroreticular resins on the oxidation of homogentisic acid (I).
Cu(II) content: 2×10^{-4} g atom, catalyst: RMT–Cu(II) chelate. Repetition number; ◑: 1, ◐: 2, ◓: 3, ◒: 4. ●: The amount of Cu(II) adsorbed.

TABLE 3. KINETIC PARAMETERS FOR THE OXIDATION OF HOMOGENTISIC ACID CATALYZED BY RESIN-Cu(II) CHELATES

No.	Catalyst [a] (Resin-Metal chelate)	V_{max} / 10^{-5} mol min^{-1}	K_m / 10^{-4} mol	k_3 / 10^{-2} min^{-1}
1	RST-L-Cu(II)	2.00	7.83	5.01
2	RGT-Cu(II)	1.46	6.16	3.61
3	RMH 5-50-Cu(II)	1.45	6.07	3.62
4	RMT 5-50-Cu(II)	1.49	8.21	3.71
5	Cu^{2+}	2.67	9.05	265.5

a) In the catalytic reaction by resin-Cu(II) chelates, Cu(II) content in the reaction system was 2×10^{-4} g atom, whereas in the catalytic reaction by Cu^{2+} only, Cu(II) content was 5×10^{-6} g atom.

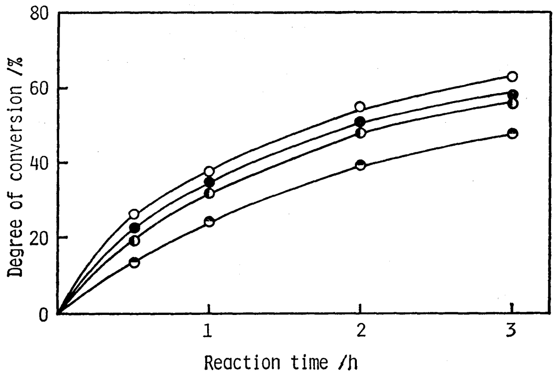


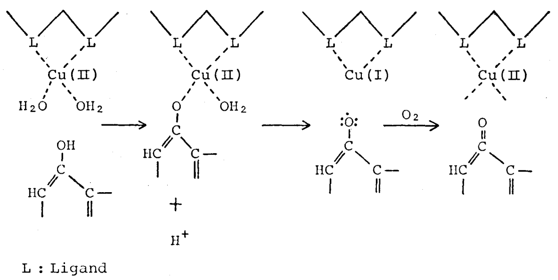
Fig. 8. Effect of the porosity of macroreticular chelating resins on the oxidation of homogentisic acid (II). Cu(II) content: 2×10^{-4} g atom, catalyst: RST-Cu(II) chelate. ○: RST-I, ●: RST-II, ◐: RST-III, ◓: RST-IV.

with an increase in the specific surface area of the resins and was little affected by the pore volume and average pore radius.

Kinetic Behavior of the Oxidation of Homogentisic Acid Catalyzed by Resin–Cu(II) Chelates. The catalytic activity of the RST–Cu(II) chelate for the oxidation of homogentisic acid was investigated under nitrogen, but it was not recognized. The result shows that molecular oxygen is necessary for this reaction.

The oxidation rate of homogentisic acid was observed at its various concentrations. The rate is proportional to the concentration of homogentisic acid in the lower concentrations and becomes independent of it in the higher concentrations. This is the kinetic behavior of a typical Michaelis-Menten type, which indicates the presence of a catalyst-substrate complex. These results suggest that the oxidation of homogentisic acid catalyzed by resin–Cu(II) chelates proceeds through the following mechanism which is similar to that of the oxidation of ascorbic acid catalyzed by ascorbic acid oxidase or lactose.

The plots of the reciprocal of the rate *vs.* the reciprocal of the substrate concentration gave straight lines in this oxidation reaction catalyzed by resin–Cu(II) chelates. From the intercept of each line and its slope, the specific rate for the decomposition of the reaction intermediate (k_3) and Michaelis-Menten constant (K_m) can be calculated. The data are listed in Table 3. For comparison, the results observed for Cu(II) ion are also listed in Table 3. The highest V_{max} value was observed for RST–Cu(II) chelate except the value observed for Cu(II) ion only. The lowest K_m value was observed for RMH–Cu(II) chelates. These results suggest that the oxidation rate of homogentisic acid catalyzed by RST–Cu(II) chelate is larger than that catalyzed by other resin–Cu(II) chelates and the affinity of RMH–Cu(II) chelate to the substrate is larger than that of other resin–Cu(II) chelates.



From the results mentioned above, the macroreticular resin–Cu(II) chelates were found to be suitable as catalysts for the oxidation of substrates such as homogentisic acid, hydroquinone, *etc.* and the catalytic activity of the resin–Cu(II) chelates was affected by the porosity of the resins. The macroreticular resin–Cu(II) chelates can be used repeatedly for these catalytic reactions.

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