Direct Oxidation of Benzene by Electron Transfer in a Multi-functionalized Chelate Resin System

Toshiharu Teranishi and Naoki Toshima *

Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

A polystyrene-based chelate resin, functionalized by tridentate iminodiacetate (ida) moieties, can easily immobilize various components by ion exchange or co-ordination. A multi-functionalized chelate resin immobilized with both ultrafine platinum particles and Fe^{II} ions has been prepared successfully by co-ordinating Fe^{II} ions to ida moieties after supporting ultrafine platinum particles. Electron transfer from the Fe^{II} ions to oxygen produced Fe^{III} ions and activated oxygen in the system, while the Fe^{III} ions were reduced again to Fe^{II} ions by molecular hydrogen *via* the platinum particles. The activation of oxygen molecules and/or a C–H bond of benzene are essential to the direct oxidation of benzene. Thus, benzene has been oxidized directly by activated oxygen to produce *p*-benzoquinone as the main product, indicating that the multi-functionalized chelate resin works like a dioxygenase enzyme. The oxidizing species for benzene was concluded to be the Fe^{II}–dioxo complex, the co-ordinating oxygen of which is activated.

Much attention has been paid to the oxidation of aromatic compounds from the point of view of both organic synthesis and enzyme models. In general, it is quite difficult to oxidize an aromatic ring directly, especially benzene itself because of its resonance stability. However, the standard Gibbs free-energy changes for the oxidation of aromatic compounds are negative, which means that oxidation can proceed under special conditions, especially in the presence of an effective catalyst. The activation of molecular oxygen is essential to the oxidation of aromatic compounds by using molecular oxygen as an oxidant. Therefore, developing a catalyst for the activation of oxygen is expected to make the direct oxidation of aromatic compounds possible.

In organisms the enzymes, which work as oxygenase by using molecular oxygen as an oxidant, often contain a transition-metal ion such as iron or copper. Biomimetic oxidation catalysts have been extensively studied.[1–6] After Groves *et al.*[7–9] elucidated the oxidation process of P-450, which is a representative oxygenase having an iron(II) haem in the organism, the oxidation of aromatic compounds by activated oxygen generated by metal–porphyrin complexes was investigated extensively.[10–13] Recently, much attention has been paid to the synthesis of enzyme-mimic complexes including non-haem iron or copper as a reaction centre.[14–19] In organisms or these biomimetic systems, oxidation proceeds by sequential electron transfer to the oxygen and continuously by the redox cycle of the metal ions contained in the system. The accumulation of special components in the resin can help achieve the sequential electron transfer and the redox cycle of the metal ions.

On the other hand, oxidation using Fenton's,[20,21] Udenfriend's[22,23] or Hamilton's reagent[24,25] has been investigated including an analysis of the mechanism.[26–29] In parallel with the above reagents, oxidation using semiconductors[30] such as TiO_2 or photosensitizers[31,32] has also been conducted.

As an example of the biomimetic system, Tabushi and co-workers[33] substituted the artificial system H_2/Pt colloid/Mn–porphyrin/O_2 for the oxidation system in the organism NADPH/P-450 reductase/Fe–porphyrin/O_2 (NADPH = nicotinamide-adenine dinucleotide phosphate), and applied it to the oxidation of various substrates. Sasaki and co-workers[34,35] succeeded in oxidizing benzene directly to phenol by hydroxyl radicals generated by feeding hydrogen and oxygen to a SiO_2-supported Cu^{II}–Pd catalyst. In these artificial systems, it has been found that sequential electron transfer from hydrogen to the metal ion is achieved, resulting in the activation of an oxygen molecule, and that the redox cycle of the metal ions promotes the reaction.

So far we have successfully immobilized ultrafine noble metal particles and metal ions simultaneously in a chelate resin[36,37] and the multi-component biomimetic systems mentioned above are quite similar. Electron transfer between components in a polymer system is supposed to achieve the activation of oxygen molecules. In order to activate oxygen molecules by reduction, Fe^{II} ions are employed in the present system because Fe^{II} ions co-ordinating to iminodiacetate (ida) moieties are expected to have greater reducing powers than the corresponding aqua ions due to the electron-donating properties of the ida moieties. On the other hand, employing Fe^{II} ions requires the reduction of the Fe^{III} ions generated back to Fe^{II}.

Ultrafine platinum particles can catalyse the evolution of hydrogen [equation (1)] and are also expected to catalyse the

$$H^+ + e^- \longrightarrow \tfrac{1}{2}H_2 \qquad (1)$$

reverse reaction [equation (2)]. We have already found that

$$\tfrac{1}{2}H_2 \longrightarrow H^+ + e^- \qquad (2)$$

Fe^{III} ions in a resin are easily reduced to Fe^{II} by hydrogen in the presence of ultrafine platinum particles,[38] suggesting that these particles work as good electron carriers [equation (3)].

$$H_2 + Pt_n{}^0 \longrightarrow 2H^+ + Pt_n{}^{2-} \qquad (3)$$

Therefore, the accumulation of platinum particles and Fe^{II} ions in a chelate resin ought to make the construction of the electron-transfer path from hydrogen to oxygen in a chelate resin possible.

Here we have used a polystyrene-based chelate resin (cr), functionalized by iminodiacetic acid moieties as a support for platinum particles and Fe^{II} ions. The ultrafine platinum particles are produced by the reduction of $[PtCl_6]^{2-}$ before the complexation of Fe^{II} ions with the chelate resin. Thus, the catalyst system contains two kinds of metal; the platinum particles act as the electron carrier from hydrogen to the Fe^{III} ions, whereas the Fe^{II} ions activate the oxygen molecules. Benzene was selected as the substrate for oxidation, because the direct oxidation of benzene is of great interest not only from the point of view of pure science but also of industrial chemistry. In this paper, the electron-transfer process from hydrogen to oxygen is studied, as well as the dependence of the yield of oxidation product on the concentration of Fe^{II} ion and on the extent of accumulation of each component. The oxidizing species of the system is investigated by measuring the yield of the oxidation product at different pH values and by comparing the distributions of products in the oxidation of benzene and anisole using the present system with those using Fenton's reagent.

Experimental

Materials.—A chelate resin containing iminodiacetic acid moieties (abbreviated as cr, Diaion CR10; mean bead diameter 0.5 mm, chemical structure as in Scheme 1) was purchased from Mitsubishi Chemical Industry Co. It was used in the swollen state as received or in the dry state by drying after washing with a large amount of ethanol. The extent of cross-linking is 5% (w/w), and two thirds of the styrene is functionalized by ida, as determined by elemental analysis. One gram of the dry resin was determined by pH titration to contain 2.57 mmol of iminodiacetic acid moieties.

The metal salts $Fe(SO_4)\cdot7H_2O$, $Cu(SO_4)\cdot5H_2O$, $PdCl_2$ and H_2PtCl_6 and 1,1′-dimethyl-4,4′-bipyridinium (methyl viologen) dichloride were used as received without further purification. Benzene and anisole were of guaranteed grade and used as received without further purification.

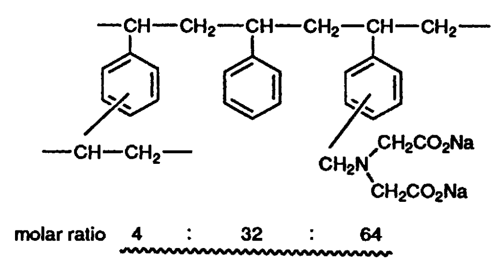
Preparation of the Catalyst.—Platinum ions were immobilized on 2.0 g of the acidic form of the chelate resin (abbreviated cr-H; metal free) by contact with H_2PtCl_6 solution (9.2 cm^3, 2.17 mmol dm^{-3}). The platinum ions were reduced by an aqueous solution of $LiBH_4$ (50 cm^3, 0.235 mol dm^{-3}) to produce Pt particles (cr–Pt). Then, $Fe(SO_4)\cdot7H_2O$ (0.0556 g) was added to the resin, cr–Pt, in water under nitrogen to give the catalyst, cr–Pt–Fe^{II}, which contained 20 μmol of Pt particles and 2.0 mmol of Fe^{II} ions in 2.0 g of the resin.

Copper ions were also used for the activation of oxygen molecules instead of Fe^{II} ions. Ultrafine palladium particles were also used as the electron carrier.

Measurements.—The electronic spectrum of $[PtCl_6]^{2-}$ in the supernatant was measured with a Hitachi model 340 spectrophotometer. The concentration of Fe^{II} ions in the supernatant was measured by atomic absorption spectroscopy (AAS) with a Shimadzu AA-646 atomic absorption/flame emission spectrophotometer. The amount of metal ion complexed was calculated from the discrepancy between the amount charged initially and that remaining in the supernatant after complexation.

Scanning electron microscopy (SEM) and electron-probe microanalysis (EPMA) on the catalyst were carried out by the use of a Hitachi model X-650 micro-scanning X-ray analyser, the resolution of the X-ray image being around 100 Å. The samples used were cr–Pt–Fe^{II} and cr–Pt10–Fe^{II}, ten times the number of platinum particles being immobilized in the latter. The sample beads were cut at around the maximum diameter with a stainless-steel knife and then coated with carbon so that cross-sections of the beads could be measured by irradiation with an electron beam. The metal distributions were evaluated from the intensity of the characteristic X-ray.

Oxidation of Benzene.—The oxidation of benzene was carried out as follows: the catalyst (2.0 g, containing 20 μmol of Pt particles and 2.0 mmol of Fe^{II} ions), a standard phosphate buffer solution (40 cm^3) at a specific pH, and benzene (10 cm^3) were mixed under stirring in a 100 cm^3 flask at 20 °C. The passage of hydrogen for 30 min was conducted followed by oxygen for 15 min and the cycle repeated three times. Then, the solution was acidified by adding 0.5 mol dm^{-3} HCl (10 cm^3).



Scheme 1 Chemical structure of the chelate resin

To investigate the oxidation products using the hydroxyl radical, the oxidation of benzene was carried out with Fenton's reagent as well as the chelate resin system. Fenton's reagent generates the hydroxyl radical (•OH) according to equation (4).[20] Thus, benzene (10 cm^3), H_2O_2 (2.66 mmol) and

$$H_2O_2 + Fe^{II} + H^+ \longrightarrow {}^{\bullet}OH + Fe^{III} + H_2O \quad (4)$$

$Fe(SO_4)\cdot7H_2O$ (2.0 mmol) were added 0.05 mol dm^{-3} H_2SO_4 (40 cm^3) under nitrogen, and the mixture stirred for 2 h at room temperature.

The oxidation products were measured quantitatively and qualitatively with a Nihon Seimitsu Kagaku Co. liquid chromatograph equipped with a Merck Lichrosorb HP-18 column (10 mm diameter × 250 mm) and a UV detector at 256 nm. Water–acetonitrile (3:1 v/v) was used as the eluent. In addition to the liquid chromatograph, a gas chromatograph with an OV-1 column was used for the product analysis.

Results and Discussion

Preparation and Characterization of the Catalyst.—On the basis of the electronic spectra of the supernatants, 96% of $[PtCl_6]^{2-}$ ions were immobilized on the cr-H resin by contact with the H_2PtCl_6 solution. Ultrafine platinum particles were produced by reduction of the platinum ions by $LiBH_4$ as shown by a colour change from yellow (cr–$[PtCl_6]^{2-}$) to grey (cr–Pt). In the electronic spectra, the cr–$[PtCl_6]^{2-}$ has a maximum at 260 nm while cr–Pt has a gentle absorption in the visible region due to reflection, indicating the reduction of platinum ions to the particles. This was confirmed from the electronic spectrum of platinum ions eluted by contacting 10 cm^3 of 0.5 mol dm^{-3} HCl solution with 2.0 g of cr–Pt; more than 98% of the immobilized platinum ions were reduced to atoms. On the other hand, all of the Fe^{II} ions (2.0 mmol) formed complexes with the chelate resin by ion exchange.

The distributions of Fe^{II} ions and Pt particles in cr–Pt–Fe^{II} and cr–Pt10–Fe^{II}, which has ten times as many Pt particles as cr–Pt–Fe^{II}, were measured by EPMA, as shown in Fig. 1. Fig. 1(*a*) shows the Fe^{II} distribution in cr–Pt–Fe^{II}, whereas Fig. 1(*b*) and 1(*c*) show the distributions of Fe^{II} and Pt in cr–Pt10–Fe^{II}, respectively. The Fe^{II} ions are distributed uniformly in each sample, indicating that the Fe^{II} ions co-ordinate to the ida moieties by ion exchange. In contrast, Fig. 1(*c*) clearly shows that the concentration of Pt decreases with increasing distance from the surface of the resin bead, and that the Pt:Fe^{II} molar ratios are 5:95 at the surface and 0:100 at the centre of the resin, respectively. Fig. 2 shows the TEM photograph of the cr–Pt–Fe^{II} dried from ethanol. The Pt particles are mainly distributed on the surface of the resin. These facts indicate that the Pt ions approach the surface of the resin by diffusion to form complexes with the ida moieties, and find it difficult to move inside the resin because cr–H has no anion-exchange ability. The distribution of each component during the preparation process is illustrated in Fig. 3.

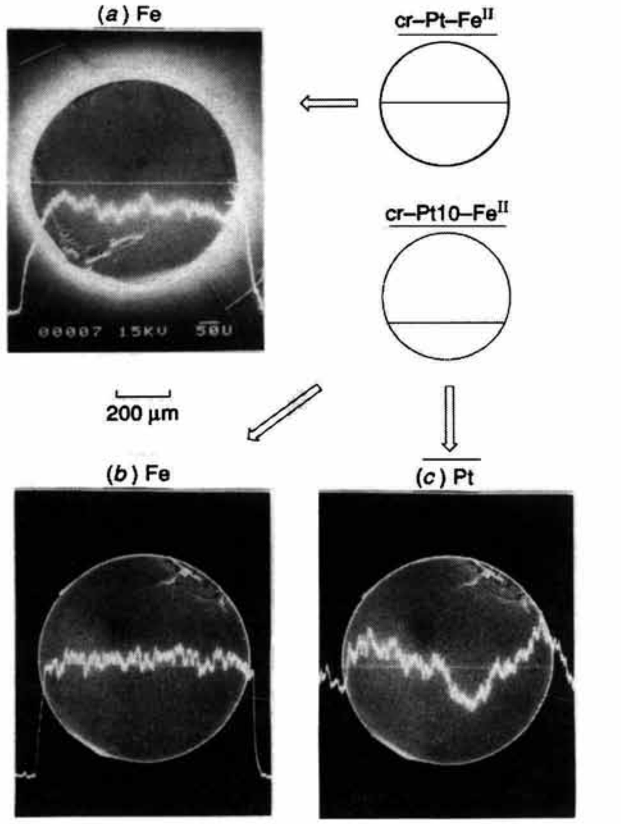


Fig. 1 SEM photographs and EPMA data of cross-sections of cr–Pt–Fe^{II} (*a*) and cr–Pt10–Fe^{II} (*b*,*c*) dried from ethanol

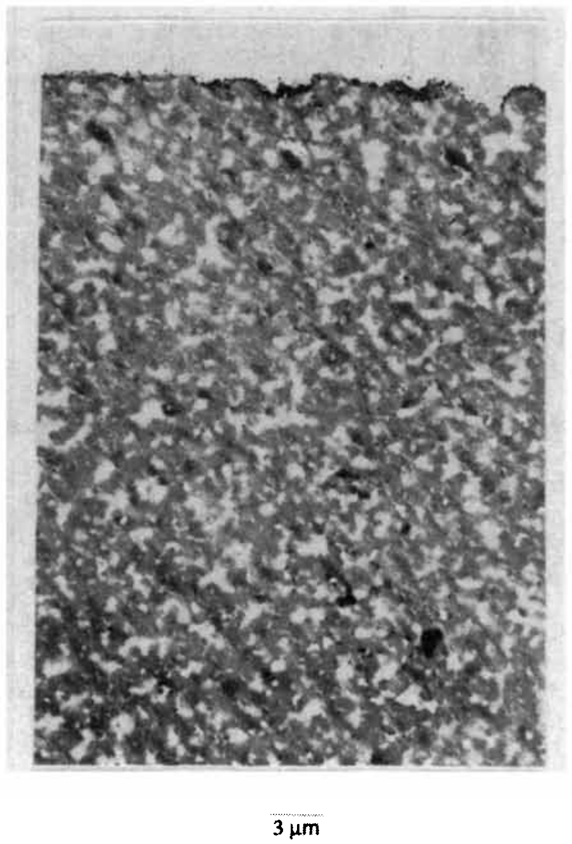


Fig. 2 Representative transmission electron micrograph (TEM) of the ultrafine platinum particles in slices of the cr–Pt–Fe^{II} beads. The magnification factor is 5000

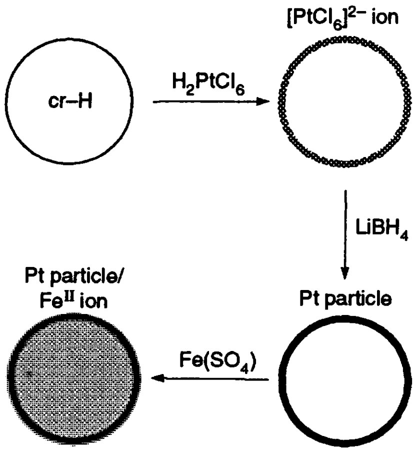
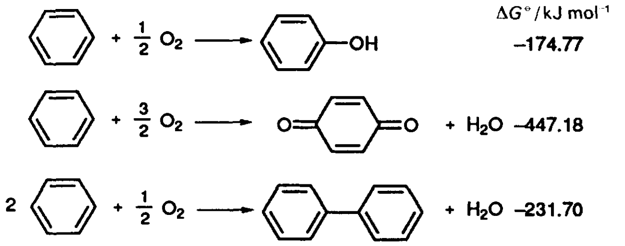


Fig. 3 Distribution of each component during the preparation of the catalyst



Scheme 2 Standard free-energy changes in the oxidation of benzene

Table 1 Effect of each chemical species on the oxidation of benzene

cr–H/g	Pt/µmol	Fe^{II}/ mmol	Solvent	Gas	Yield*/ µmol
2.0	0	0	H_2O	H_2, O_2	0
2.0	20	0	H_2O	H_2, O_2	0
2.0	20	2.0	H_2O	H_2, N_2	0
2.0	0	2.0	H_2O	H_2, O_2	0.8
2.0	20	2.0	H_2O	H_2, O_2	5.9

* Yield of *p*-benzoquinone from the oxidation of benzene. Benzene = 10 cm^3, solvent = 40 cm^3, pH 9.18, room temperature.

Electron-transfer Process.—Standard free-energy changes in the oxidation of benzene are given in Scheme 2; each oxidation reaction has a negative ΔG° value. The activation of molecular oxygen and/or the C–H bond of benzene is necessary for the direct oxidation of benzene by molecular oxygen. The cr–Pt–Fe^{II} catalyst is expected to activate molecular oxygen by electron transfer from the Fe^{II} ions.

The oxidation was conducted at pH 9.18 under various conditions to investigate the electron-transfer process in the chelate resin and the results are presented in Table 1. It is clear that without platinum particles or Fe^{II} ions the chelate resin gives no oxidation products. With only platinum particles supported on the chelate resin, no oxidation products are detected indicating that electron transfer from hydrogen to oxygen *via* these particles does not proceed. Even if both platinum particles and Fe^{II} ions exist in the resin, no oxidation products are produced without the passage of oxygen. However when Fe^{II} ions and oxygen exist together, then oxidation products are detected for the first time. It is clear that Fe^{II} ions and oxygen molecules are essential for the direct oxidation of benzene in this system.

The main oxidation product was *p*-benzoquinone and a small amount of phenol, but no biphenyl was detected. Many catalytic systems for dioxidizing benzene have been found so far besides the present system.[39–41] Here, the oxygen molecules might be activated by electron transfer from the Fe^{II} ions, resulting in the generation of the oxidizing species. Since the Fe^{III} ions, produced from oxidation of the Fe^{II} ions, cannot be reduced to Fe^{II} ions by molecular hydrogen, the yield of *p*-benzoquinone is not high in the system without platinum particles. Coexistence with the ultrafine platinum particles makes electron transfer from hydrogen to the Fe^{III} ions possible because the platinum particles are good electron carriers. Therefore, the regenerated Fe^{II} ions could activate the oxygen molecules again, resulting in an increased yield of *p*-benzoquinone.

Fig. 4 shows the yield of *p*-benzoquinone obtained *vs.* time. *p*-Benzoquinone could only be obtained under an oxygen atmosphere. Since the rate of production of *p*-benzoquinone decreases gradually with repetition of the redox cycle, the yield is expected to become constant. This will be caused by destruction of the resin beads and a decrease in the number of active sites. Since the reactions were carried out in a water–benzene mixture, the reaction proceeded in two liquid phases. As vigorous agitation was expected to increase the rate of reaction, this was kept constant throughout.

The overall electron-transfer process is summarized in Fig. 5. The system is similar to the organism system NADPH/P-450 reductase/Fe–porphyrin/O_2.[42]

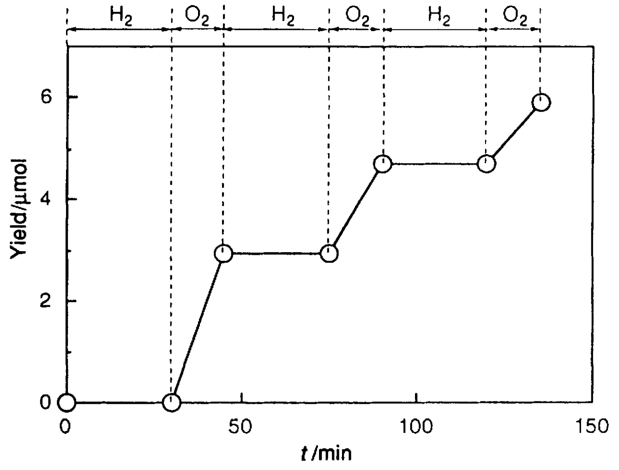


Fig. 4 Yield of *p*-benzoquinone obtained during alternate passages of hydrogen for 30 min and oxygen for 15 min

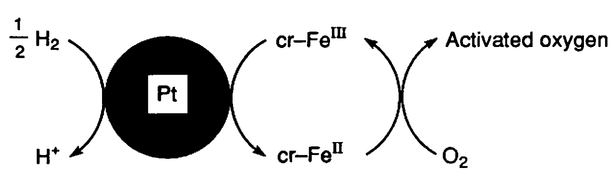


Fig. 5 Electron-transfer process from H_2 to O_2 in the chelate resin system

It has been found based on the extended X-ray absorption fine structure (EXAFS) measurements of the cr–Fe complexes in water (Fig. 6) that the co-ordination number of the Fe^{II} ions in cr–Fe^{II} is four, whereas it is six for the Fe^{III} ions so that every Fe^{II} ion has vacant co-ordination sites.[43] Oxygen molecules are thought to be activated by co-ordination at these vacant sites.

In order to investigate the path of oxidation of benzene to *p*-benzoquinone, the oxidation was carried out in the absence and presence of phenol. The results are presented in Table 2. Addition of phenol did not lead to a drastic increase in the yield of *p*-benzoquinone, suggesting that *p*-benzoquinone is produced directly from benzene and not *via* phenol in the present system. Although the selective generation of *p*-benzoquinone is a very interesting aspect, it remains unsolved as to why and how *p*-benzoquinone is generated at present.

Amount of Fe^{II} *Ions participating in Oxidation.*—Fig. 7 shows the yield of *p*-benzoquinone against the amount of Fe^{II} ions co-ordinating in the chelate resin at pH 4.02 and 9.18. The yield of *p*-benzoquinone increases with increasing amounts of Fe^{II} ions at each pH, indicating that increasing amounts of Fe^{II} ions participate in the activation of oxygen molecules.

The accumulation of the ultrafine platinum particles and Fe^{II} ions in the chelate resin were determined. Thus 9.2 cm^3 of aqueous 2.17 mmol dm^{-3} H_2PtCl_6 solution (20 µmol Pt) and 1.0 mmol of Fe^{II} ions were allowed to make contact with 1.0, 1.5 and 2.0 g of the chelate resin support (cr–H). From the electronic spectra 92, 94 and 96% of the $[PtCl_6]^{2-}$ ions were immobilized on 1.0, 1.5 and 2.0 g of the chelate resin, respectively, and from the atomic absorption spectra all of the Fe^{II} ions were co-ordinated in the chelate resin. The effect of accumulation on the yield of *p*-benzoquinone is illustrated in Fig. 8. The yield of *p*-benzoquinone increases as the Fe^{II} ions and platinum particles accumulate, that is, the amount of resin support decreases.

As mentioned above, the Fe^{II} ions are distributed uniformly in the resin (Fig. 1), while the platinum particles are distributed on the surface of the resin only (Fig. 2). Therefore, the Fe^{II} ions near the platinum particles are thought to participate in all cyclic redox reaction between Fe^{II} and Fe^{III}. For example, in Fig. 2, most of the platinum particles are distributed within 0.4 µm of the surface of the resin beads (resin diameter is 500 µm).

Table 2 Effect of addition of phenol on the yield of *p*-benzoquinone

cr–H/g	Pt/µmol	Fe^{II}/ mmol	Phenol/ mmol	Gas	Yield*/ µmol
2.0	20	2.0	—	H_2, O_2	5.9
2.0	20	2.0	0.92	H_2, O_2	6.7

* Yield of *p*-benzoquinone from the oxidation of benzene. Benzene = 10 cm^3, solvent = 40 cm^3, pH 9.18, room temperature.

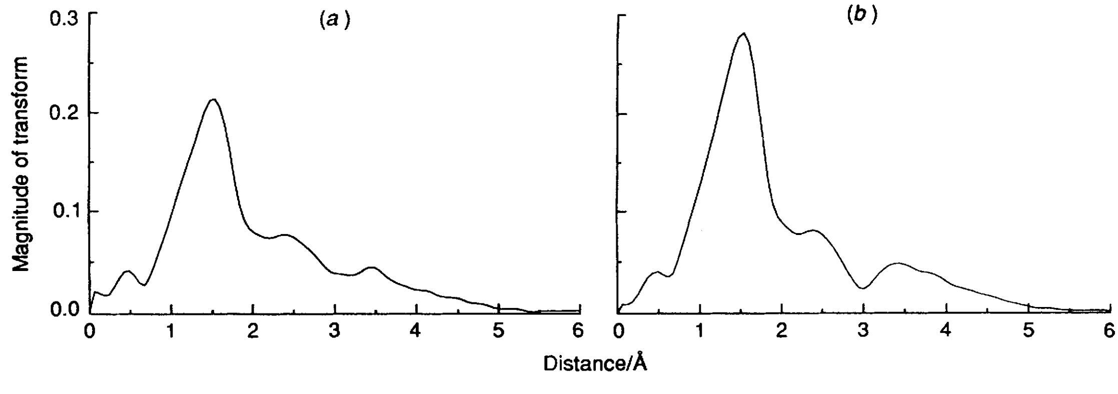


Fig. 6 Fourier transformation of the normalized k^1-weighted EXAFS spectra of cr–Fe^{II} (*a*) and cr–Fe^{III} (*b*) in water

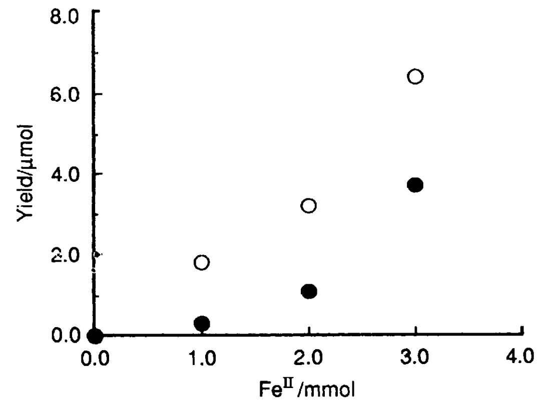


Fig. 7 Dependence of the yield of *p*-benzoquinone on the amount of Fe^{II} ions co-ordinating in 2 g of the chelate resin at pH 4.02 (●) and 9.18 (○); benzene, 10 cm^3; solvent, 40 cm^3, room temperature (r.t.)

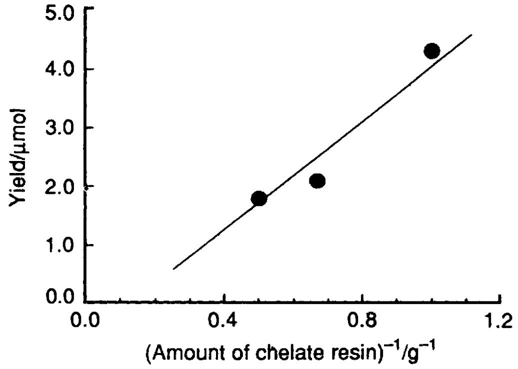


Fig. 8 Effect of the accumulation of Fe^{II} ions and Pt particles on the yield of *p*-benzoquinone; (amount of chelate resin)$^{-1}$/g^{-1} indicates the extent of the accumulation; benzene, 10 cm^3; solvent, 40 cm^3; pH 9.18; r.t.

Considering the uniform distribution of the Fe^{II} ions, then *ca.* 0.5% may participate in the oxidation. The results of Figs. 7 and 8 make it clear that increasing the concentration of Fe^{II} ions around the platinum particles causes an increase in the yield of *p*-benzoquinone. This confirms that only the Fe^{II} ions around the platinum particles participate in the redox reaction during the alternating supply of hydrogen and oxygen, and that the inner Fe^{III} ions produced by oxidation of the Fe^{II} ions remain unchanged. The concentration of the Fe^{II} ions around the platinum particles is thus an important factor for improving the yield of *p*-benzoquinone. In other words, the chelate resin works to accumulate Fe^{II} ions around the platinum particles.

Oxidizing Species of Benzene.—Fig. 9 shows the dependence of the yield of *p*-benzoquinone on the pH of the solvent. Phosphate buffer solutions at pH 1.68, 4.02, 6.88, 9.18 and 10.02 were used as the solvent. At a pH of less than 2, the Fe^{II} ions were rinsed from the resin to the supernatant. In an acidic or neutral solution, the yield of *p*-benzoquinone was low. As the solution became basic, however, the yield increased drastically. Since $Fe^{II} \longrightarrow Fe^{III}$ has a redox potential of −0.771 V in acidic solution, and 0.56 V in basic solution (measured as the hydroxides), the co-ordination of oxygen to the iron ion and the reduction of Fe^{III} to Fe^{II} are thought to proceed preferably in a basic solution, resulting in an increased yield of *p*-benzoquinone.

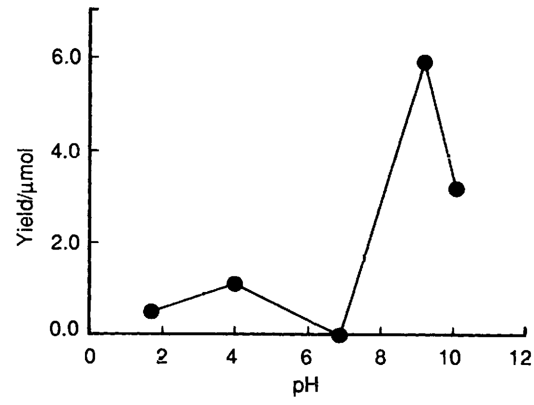


Fig. 9 Dependence of the yield of *p*-benzoquinone on the pH of the aqueous phosphate solution; cr–Pt–Fe^{II}, 2.0 g; benzene, 10 cm^3; solvent, 40 cm^3, r.t.

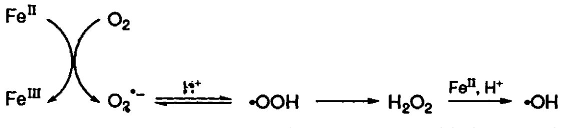


Fig. 10 Generation of radical species from superoxide ions produced by electron transfer from Fe^{II} to oxygen

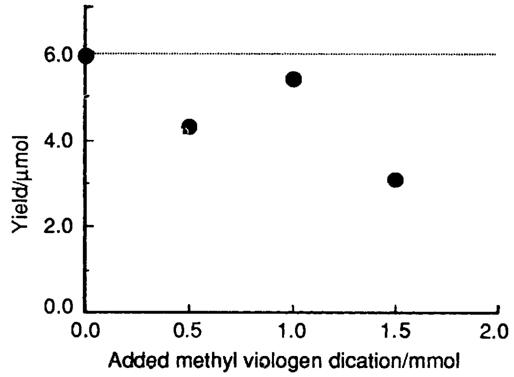


Fig. 11 Additional effect of the methyl viologen dication on the yield of *p*-benzoquinone; cr–Pt–Fe^{II}, 2.0 g; benzene, 10 cm^3; solvent, 40 cm^3; pH 9.18; r.t.

In general, oxidation of the benzene ring is achieved by radical species.[20,21,31,32] In the present system, assuming that the oxidizing species are the radicals, they are supposed to be generated from a superoxide radical ($O_2^{•-}$) produced from the reduction of oxygen, as shown in Fig. 10. The superoxide radical can generate a hydroperoxy radical (•OOH), from which a hydroxyl radical (•OH) can then be generated *via* hydrogen peroxide.[20,44] Both radicals are active enough to react with benzene. Although the acidity of the solution promotes the generation of these radicals, the present system actually gives a higher yield of *p*-benzoquinone at a high pH rather than at neutral pH. This suggests that highly active radical species like hydroperoxy and hydroxyl radicals were not generated in this system.

In order to investigate the actual oxidation products using the hydroxyl radical, the oxidation of benzene was carried out using Fenton's reagent. As a result, 630 μmol of phenol and 3.5 μmol of *p*-benzoquinone were obtained. Such a distribution of oxidation products strongly suggests that highly reactive radical species such as the hydroxyl radical were not produced in the chelate resin system.

On the other hand, it is possible that the superoxide radical, a precursor of the hydroperoxy and hydroxyl radicals, works as the oxidizing species, even though it is stable in alkaline solution and less reactive than the highly active radical species. A methyl viologen radical cation, generated from the reduction of the methyl viologen dication, can be an effective electron donor to oxygen in the present system.[45] Thus, 0.5, 1.0 and 1.5 mmol of methyl viologen chloride were immobilized in the resin by ion exchange by contacting with 2.0 g of cr–Pt–Fe^{II} in water under nitrogen. The electronic spectra of the supernatants at 257 nm indicated that all of the methyl viologen had been immobilized in the resin. The oxidation reaction was carried out at pH 9.18 to prevent the superoxide radical from changing into other radical species or hydrogen peroxide. Hydrogen bubbling made

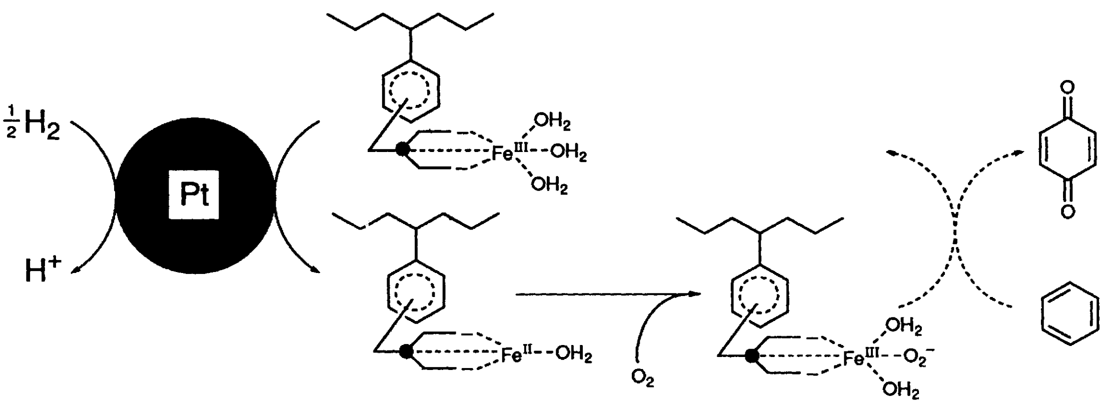


Fig. 12 Generation of active oxygen species and the redox process of the Fe ions

Table 3 Redox potentials[a] of MY [Y = edta or $(OH_2)_n$][b]

	E_0/V	
Metal complex (MY)	Y = edta	Y = $(OH_2)_n$
$Cr^{II}Y-Cr^{III}Y$	≈ −1	−0.41 (n = 6)
$V^{II}Y-V^{III}Y$	−1.03	−0.25 (n = 6)
$Cu^{I}Y-Cu^{II}Y$	—	+0.167 (n = 4)
$Fe^{II}Y-Fe^{III}Y$	+0.12	+0.77 (n = 6)
$Mn^{II}Y-Mn^{III}Y$	+1.0	+1.50 (n = 6)
$Co^{II}Y-Co^{III}Y$	+0.60	+1.82 (n = 6)

[a] *vs.* Normal hydrogen electrode (NHE). [b] Ref. 45.

the resin turn deep blue, as a result of the generation of methyl viologen radical cations by electron transfer from hydrogen *via* the ultrafine platinum particles. When hydrogen was replaced by oxygen, the deep blue colour disappeared, resulting in the production of the superoxide radicals. The effect of adding methyl viologen on the yield of *p*-benzoquinone is presented in Fig. 11. The yield does not increase, indicating that the superoxide radical does not participate in the oxidation of benzene in the present system.

In order to identify the oxidizing species, anisole was employed as the substrate instead of benzene. Although the oxidation of anisole with Fenton's reagent gave no ring-oxidized products, cr–Pt–Fe^{II} gave a small amount of *p*-methoxyphenol, which was also detected in the oxidation of anisole with the Fe–porphyrin system.[14] It is thought that, as in the Fe–porphyrin system, cr–Pt–Fe^{II} generates an active oxidizing iron–dioxo complex from reduction after the co-ordination of molecular oxygen to the Fe^{II} ion. A speculative redox process with the structure of the active oxidizing species is illustrated in Fig. 12. Co-ordination of molecular oxygen to the Fe^{II} ion is reasonable, since Fe^{II} ions have been found to have some vacant co-ordination sites.[43]

Other Metals.—The Cu^{II} ion was also used as the redox catalyst instead of Fe^{II} in the present system. The cr–Pt–Cu^{II} was prepared from the contact of 2.0 mmol of $Cu(SO_4)\cdot 5H_2O$ with 2.0 g of cr–Pt in water. As a result of the oxidation of benzene over cr–Pt–Cu^{II} at pH 9.18, the colour of the resin did not change and no oxidation products were detected. This is because Cu^{II} is not reduced to Cu^{I} by the passage of hydrogen. In general, the redox potential of the metal ion determines whether or not the metal ion in the resin is reduced. Table 3 gives the redox potentials of metal–ethylenediaminetetraacetate (edta) complexes, which have similar structures to metal–ida complexes. Co-ordination of the edta ligand makes the redox potential more negative than the corresponding aqua complexes, indicating that the metal oxidation states are more stable in the former. The redox potential of Cu^{II}–edta/Cu^{I}–edta is not known because the Cu^{I}–edta complex is unstable. However, it is estimated that the Cu^{II}–edta complex is hardly reduced compared with the Fe^{II}–edta complex since the redox potential of the aqua ion is +0.167 V (*vs.* NHE). Moreover, structural changes between Cu^{I} and Cu^{II} in the resin are thought to be difficult compared with those between Fe^{II} and Fe^{III}. A decrease in the redox potential upon co-ordination of the edta ligand is probably caused by increasing electron density at the metal ion due to the electron-donating property of edta. In the chelate resin system, by considering the co-ordination state and the electron-withdrawing capacity of the benzyl group in the matrix, the electron-donating capacity of the ida moiety is estimated to be about half that of edta. Therefore, the decrease in the redox potential of the metal ion in the resin is thought to be suppressed by about half that of metal–edta complex.

Finally, palladium particles were used as the electron carrier as well as platinum particles. The ultrafine palladium particles were supported in the same way as the platinum particles by using 3.33 mol dm^{-3} of aqueous H_2PdCl_4 solution. The oxidation of benzene at pH 9.18 gave 4.96 μmol of *p*-benzoquinone, equivalent to 84% in the case of the platinum particles. Although palladium particles work as good electron carriers to Fe^{III} ions, they have a lower ability than platinum particles to carry electrons.[33]

Conclusion

Ultrafine platinum particles and Fe^{II} ions have been immobilized successfully in a chelate resin. The present system is a biomimetic one, substituting the artificial system H_2/Pt particles/Fe–ida/O_2 for the oxidation system in the organism NADPH/P-450 reductase/Fe–porphyrin/O_2. The oxidation of benzene proceeds by sequential electron transfer from hydrogen to oxygen and continuously by the redox cycle of co-ordinating Fe ions. That the main product of the oxidation of benzene is *p*-benzoquinone indicates that the multi-functionalized chelate resin works like a dioxygenase enzyme. The oxidizing species in the present system is concluded to be the Fe^{II}–dioxo complex. Further elucidation of the oxidizing species will lead to the development of artificial enzymes, especially dioxygenase.

Acknowledgements

The authors express their thanks to Dr. Yasuhisa Hirohata and Dr. Kouichi Adachi for the TEM measurements and Dr. Shigeru Ohtsuka for the SEM and EPMA measurements. This work was supported by the Grant-in-Aid for Scientific Research (C) (No. 01550611) and (B) (No. 05453141) from the Ministry of Education, Science and Culture, Japan.

References

1 R. A. Sheldon and J. K. Kochi, *Metal-Catalysed Oxidation of Organic Compounds*, Academic Press, New York, 1981.
2 A. E. Shilov, *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Reidel, Dordrecht, 1984.

3 R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245.

4 C. L. Hill, *Activation and Functionalization of Alkanes*, Wiley, New York, 1989.

5 S. Takagi, E. Takahashi, T. K. Miyamoto and Y. Sasaki, *Chem. Lett.*, 1986, 1275.

6 N. Herron and C. A. Tolman, *J. Am. Chem. Soc.*, 1987, **109**, 2837.

7 J. T. Groves, T. E. Nemo and R. S. Myers, *J. Am. Chem. Soc.*, 1979, **101**, 1032.

8 J. T. Groves and R. Neumann, *J. Am. Chem. Soc.*, 1987, **109**, 5045.

9 J. T. Groves and R. Neumann, *J. Am. Chem. Soc.*, 1989, **111**, 2900.

10 I. Tabushi and M. Kodera, *J. Am. Chem. Soc.*, 1986, **108**, 1101.

11 E. I. Kavasevich, A. M. Khenkin and A. E. Shilov, *J. Chem. Soc., Chem. Commun.*, 1987, 731.

12 P. Battioni, J. F. Bartoni, P. Leduc, M. Fontecave and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1987, 791.

13 M. N. Carrier, C. Scheer, P. Gourine, J. F. Bartoni and D. Mansuy, *Tetrahedron Lett.*, 1990, **31**, 6645.

14 D. H. R. Bartin, J. Boivin, M. J. Gastiger, J. Morzycki, R. S. Hay-Motherwell, W. B. Motherwell, N. Ozbalik and K. M. Schwartzentruber, *J. Chem. Soc., Perkin Trans. 1*, 1986, 947.

15 D. H. R. Barton, F. Halley, N. Ozbalik, M. Schmitt, E. Young and G. Balvoine, *J. Am. Chem. Soc.*, 1989, **111**, 7144.

16 N. Herron and C. A. Tolman, *J. Am. Chem. Soc.*, 1987, **109**, 2837.

17 B. P. Murch, F. C. Bradley and L. Que, jun., *J. Am. Chem. Soc.*, 1986, **108**, 5027.

18 T. Funabiki, T. Toyoda, H. Ishida, M. Tsujimoto, S. Ozawa and S. Yoshida, *J. Mol. Catal.*, 1990, **61**, 235.

19 N. Kitajima, H. Fukui and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1988, 485; N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1988, 152; N. Kitajima, K. Fujisawa, Y. Moro-oka and K. Toriumi, *J. Am. Chem. Soc.*, 1989, **111**, 8975.

20 C. Walling, *Acc. Chem. Rev.*, 1975, **8**, 125.

21 T. Kuruta, Y. Watanabe, M. Katoh and Y. Sawaki, *J. Am. Chem. Soc.*, 1988, **110**, 7472.

22 S. Udenfriend, C. T. Clark, J. Axelrod and B. B. Brodie, *J. Biol. Chem.*, 1954, **208**, 1731.

23 M. B. Dearden, C. R. E. Jefcoate and J. R. L. Smith, *Adv. Chem. Ser.*, 1968, **77**, 260.

24 G. A. Hamilton, J. W. Hanifin, jun. and J. P. Friedman, *J. Am. Chem. Soc.*, 1966, **88**, 5269.

25 G. A. Hamilton, in *Molecular Mechanism of Oxygen Activation*, ed. O. Hayashi, Academic Press, New York, 1974, p. 405.

26 H. Orita, T. Hayakawa, M. Shimizu and K. Takehira, *J. Mol. Catal.*, 1987, **42**, 99.

27 M. Blanchard, C. Bouchoul, G. Djaneye-Boundjou and P. Canesson, *Tetrahedron Lett.*, 1988, **29**, 2177.

28 E. A. Karakhanov, S. Yu. Narin, V. A. Artemov, T. Yu. Filippova and A. G. Dedov, *Neftekhimiya*, 1988, **28**, 352.

29 S. Tamagaki, K. Suzuki and W. Tagaki, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 148.

30 M. Fujihira, Y. Satoh and T. Osa, *Nature (London)*, 1981, **293**, 206.

31 S. L. Mattes and F. Farid, *Organic Photochemistry*, ed. A. Padws, Marcel Dekker, New York, 1983, vol. 6, p. 293 and refs. therein.

32 M. Sako, S. Ohara, K. Shimada, K. Hirota and Y. Maki, *J. Chem. Soc., Perkin Trans. 1*, 1990, 863.

33 I. Tabushi and A. Yazaki, *J. Am. Chem. Soc.*, 1981, **103**, 7371; I. Tabushi and K. Morimitsu, *J. Am. Chem. Soc.*, 1984, **106**, 6871.

34 A. Kunai, S. Hata, S. Ito and K. Sasaki, *J. Am. Chem. Soc.*, 1986, **108**, 6012.

35 T. Kitano, Y. Kuroda, A. Itoh, J. Li-Fen, A. Kunai and K. Sasaki, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1991.

36 N. Toshima, T. Teranishi, H. Asanuma and Y. Saito, *J. Phys. Chem.*, 1992, **96**, 3796.

37 N. Toshima, T. Teranishi and Y. Saito, *Makromol. Chem., Makromol. Symp.*, 1992, **59**, 327.

38 T. Teranishi and N. Toshima, unpublished work.

39 J. van Gent, A. A. Wismeijer, A. W. P. G. P. Rit and H. van Bekkum, *Tetrahedron Lett.*, 1986, **27**, 1059.

40 S. Ito, A. Kunai, H. Okada and K. Sasaki, *J. Org. Chem.*, 1988, **53**, 296.

41 H. Orita, M. Shimizu, T. Hayakawa and K. Takehira, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1652.

42 *Cytochrome P-450, Structure, Mechanism, and Biochemistry*, ed. P. R. Oritz Montellano, Plenum Press, New York and London, 1986.

43 T. Teranishi, M. Harada, K. Asakura, H. Asanuma, Y. Saito and N. Toshima, *J. Phys. Chem.*, 1994, **98**, 7967.

44 A. A. Frimer, *The Chemistry of Peroxides*, Wiley, New York, 1983, p. 429.

45 Y. Kurimura, M. Nagashima, K. Takato, E. Tsuchida, M. Kaneko and A. Yamada, *J. Phys. Chem.*, 1982, **86**, 2432.

46 F. P. Dwyer and D. P. Mellor, *Chelating Agents and Metal Chelates*, Academic Press, New York, 1964.

Received 1st *July* 1994; *Paper* 4/03986F