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The oxidation of 2,6-xylenol catalysed by polymer supported copper complexes

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The synthesis and characterisation of copolymers containing tertiary nitrogen to which Cu(I) or Cu(II) species are anchored is described. The anchored species function as catalysts for the oxidation of 2,6-xylenol by O_2 under basic conditions. The kinetics of these oxidations have been followed by monitoring oxygen uptake as a function of pH, temperature, reactant concentrations, oxygen partial pressure and catalyst loading. A suitable mechanism is proposed to account for the kinetics as well as the formation of the product, diphenoquinone. Recycling efficiencies of the catalysts are found to be good. © 1997 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: polymer supported catalysts; 2,6-xylenol oxidation; Cu(II) species)

INTRODUCTION

The oxidative coupling of 2,6-xylenol leads to polyphenylene oxide (C–O coupling) or diphenoquinone (C–C coupling) [1]. The reaction has been carried out using various homogeneous catalysts based on copper–amine systems [2–4] and several other heterogeneous catalysts [5–7]. Tsuchida *et al.* have studied the kinetics of oxidative polymerisation of 2,6-xylenol catalysed by homogeneous polyvinylpyridine–Cu(I) complexes [4,8–11]. Cu(II) complexes of poly [styrene-co-4-(*N*-methyl-*N*-p-vinylbenzylamino) pyridine] [12–15] and poly (styrene-co-*N*-vinylimidazole)[16] have also been used as catalysts for this reaction under homogeneous conditions. In the present paper we report the study of oxidative coupling of 2,6-xylenol catalysed by Cu(II) complexes anchored on some functional copolymers.

EXPERIMENTAL

The monomers 2,3-epoxypropyl methacrylate (GMA), 4-vinylpyridine (4-VP) and *N*-vinylpyrrolidinone (N-VP) were purified by vacuum distillation under nitrogen atmosphere. N,N^1-methylenebisacrylamide (MBAm) was recrystallised from methanol. 2,6-Xylenol from Fluka was purified by recrystallisation from n-hexane (m.p. 122°C). Cuprous chloride (CuCl) and cupric acetate ($Cu(OAc)_2{\cdot}H_2O$) were from Merck-India and used as received. Infrared spectra were recorded on a Shimadzu-IR 470 using KBr pellets. ^{1}H-NMR spectra were recorded on a Hitachi R600 NMR spectrometer with tetramethylsilane as the internal standard. UV spectra were recorded on a Hitachi 200A double beam spectrometer using 10 mm quartz cells. A Carl-Zeiss PMQ II spectrometer with cells of 1 cm path length was used for light absorption measurements. Average particle sizes of the catalysts were measured using a Malvern particle size analyser 3600E.

Synthesis of copolymers

Copolymer 1 (P1). This was prepared by the suspension copolymerisation of 48 mol.% each of *N*-vinylpyrrolidinone (N-VP), 2,3-epoxypropyl methacrylate (GMA) and 4 mol.% of methylenebisacrylamide (MBAm) in 500 ml of 30% aqueous sodium chloride. The detailed procedure has been described elsewhere [17]. The yield of the copolymer [P(1)] was ~80%. The epoxy group of the copolymer [P(1)] was opened by diethylenetriamine or triethylenetetramine. The reaction was carried out by heating about 5 g of the copolymer with 10 ml of diethylenetriamine or triethylenetetramine in 100 ml dry DMF at 100°C for 10 h. The copolymer with diethylenetriamine or triethylenetetramine functions have been denoted P2 and P3 respectively. IR spectrum of the copolymers showed the following absorbances: 3424 cm^{-1} (NH or OH), 1718 cm^{-1} (ester carbonyl), 1651 cm^{-1} (carbonyl-N-VP) and 1260 cm^{-1} (> C–O–C < , epoxy).

Copolymer 4 (P4). Monomers capable of co-ordinating to transition metal ions were polymerised by the template method [18]. About 4 g of $MnCl_2{\cdot}2H_2O$ (0.02 moles) was dissolved in 100 ml of hot ethanol to which was added 8.7 ml (0.08 moles) of freshly distilled 4-vinylpyridine and the mixture was cooled in an ice bath. The complex which precipitated out was filtered, washed thoroughly with ethanol, acetone and vacuum dried. The composition of $Mn(4VP)_4Cl_2$ was confirmed by the elemental analysis and the estimation of Mn content. Elemental analysis: Calcd.: 61.48% C, 5.12% H, 10.25% N; Found: 61.2% C, 5.18% H, 10.28% N. Mn content: Calcd.: 23.04%; Found: 22.84%.

The complex was copolymerised with methylenebisacrylamide as follows. About 6.5 g $Mn(4VP)_4Cl_2$ (0.012 moles) was dissolved in 50 ml distilled DMF with constant stirring. The mixture was deoxygenated with nitrogen. To this solution, 3 g of methylenebisacrylamide (0.019 moles) was added followed by 200 mg of AIBN in toluene (20 ml) and the mixture was heated to 80°C under nitrogen with vigorous stirring. The polymerisation was

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carried out for approximately 5 h. The initially homogeneous mixture yielded the copolymer as discrete fine particles upon polymerisation. The polymer was filtered, washed thoroughly by stirring with hot distilled water followed by a similar treatment with methanol, followed by acetone and then vacuum dried. The yield of the copolymer was ~90%.

The Mn^{2+} coordinated to the polymer was removed by stirring 8 g of the copolymer with 400 ml of aqueous EDTA (3 g) for 24 h at room temperature. The polymer was filtered, washed free of EDTA and the process repeated to obtain Mn^{2+} free copolymer. The complete removal of Mn^{2+} was confirmed by carrying out the test for Mn^{2+} [19]. IR spectrum of the copolymer showed the following absorbances: 3392 cm^{-1} (amide NH), 1644 cm^{-1} ($>C{=}N-$), and 822 cm^{-1} (out-of-plane bending of aromatic C–H).

All the copolymers were powdered and sieved through standard mesh sieves. The data on elemental analysis of copolymers are given in *Table 1*.

Loading of metal ions on polymer supports

Loading of CuCl. About 500 mg of CuCl was dissolved in 20 ml of 1:1 HCl–water mixture and added to 20 ml of DMF. About 4 g of P3 or P4 was stirred with this mixture for about 24 h at room temperature. The loaded polymer was filtered, washed thoroughly with water, methanol, acetone and vacuum dried.

Loading of $Cu(OAc)_2{\cdot}H_2O$. About 500 mg of cupric acetate was dissolved in 40 ml of 1:1 DMF–water mixture and to that was added 0.5 ml of acetic acid. About 4 g of P2 was stirred with this mixture for 24 h at room temperature. The loaded polymer was filtered, washed thoroughly with water, methanol, acetone and vacuum dried.

Since the loading process involved stirring for 24 h further subdivision of particles is likely. The particle size distribution analysis was carried out on the final loaded copolymers. The average size of the particles were estimated using the equation

$$dp = \frac{1}{\sum_{i=1}^{n} X_i/dp_i}$$

where X_i is the weight percentage of particles of size dp_i. Care was taken to use only samples with reasonably narrow distribution.

The metal content of the catalyst was determined as follows. About 50–100 mg of the catalyst were digested using hot concentrated H_2SO_4 (~3 ml) and the solution was cleared using hydrogen peroxide (~2 ml). The metal content was then determined spectrophotometrically using diethyldithiocarbamate [20]. The polymer supports employed, the metal salt loaded, and their average particle diameters are given in *Table 2*.

Oxidative coupling of 2,6-xylenol

The experimental set-up used was similar to the one used for study of hydrogenation using polymer-supported catalysts [21] except that hydrogen gas was replaced by oxygen. Sodium hydroxide was used as methanolic solution and its strength was determined by titrating with standard oxalic acid solution. The required amount of base was taken in the separating funnel and bubbled with O_2 for 15 min. This was run into the reaction vessel and the separating funnel was filled with 10 ml of methanolic solution of 2,6-xylenol of required concentration. This was bubbled with O_2 for 15 min while the solvent mixture and catalyst was stirred mechanically. Addition of substrate was followed by opening the system to the gas burette while closing the exit stop cork. The rate of oxidative coupling reaction was calculated from dioxygen consumption against time as

$$\frac{(-dO_2)}{dt} = \frac{4(-d[DMP])}{dt}$$

The reaction temperature was varied between 30 and 50 ± 1°C.

The solubility of molecular oxygen in methanol was determined by an electrochemical method [22]. The solubility of O_2 at 1 atm pressure was found to be 2×10^{-3} mol l^{-1} (303 K), 1.75×10^{-3} mol l^{-1} (313 K) and 1.48×10^{-3} mol l^{-1} (323 K).

The variation of partial pressure of O_2 was carried out by using mixtures of argon and oxygen with the total pressure being 1 bar.

Table 1 Data on elemental analysis of the copolymers

Number	Polymer	C (%)	H (%)	N (%)
1	P1	55.01	6.91	5.88
2	P2	47.93	7.30	8.75
3	P3	48.62	7.78	8.07
4	P4	58.35	6.69	12.93

Table 2 Characteristics of the catalysts employed

Number	Polymer	Metal salt	Catalyst	Metal content (%)	Average particle diameter (μ)
1	P2	$Cu(OAc)_2$	Cat 1	4.75	77.86
2	P3	CuCl	Cat 2	6.50	44.53
3	P4	CuCl	Cat 3	5.37	14.51

Product analysis

2,6-Xylenol (0.13 mol l^{-1}) in 20 ml of methanol was oxidised using 500 mg of Cat 3 at 303 K and 1 atm pressure for 5 h. The reaction mixture was filtered free of catalyst and added to methanol containing HCl to neutralise the excess base. The excess methanol was removed under reduced pressure and the residue was dissolved in chloroform. The unreacted xylenol was removed by extracting with aqueous NaOH. The chloroform layer was analysed using a UV spectrometer. The $CHCl_3$ solvent was removed under reduced pressure and the residue was taken up in CCl_4 for ^1H-NMR analysis.

RESULTS AND DISCUSSION

The CuCl loaded on P3 or P4 would be oxidised to Cu(II) *in situ* in the presence of molecular oxygen and sodium hydroxide. It has been already reported that the Cu(I) amine system which is oxidised to Cu(II) amine *in situ* by molecular oxygen was found to be active under mild conditions [8]. Tsuchida *et al.* have prepared the insoluble catalytically active Cu(II) poly-4-vinylpyridine complexes by treating $CuCl_2$–poly-4-vinylpyridine with water or potassium hydroxide [9]. The UV spectrum of the product showed a broad band at $\lambda_{max} = 421$ nm which corresponds to that of tetramethyldiphenoquinone. The ^1H-NMR spectrum showed two signals at δ7 and δ2.2 with the area ratio 1:3. The former signal was assigned to the aromatic ring protons and the latter to methyl protons. IR spectrum showed the following absorbances: 2912 cm^{-1} (CH_3), 1712 cm^{-1} (carbonyl), 1635, 1587 and 1520 cm^{-1} (C=C, stretching), 803 and 777 cm^{-1} (out-of-plane bending of aromatic C–H). The melting point of the product was found to be 214°C which agreed with the literature value [23]. Based on these observations the reaction product was confirmed to be 3,3′, 5,5′-tetramethyl-4,4′-diphenoquinone. The yield was ~58%. No polymer was obtained. The cent percent selectivity for C–C coupling as against C–O coupling is dependent upon the N/Cu ratio and the reaction conditions. Endres *et al.* have shown that at low values of N/Cu of ~0.67 to 10, the oxidation gave predominantly C–C coupled product under homogeneous conditions [2]. If the ratio were ~10 to 100, predominantly C–O coupled products were obtained. In the present study the N/Cu ratios were 1.87 (Cat 1), 1.27 (Cat 2) and 2.4 (Cat 3) respectively. An additional feature could be the heterogeneous nature of the reaction conditions.

As shown in the mechanism of oxidation (*Scheme 1*)

$$2(\mathrm{DMP}) \rightarrow (\mathrm{DMP})_2 \xrightarrow{\frac{1}{2}O_2} \mathrm{DPQ}$$

Thus one mole of O_2 consumption corresponds to two moles of diphenoquinone formed. The turnover number (TON) can be defined as the number of moles of DPQ formed $[2(-dO_2)/dt]$ per g atom of Cu per hour. A sample calculation is shown for Cat 3.

$$-(dO_2)/dt = 2.34 \times 10^{-6}\ \mathrm{mol\ l^{-1}\ s^{-1}}$$

$$+(\mathrm{DPQ})/dt = 4.68 \times 10^{-6}\ \mathrm{mol\ l^{-1}\ s^{-1}}$$

$$[\mathrm{Cat3}] = 10.57 \times 10^{-3}\ \mathrm{g\ atom\ Cu\ l^{-1}}$$

$$\mathrm{TON} = \frac{4.68 \times 10^{-6}}{10.57 \times 10^{-3}} \times 3600$$

$$= 1.59\ \mathrm{mol\ (g\ atom\ Cu)^{-1}\ h^{-1}}$$

For Cat 1 and Cat 2 the TON values were 0.52 and 0.75 mol (g atom Cu)$^{-1}$ h^{-1} respectively.

The plots of percentage of DMP reacted versus time are depicted in *Figure 1*. The low reactivity of the catalysts is due to the heterogeneity of the systems. However data on the initial rates only were used for the kinetic analysis. It has already been reported that the oxidation of xylenol did not proceed when the copper–cation exchange resin complex was used as the catalyst [24]. The reaction rates are plotted as a function of $[OH]^-$ in *Figure 2*. With all three catalysts no reaction takes place in the absence of base at all temperatures studied. The increase in $[OH]^-$ increases the rate of oxidation. Such effects were also reported in the literature [12,16,25] and proved that deprotonation of DMP by hydroxide is essential for co-ordination of phenolate ion to

$$\begin{aligned}
&\mathrm{DMP} + {}^{\ominus}\mathrm{OH} \rightleftharpoons \mathrm{DMP}^{\ominus} + \mathrm{H_2O}\\
&\mathrm{DMP}^{\ominus} + \text{Ⓟ}\!-\!\mathrm{Cu^{2+}} \overset{K}{\rightleftharpoons} \mathrm{C^*}\\
&\mathrm{C^*} + \mathrm{O_2} \xrightarrow{k} \text{Ⓟ}\!-\!\mathrm{Cu^{+}} \cdots\cdots\cdots \mathrm{O_2} + \mathrm{DMP^{\bullet}}\\
&2\mathrm{DMP^{\bullet}} \xrightarrow{\text{Fast}} (\mathrm{DMP})_2 \xrightarrow[\frac{1}{2}O_2]{\text{Fast}} \mathrm{DPQ}\\
&2\mathrm{Cu^+} + \mathrm{O_2} + 2\mathrm{H^+} \xrightarrow{\text{Fast}} \mathrm{H_2O_2} + 2\mathrm{Cu^{2+}}\\
&\qquad\qquad\text{(or)}\\
&2\mathrm{Cu^+} + \mathrm{O_2} + 2\mathrm{H_2O} \xrightarrow{\text{Fast}} \mathrm{H_2O_2} + 2\mathrm{Cu^{2+}} + 2\overset{\ominus}{\mathrm{O}}\mathrm{H}\\
&2\mathrm{H_2O_2} \xrightarrow{\text{Fast}} 2\mathrm{H_2O} + \mathrm{O_2}
\end{aligned}$$

Scheme 1 Mechanism of oxidation

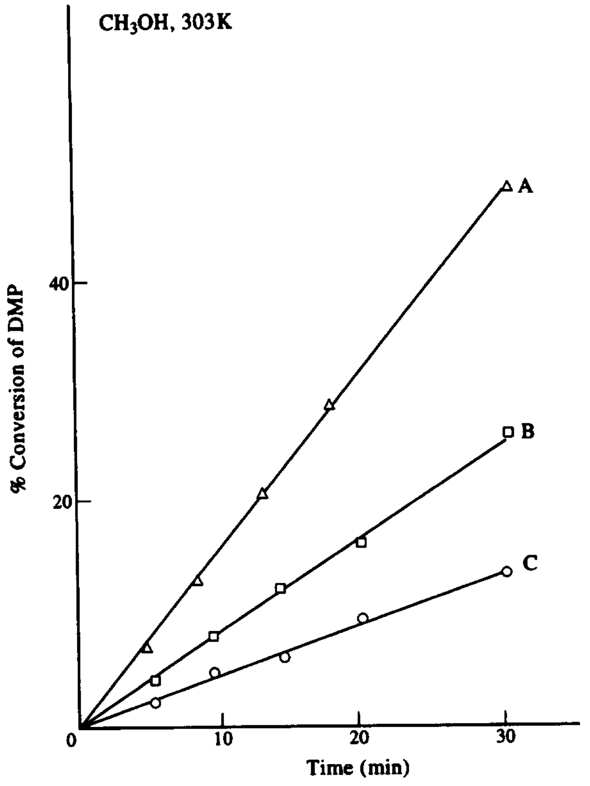

Figure 1 Plots of percentage conversion of DMP versus time. [DMP] = 0.13 mol l^{-1}, $[OH]^-$ = 0.5 N, pO_2 = 578 mm Hg, M = 12.5 × 10^{-3} g cm^{-1}. A, Cat 3; B, Cat 2; C, Cat 1

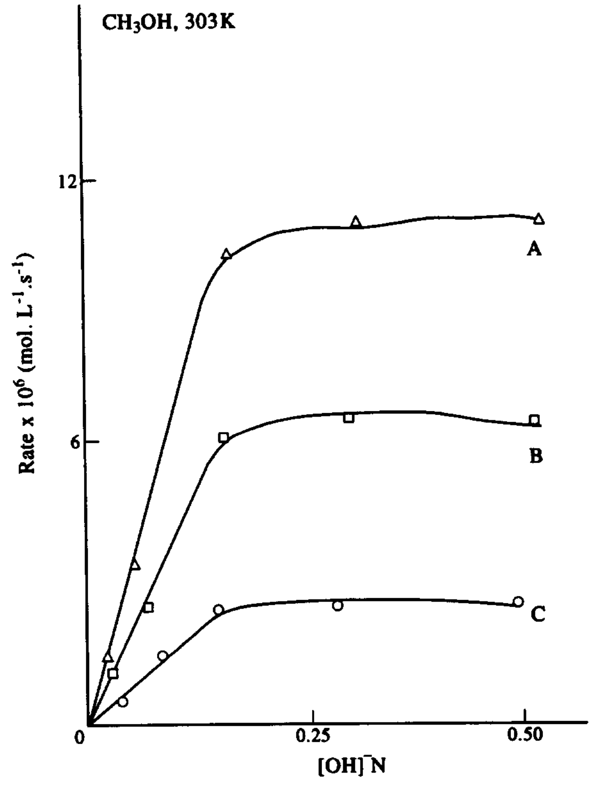

Figure 2 Plots of rate of oxidation versus [OH]. [DMP] = 0.13 mol l^{-1}, pO_2 = 578 mm Hg, M = 12.5 × 10^{-3} g cm^{-1}. A, Cat 3; B, Cat 2; C, Cat 1

P–Cu(II) complexes. Increasing the hydroxide concentration promotes formation of phenolate anions resulting in enhanced reaction. Beyond

$$\frac{[\mathrm{OH}]}{[\mathrm{DMP}]}=1$$

a further increase in $[\mathrm{OH}]^-$ does not have any effect on reaction rates. However, Chen *et al.* have reported that excess hydroxide some how destroyed the catalyst causing a decrease in rate [16]. The saturation rates at high base concentration, namely 0.5 N, indicates the stability of the present catalyst systems under the basic conditions. *Figure 3* depicts the variation of initial rates of oxidation with [substrate] at high base concentration. It can be seen that with all the catalyst systems saturation rates are obtained at high [DMP]. This is similar to saturation rates being obtained in enzyme catalysed reactions where Michaelis–Menten type kinetics are obtained. The rates of oxidation as a function of catalyst loading are plotted in *Figure 4*. The rates are directly proportional to the catalyst loading in the range studied. The direct dependence of rates on partial pressure of oxygen is shown in *Figure 5*. The data support the mechanism involving reaction of an initially formed substrate–catalyst complex with O_2 in the rate determining step (*Scheme 1*). No attempt was made to study the reaction at higher pressures of O_2.

A one electron transfer from the phenolate ion to the Cu(II) is well documented in the literature [26–29]. The phenoxy radical formed is immediately desorbed into the solution phase. As the dissociated phenoxy radicals would have an electron density about twice as high at the p-carbon position ($\rho = 0.45$) compared to that at oxygen ($\rho = 0.23$) [29], the free radicals would lead predominantly to the C–C coupled product (DPQ formation).

As under optimum conditions only DPQ was obtained as

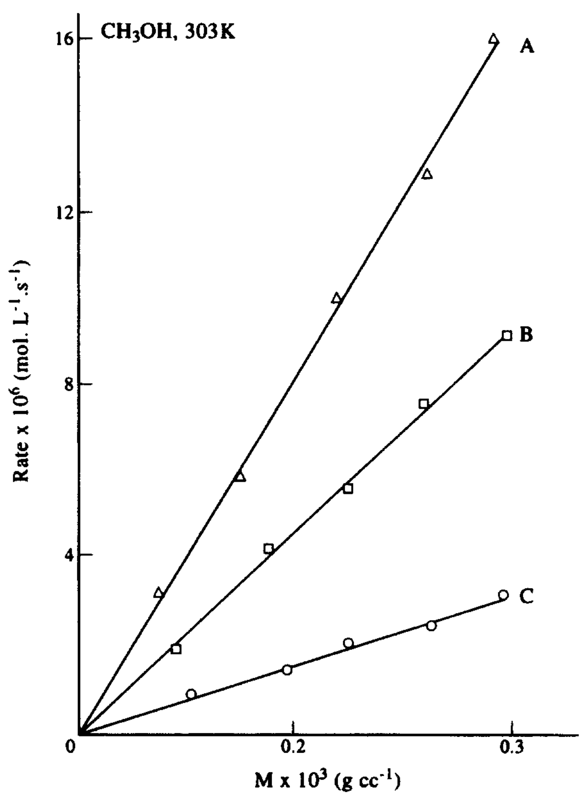

Figure 4 Dependence of rate of oxidation on catalyst loading (M). $[\mathrm{OH}]^- = 0.5$ N, $pO_2 = 578$ mm Hg, [DMP] = 0.13 mol l^{-1}. A, Cat 3; B, Cat 2; C, Cat 1

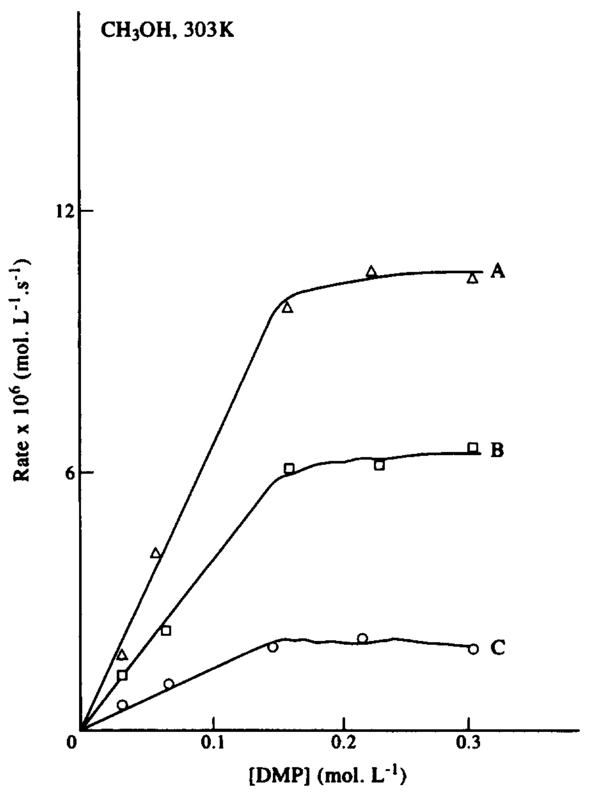

Figure 3 Dependence of rate of oxidation on [DMP]. $[\mathrm{OH}]^- = 0.5$ N, $pO_2 = 578$ mm Hg, $M = 12.5 \times 10^{-3}$ g cm^{-1}. A, Cat 3; B, Cat 2; C, Cat 1

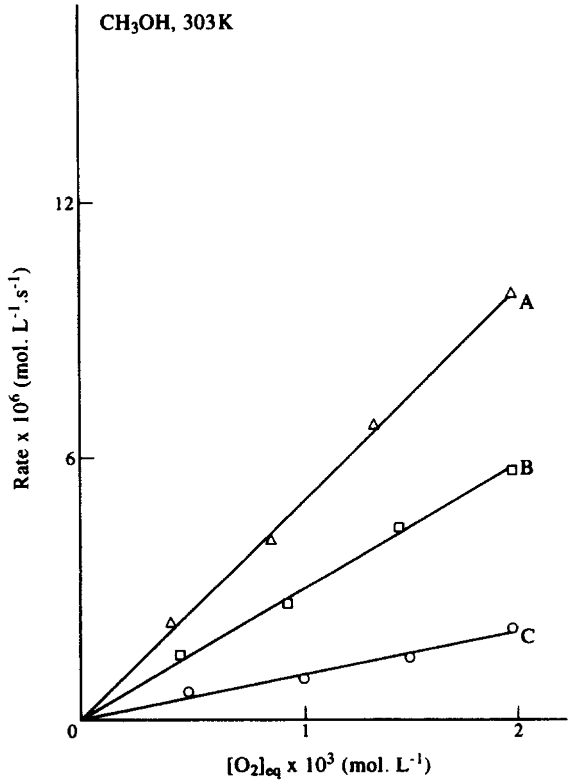

Figure 5 Dependence of rate of oxidation on equilibrium concentration $[O_2]_{eq}$ in solution. [DMP] = 0.13 mol l^{-1}, $[\mathrm{OH}]^- = 0.5$ N, $M = 12.5 \times 10^{-3}$ g cm^{-1}. A, Cat 3; B, Cat 2; C, Cat 1

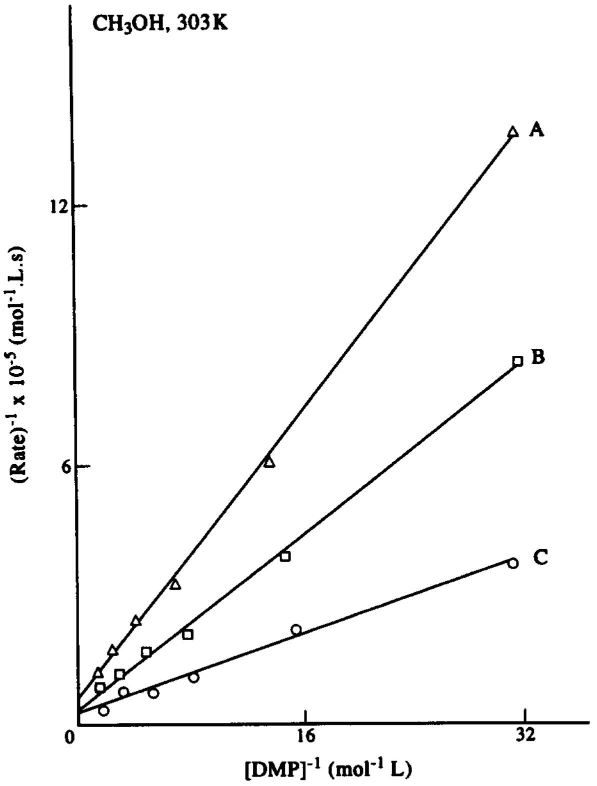

Figure 6 Plots of (rate)$^{-1}$ versus $[H_2O_2]^{-1}$. [DMP] = 0.13 mol l^{-1}, $[OH]^- = 0.5$ N, $pO_2 = 578$ mm Hg, $M = 12.5 \times 10^{-3}$ g cm^{-1}. A, Cat 1; B, Cat 2; C, Cat 3

the oxidation product by the present catalysts, it seems more likely that the phenoxy radical would dissociate from the complex. A similar type of radical mechanism for DPQ formation has already been proposed by Kresta *et al.* [29].

For the polymeric catalyst, the local copper concentration within the polymer backbone is relatively high and hence the oxidation of Cu(I) is accelerated [30]. It is known that the autoxidation rates of Cu(I) complexes can be quite high [31], although the low redox potential (− 0.33 V) for the O_2/O_2^- couple [32,33] would be very unfavourable. This problem can be overcome by a two electron reduction of O_2 in a dimeric transition state $(Cu^+(O_2)Cu^+)$ avoiding the formation of free O_2 [32].

Therefore, the formation of such an intermediate which has already been suggested by Battleheim *et al.* [34] is highly probable. In analogy, in hemocyanin two Cu(I) ions are known to reversibly bind one dioxygen molecule in a dinuclear complex [35]. In this dimeric species $(Cu^+(O_2)Cu^+)$, molecular oxygen is thought to form a bridge between the two Cu(I) ions. This type of species has been proposed in the autoxidation mechanism of other Cu(I) complexes [36–40]. In fact the dimeric intermediate $(Cu^{2+}(O_2)Cu^{2+})$ has also been suggested by Schouten *et al.* [27] in the copper catalysed oxidative coupling of 2,6-Xylenol. Hence in the present system, it can be envisaged that the two neighbouring Cu(I) ions on the polymer back bone form a dimeric species like $(Cu^+(O_2)Cu^+)$ for Cu(I) re-oxidation. The H_2O_2 formed during the re-oxidation of Cu(I) species immediately decomposes to water and oxygen. The decomposition of H_2O_2 by Cu(II) species is a well established process [41–43].

It has been well established that the role of oxygen in the oxidative coupling reaction of 2,6-xylenol is to oxidise the Cu(I) ions to the dimeric state [3]. Thus, 2,6-xylenol can be reacted in the absence of oxygen provided more than an equivalent of Cu(II) ion is present. However, Tsuruya *et al.* have found no product could be obtained with the $CuCl_2$/KOH system under nitrogen atmosphere [44]. Tsuchida *et al.* have also found that even with an excess of Cu(II) complexes, the oxidation did not proceed at all in the absence of oxygen when aliphatic amines are used as ligands [26]. The oxygen seems to have another role in addition to keeping copper ion in the divalent state. They suggested a ternary complex (O_2–Cu(II)–DMP) between the copper–amine complex, phenol and oxygen as the intermediate involved in the oxidative coupling of phenol derivatives. The oxygen was assumed to promote the electron transfer from the DMP to the metal ion by acting as an electron acceptor or the dissociation of the activated phenoxy radicals or both. Taking these factors into account it can be envisaged that the molecular oxygen forms a ternary complex with the already formed Cat–DMP complex in the rate determining step (*Scheme 1*) and induces the electron transfer process from phenolate ion to Cu(II) ions as well as inducing the dissociation of phenoxy radicals from the catalyst particles.

The above mechanism would lead to the rate law

$$\text{Rate} = \frac{kK[\text{Cat}][\text{DMP}][O_2]}{1 + K[\text{DMP}]} \qquad (1)$$

where k is the rate constant and K is the equilibrium constant. The experimental results are in good agreement with the above rate law indicating that the reaction follows the proposed mechanistic route. Equation (1) can be rearranged as

$$\frac{1}{\text{rate}} = \frac{1}{kK[\text{Cat}][\text{DMP}][O_2]} + \frac{1}{k[\text{Cat}][O_2]} \qquad (2)$$

Thus, a plot of (rate)$^{-1}$ versus [DMP]$^{-1}$ at constant [Cat] and $[O_2]$ is a straight line with a positive intercept on the *Y* axis. From the values of slope and intercepts of the plots and using equation (2), the rate and equilibrium constants were evaluated.

Since the system is heterogeneous these plots would not lead to absolute rate or equilibrium constants. Unless the total surface area of the catalyst as well as distribution of

Table 3 Kinetic parameters of the oxidation of 2,6-xylenol [a]

Number	Catalyst	303 K		313 K		323 K	
		k	K	k	K	k	K
1	Cat 1	1.77	0.48	3.06	0.60	5.15	0.72
2	Cat 2	2.60	0.59	3.73	0.69	5.56	0.81
3	Cat 3	4.28	0.93	6.00	1.10	8.51	1.24

[a] k in mol^{-1} l s^{-1}, K in mol^{-1} l.

[Cat 1] = 9.34 × 10^{-3} (g atom Cu) l^{-1}; [Cat 2] = 12.78 × 10^{-3} (g atom Cu) l^{-1}; [Cat 3] = 10.57 × 10^{-3} (g atom Cu) l^{-1}

.[DMP]/[Cat 1] = 3.47–53.5; [DMP]/[Cat 2] = 2.54–39.0; [DMP]/[Cat 3] = 3–47.3.

Solvent, methanol; pO_2 = 760-vapour pressure of methanol (mm); $[OH]^-$ = 0.5 N.

number of reactive sites per unit surface area are available, the data on k or K will be tentative. They are used here merely to compare the catalysts among themselves.

Determination of the formation constant of the Cat–DMP complex by equilibrating the two in the absence of O_2 was not possible because of the possible adsorption of the phenolate anion by the polymer matrix.

The plots of $(\text{rate})^{-1}$ versus $[\text{DMP}]^{-1}$ for all the catalysts are given in *Figure 6*. The data on estimated rate and equilibrium constants are given in *Table 3*. Both rate constant (k) and equilibrium constant (K) increase in the order of Cat 1 < Cat 2 < Cat 3. The high reactivity of Cat 3 is due to the smaller average particle diameter of Cat 3 (14.51μ) as well as the difference in the ligand binding the Cu(II) ions.

As detailed in previous communications from our laboratory [17,45], the analysis of kinetic data using the treatment of Satterfield [46] can be carried out here. The rate of hydrogenation under excess substrate for slurry reactors is given by

$$\frac{Ce}{Nv} = \frac{1}{k_L A_b} + \frac{d p \rho_p}{6M}(1/k_c + 1/k_s)$$

where Ce is the equilibrium concentration of H_2 in the solvent, Nv is the rate of hydrogenation ($\text{mol l}^{-1}\ \text{s}^{-1}$), k_L is the mass transfer coefficient for the transport of H_2 from gaseous phase to the liquid phase (cm s^{-1}), k_c is the mass transfer coefficient for the transport of dissolved H_2 from the liquid phase to the surface of the catalyst particles (cm s^{-1}), k_s is the pseudo-first-order reaction rate constant (cm s^{-1}), A_b is the interfacial area per unit volume of the slurry, dp is the average particle diameter (cm), ρ_p is the density of the catalyst particle (g cm^{-1}) and M is the weight of catalyst per unit volume of the slurry (g cm^{-1})

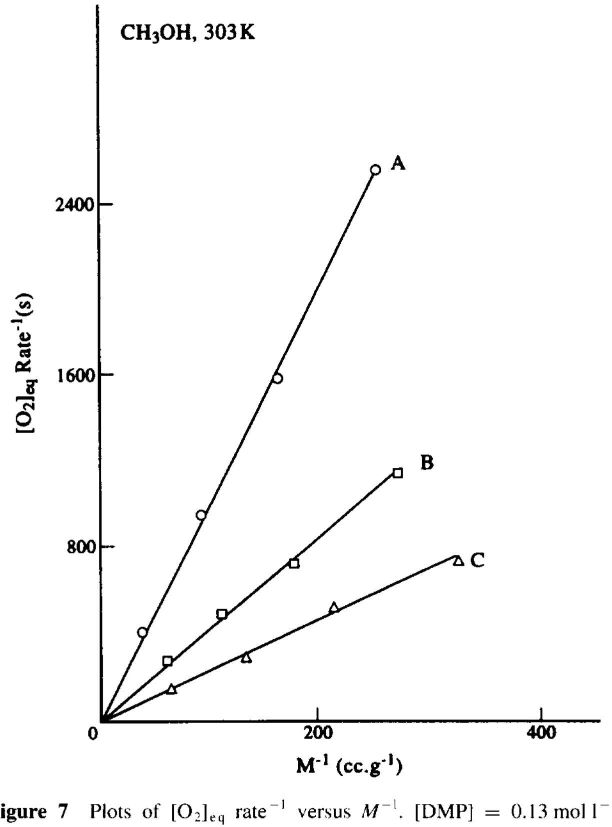

Figure 7 Plots of $[O_2]_{eq}$ rate^{-1} versus M^{-1}. $[\text{DMP}] = 0.13\ \text{mol l}^{-1}$, $[\text{OH}]^- = 0.5$ N, $pO_2 = 578$ mm Hg. A, Cat 1; B, Cat 2; C, Cat 3

Table 4 Data on k_c and k_s values [a]

	$k_c \times 10^4$	$k_s \times 10^3$
Cat 1 (77.86μ)	2.23	9.96
Cat 2 (44.53μ)	2.14	5.40
Cat 3 (14.51μ)	1.28	3.80

[a] k_c, k_s in cm s^{-1}.Solvent, methanol; temperature, 303 K.

Table 5 Recycling efficiencies of the catalysts

	Number of cycles	
	0	2
Cat 1 Cu content (mg g^{-1})	47.5	46.25
Rate × 10^5 ($\text{mol l}^{-1}\ \text{s}^{-1}$)	0.26	0.22
Cat 2 Cu content (mg g^{-1})	65.0	64.10
Rate × 10^5 ($\text{mol l}^{-1}\ \text{s}^{-1}$)	0.51	0.49
Cat 3 Cu content (mg g^{-1})	53.75	53.0
Rate × 10^5 ($\text{mol l}^{-1}\ \text{s}^{-1}$)	1.0	0.84

$[\text{DMP}] = 0.13\ \text{mol l}^{-1}$, $[\text{OH}]^- = 0.13$ N.Temperature = 303 K; $pO_2 = 760$-vapour pressure of methanol (mm); $[\text{Cat}] = 12.5 \times 10^{-3}\ \text{g cm}^{-1}$.

Unlike in the case of hydrogenation reactions, oxidation of 2,6-xylenol is a slow reaction where O_2 diffusion always remains faster than the surface reaction since rates are directly proportional to catalyst loading up to very high values of M (*Figure 4*). Thus plots of $-\,d(O_2)/dt$ vs. $[O_2]_{eq}$ can be used to evaluate k_c (*Figure 5*). The plots of $[O_2]_{eq}(\text{rate})^{-1}$ vs. M^{-1} appear in *Figure 7*. The slope of the plots yield the value of $1/k_c + 1/k_s$. The estimated values of k_c and k_s appear in *Table 4*. It can be seen that the order of magnitude of k_c is the same with all three catalysts. The larger particle sizes of Cat 1 and Cat 2 give rise to larger values of k_s.

Recycling efficiencies

The catalysts prepared in the present study were periodically analysed for their metal content. With DMP as the substrate the rates were measured after 2 cycles of use. The data appear in *Table 5*. With Cat 1 there is a loss of ~1.31% Cu per cycle whereas the percentage loss of Cu per cycle for Cat 2 and Cat 3 is ~0.69%. However all the three catalyst retained more than ~90% of their original activity. It is clear that the multiple ligation of the metal leads to higher recycling efficiency.

REFERENCES

1. Hay, A.S., Blanchard, H.S., Endres, G.F. and Eustance, J.W., *J. Am. Chem. Soc.*, 1959, **81**, 6335.
2. Endres, G.F., Hay, A.S. and Eustance, J.W., *J. Org. Chem.*, 1963, **28**, 1300.
3. Hay, A.S., *Adv Polym. Sci.*, 1967, **4**, 496.
4. Tsuchida, E., Nishiyama, H. and Terada, E., *J. Polym. Sci. Polym. Chem. Ed.*, 1976, **14**, 825.
5. Linger, B.O., *Acta Chem. Scand.*, 1960, **14**, 1203.
6. McNelis, E., *J. Org. Chem.*, 1966, **31**, 1255.
7. Kon, E. and McNelis, E., *J. Org. Chem.*, 1975, **40**, 1515.
8. Tsuchida, E., Kaneko, M. and Nishide, H., *Makromol. Chem.*, 1972, **151**, 221.
9. Tsuchida, E., Kaneko, M. and Nishide, H., *Makromol. Chem.*, 1973, **164**, 203.
10. Tsuchida, E., Nishide, H. and Nishiyama, T., *J. Polym. Sci. Polym. Symp.*, 1974, **47**, 35.
11. Tsuchida, E., Nishide, H. and Nishiyama, T., *Makromol. Chem.*, 1974, **175**, 3047.
12. Verlaan, J.P.J., Bootsma, J.P.C., Koning, C.E. and Challa, G., *J. Mol. Catal.*, 1983, **18**, 159.
13. Koning, C.E., Challa, G., Hulsbergen, F.B. and Reedijk, J., *J. Mol. Catal.*, 1986, **34**, 493.

14. Koning, C.E., Eshui, J.J.W., Viersen, F.J. and Challa, G., *Reactive Polymers,*, 1986, **4**, 493.
15. Koning, C.E., Brinkhuis, R., Wevers, R. and Challa, G., *Polymer,*, 1987, **28**, 2310.
16. Wei Chen and Challa, G., *Polymer*, 1990, **31**, 2171.
17. Xavier, R. and Mahadevan, V., *J. Polym. Sci. Part A: Polym. Chem.*,, 1992, **30**, 2665.
18. Tezuke, S., Shimada, K. and Okamura, S., *J. Polym. Sci. Part. A1.*, 1969, **7**, 879.
19. Noyes, Arthur A., *Qualitative Chemical Analysis of Inorganic Substances* 10th edn., The MacMillan Company, New York, 1956.
20. Vogel, A.I., *Text book of Quantitative Inorganic Chemistry*, ELBS, 1978, p. 156.
21. Nayak, Suchita D., Mahadevan, V. and Srinivasan, M., *J. Catal.*, 1985, **92**, 327.
22. Greef, R., Peat, R., Peter, L.M., Pletcher, D. and Robinson, J. (Eds.), *Instrumental methods in Electrochemistry*, Harwood Ltd, England, 1985, p. 178.
23. Finkbeiner, H., Hay, A.S., Blanchard, H.S. and Endres, G.F., *J. Org. Chem.*,, 1966, **31**, 549.
24. Vollmet, B. and Saatweber, S., *Angew. Makromol. Chem.*,, 1968, **2**, 114.
25. Wei Chen and Challa, G., *Eur. Polym. J.*, 1990, **26**, 1211.
26. Tsuchida, E., Kaneko, M. and Nishide, H., *Makromol. Chem.*,, 1972, **151**, 235.
27. Schouten, A.S., Challa, G. and Reedijk, J., *J. Mol. Catal.*,, 1980, **9**, 41.
28. Finkbeiner, H.L., Hay, A.S. and White, D.M., in C.E. Schildknecht and I. Skeist (Eds.), *Polymerisation Processes*, Wiley-Interscience, New York, 1977, p. 537.
29. Kresta, J., Thac, A., Prikryl, R. and Malik, L., *Makromol. Chem.*,, 1975, **76**, 157.
30. Koning, C.E., Vierson, F.J., Challa, G. and Reedijk, J., *J. Mol. Catal.*,, 1988, **44**, 245.
31. Zuberbuhler, A.D., in K.D. Karlin and J. Zubieta (Eds.), *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*, Adenine Press, New York, 1983, p. 237.
32. Sawyer, D.T. and Valentine, J.S., *Acc. Chem. Res.*,, 1981, **14**, 393.
33. Wood, R.M., *FEBS Lett.*,, 1974, **44**, 22.
34. Bettleheim, A., Farraggi, M., Hodara I., and Manassen, J., *J. Chem. Soc. Faraday Trans. 1*, 1977, **73**, 582.
35. Loutie, R. and Witters, R., in G.L. Eicchorn (Ed.), *Inorganic Biochemistry*, Elsevier, Amsterdam, 1973, Vol. 1, p. 134.
36. Karlin, K.D., Cruse, R.W., Gultneh, Y., Hayes, J.C., Mckown J.W. and Zubieta, J., in K.D. Karlin and J. Zubieta (Eds.), *Biological and Inorganic Copper Chemistry*, Adenine Press, New York. 1986, Vol. 2, p. 101.
37. Zuberbuhler, A.D., in H. Sigel (Ed.), *Metal ions in Biolgical Systems*, Mercel Dekker, New York, 1976, Vol. 5.
38. Pecht, I. and Anbar, M., *J. Chem. Soc. Ser. A*, 1968, 1902.
39. Goodwin, J.A., Stanburg, D.M., Wilson L.J., and Scott, R.A., in K.D. Karlin and Zubieta (Eds.), *Biological and Inorganic Copper Chemistry*, Adenine Press, New York, 1986, Vol. 2, p. 11.
40. Nelson, S.M., in K.D. Karlin and J. Zubieta (Eds)., *Copper Co-Ordination Chemistry: Biological and Inorganic Perspectives*, Adenine Press, New York, 1983, p. 331.
41. Nose, Y., Hatano, M. and Kambara, S., *Makromol. Chem.*,, 1966, **98**, 136.
42. Bekturov, E.A., Kudaibergenov, S.K. and Sigitov, V.B., *Polymer,*, 1986, **27**, 1269.
43. Salem, I.A., *J. Mol. Catal.*,, 1993, **80**, 11.
44. Tsuruya, S., Nakamae, K. and Yonezawa, T., *J. Catal.*,, 1976, **44**, 40.
45. Mathew, J. and Mahadevan, V., *J. Mol. Catal.*,, 1990, **60**, 189.
46. Satterfield, C.N., *Mass Transfer in Heterogeneous Catalysis*, MIT Press, Cambridge, MA, 1970, pp. 107–123.