Catalytic oxidation by polymer-supported copper(II)–L-valine complexes

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Abstract

Anchoring of an amino acid L-valine on cross-linked styrene–divinyl benzene was carried out in presence of a base. Reaction of cupric acetate with the polymeric ligand resulted in chelate formation with Cu(II) ion. The immobilized Cu(II) catalysts were characterized by elemental analyses, IR, UV-Vis, SEM, ESR and thermal analysis. Physico-chemical properties like surface area, apparent bulk density, pore volume, etc. have been determined. The supported Cu(II) complexes behave as versatile catalysts in the oxidation of various substrates such as benzyl alcohol, cyclohexanol and styrene in presence of *t*-butyl hydroperoxide as oxidant. The effect of reaction conditions on conversion and selectivity to products has been studied in detail. Preliminary kinetic experiments reveal that the Cu(II) complexes attached to polymer matrix can be recycled about four times with no major loss in activity.
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1. Introduction

The potential applications of polymer–metal complexes in organic transformations has been reviewed in detail by many groups [1,2]. The advantages derived from the use of functionalized macromolecules being simplification of the workup, ease of separation of products from reaction mixture, recovery and recycling of catalysts, etc. [3–5]. Ligands which have been commonly anchored to polystyrene prior to complexation with metal ions include dipyridylamine [6], phosphines [7], β-diketones [8], Schiff bases [9] and multidentate amines [10]. Anchoring of (N, O)-containing ligand such as an α-amino acid directly on a polymer backbone has not been well studied. One of the major problems associated with binding of optically active amino acids is the presence of reactive amino and carboxylic groups. Synthetic sequence commonly involves protection–deprotection strategy of the desired end group to overcome racemization and separation problems which are in addition sensitive

to pH of reaction medium. One of the earliest instance of an α-amino acid supported Merrifield's resin was reported by Petit and Jozefonvicz [11]. This study describes the methods for preparation of Cu(II) complexes with different polymer-bound amino acids. Catalytic activity, however, was not investigated. More recently zeolite encapsulated copper(II)–histidine complexes were shown to exhibit catalytic activity in the oxidation of olefins and alcohols with high turnovers [12]. The interest in these complexes stems from the fact that Cu(II)–amino acids resemble the active center of Cu-enzymes, which are known to participate in selective catalytic oxidation reaction in nature [13,14].

In continuation of our work on the catalytic application of bidentate Schiff base ((N, O) donor) bearing polymer-supported catalysts [15,16] we have in the present work devised a convenient synthetic strategy for anchoring an amino acid such as L-valine (L-val) on moderately cross-linked chloromethylated poly(styrene–divinyl benzene) (poly(S-DVB)) support followed by isolation of the corresponding Cu(II) complexes. These newly synthesized compounds have been evaluated as catalysts for the oxidation of benzyl alcohol, cyclohexanol and styrene in presence of *t*-butyl hydroperoxide (TBHP) as the oxidant under mild conditions. The effect of different reaction parameters on

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the kinetics of oxidation of benzyl alcohol as model substrate has been examined in detail. A brief study on the recyclability of Cu catalysts has been undertaken.

2. Experimental

2.1. Materials

Chloromethylated poly(styrene–divinyl benzene) co-polymer beads with 6 and 8% cross-link (18–44 mesh, chlorine content 16 and 17.5%, respectively) were received from Ion-Exchange India Ltd. The commercial resin was pretreated with aqueous dioxane (50:50 (v/v)) and finally washed with methanol and dried under vacuum 90 °C for 8 h before using for chemical functionalization. $Cu(OAc)_2 \cdot H_2O$ (Merck), L-valine (Merck), styrene (Merck), benzyl alcohol (Merck) and cyclohexanol (Fluka) were used as received. AR grade 1,4-dioxane, methanol, acetonitrile and ethanol were freshly distilled using standard methods [17]. *t*-Butyl hydroperoxide (70% aqueous solution, Merck), cumene hydroperoxide (CHP, 80% in cumene, Fluka) and H_2O_2 (30% (w/v), Thomas Baker) were used as received. The active oxygen content in commercial TBHP was determined iodometrically following a literature method [18].

2.2. Measurements

Elemental analyses of polymer–metal complexes were carried out using a Carlo-Erba Strumentazione microanalyzer. The total Cu content on the polymeric support after loading was estimated using an Optima 4300DV inductively coupled plasma emission spectrometer (Perkin-Elmer). Chlorine content was estimated gravimetrically by precipitation of chloride as AgCl. Surface area of supports and the Cu-anchored polymer was determined on a Carlo-Erba surface analyzer employing BET relationship. UV-Vis reflectance spectra of catalysts were recorded on a Shimadzu-UV 240 instrument using spectroscopic grade $BaSO_4$ as a reference. IR and far-IR spectra of polymer-supported Cu complexes at various stages of synthesis were recorded on a Nicolet Magna 550 spectrophotometer. Thermogravimetric analyses of compounds were carried out on Shimadzu DT-30 instrument at a heating rate of $10 \,^{\circ}C \, min^{-1}$ under an atmosphere of nitrogen. Scanning electron micrographs of catalysts and supports were taken on a CAMICA SU30 instrument with SE electrode at 20 kV. X-band (9.5 MHz) electron spin resonance spectra of polymer anchored Cu(II) complexes were recorded at room temperature on a Varian E112 spectrometer. TCNE was used as the '*g*' marker. The analyses of various liquid products obtained in the catalytic oxidation reactions were carried out on Shimadzu 15A gas chromatograph using a 15% Carbowax column (0.32 cm × 2 M) and Data lab GC 9000 using capillary column AT-1 (0.32 mm × 15 M × 0.25 μm thickness) attached to a flame ionization detector and N_2 as

carrier gas. Product identification was also carried out on a Finnigan MAT 9001 GCQ GC–MS system operated in the full scan mode and a quadrupole ion trap mass analyzer. The swelling behavior of supported catalysts in representative polar and non-polar solvents was carried out at $27 \pm 1 \,^{\circ}C$ by a procedure described previously [19].

2.3. Synthesis of polymeric supports

Pre-washed chloromethylated styrene–divinyl benzene co-polymer beads (12 g) in 35 ml methanol were mixed with an aqueous solution of L-valine (9 g) in 250 ml distilled water. The contents were refluxed for 16 h in presence of 6 ml of pyridine. The overall molar ratio of different reagents based on percent replaceable chlorine on resin approximately corresponds to l:1.25:1.25 for Cl:amino acid:base. The contents were cooled and kept aside for 1 week with occasional shaking. At the end of this period, pH of the reaction mixture came down from the initial value of 7.1–5.1. The color of the beads changed from off-white to light yellow indicating the attachment of the ligand. Finally, the L-valine linked polymer beads were filtered, washed with hot water followed by ethanol and dried under vacuum at 90 °C for 8 h to yield 13.8 g of product.

In order to confirm the presence of free –COOH group after functionalization of L-valine through amino group on the polymer support, a known weight of the dry resin (8% poly(S-DVB)L-val, 0.5 g) in 30 ml of distilled water was refluxed for 10–12 h in presence of excess NaOH (10 ml, 0.1N) containing a few drops of phenolphthalein indicator. Upon cooling, the solution was filtered, washed carefully with 2× 5 ml portions of water and the filtrate back titrated with 0.1N HCl. A simple calculation based on titer values showed that about 2.46% N equivalent to 1.76 mmol L-valine to be anchored per gram of polymer. In the case of 6% poly(S-DVB)L-val, this value was 2.43% N (1.74 mmol L-val/g). Independently estimated nitrogen from microanalysis of the same samples (Table 2) gave value of 2.56% N (1.83 mmol L-val/g) and 2.47% N (1.76 mmol L-val/g), respectively. The close agreement of these results thus allowed us to quantify unambiguously the extent of amino acid loading on the cross-linked polymeric support.

The loading of metal on the polymer was carried out as follows: liganded polymer beads (12.5 g) were kept in contact with ethanol (50 ml) for 45 mm. To this was added an ethanolic solution (100 ml) of $Cu(CH_3COO)_2 \cdot H_2O$ (4.0 g, 0.02 mol) containing 3 ml glacial acetic acid and the contents gently agitated on a shaker at constant speed for 8 days at 25 °C (pH 3.6). The color of the beads changed from light yellow to yellow during this period indicating the formation of the metal complex on the polymer matrix (pH of the solution remained around 3.5 after 8 days). At the end of this period, the light yellow colored polymer was filtered, washed thoroughly with ethanol, dioxane and methanol to ensure the removal of any unreacted metal acetate and dried in vacuum for 6 h at 90 °C.

2.4. Catalytic oxidation

A typical experimental procedure for the oxidation of alcohols and olefins using polymer anchored Cu(II) catalysts is described as follows. The catalyst (0.10 g) was taken in a two neck round bottom flask equipped with a nitrogen inlet and a condenser. To this was added 20 ml of acetonitrile, 5 mmol of the substrate alcohol/olefin followed by t-butyl hydroperoxide (7.5 mmol). A known amount of an internal standard (chlorobenzene) was added to the above solution prior to the run. The flask was stoppered and the mixture stirred magnetically at different temperatures under a blanket of nitrogen taking care to avoid any loss of solvent vapors during agitation. At the end of specified time, the contents were analyzed by GC. Control experiments in the absence of catalyst showed practically no or only traces ($\sim$0.1%) of product formation. Peak positions of various reaction products were compared and matched with the retention times of authentic samples. Identity of the products was also confirmed by GC–MS.

3. Results and discussion

3.1. Anchoring of L-valine

The direct attachment of an amino acid residue to chloromethylated poly(styrene–divinyl benzene) resin has previously been accomplished by employing one of the following routes:

(i) Substitution of chlorine by iodine on the chloromethylated polymer followed by reaction with α-amino acid [20].
(ii) Reaction of amino acid with cross-linked chloromethylated styrene–divinyl benzene co-polymer in presence of sodium iodide and a base such as tertiary amine [21].
(iii) Chlorosulfonation of the resin and subsequent reaction with sodium salt of amino acid [22].

Moderate yields were claimed in case of reaction with chlorosulfonated polystyrene (method (iii)) and low yields were noted with methods (i) and (ii).

In the present work initial attempts to react L-valine with chloromethylated poly(S-DVB) in aqueous as well as in methanolic solution including reflux conditions proved unsuccessful. After several screening experiments, the reaction of amino acid and the resin in presence of pyridine as a base showed encouraging result as it is known to work well in both aqueous as well as in organic solvents. Using slightly more than molar excess of L-valine and pyridine reproducible grafting on the resin could be achieved (Table 2). Analysis for nitrogen after ligand attachment gave values of 2.56 and 2.46%, respectively, for 8 and 6% cross-linked supports. This correspond to 1.83 and 1.76 mmol of L-valine anchored per gram of support. It is 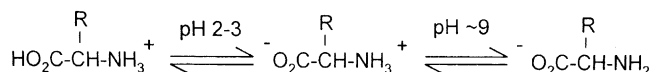known that in *non-aqueous* solvents and with *excess* pyridine quaternization of pendant benzylic rests in chloromethylated styrene–divinyl benzene readily occurs [23,24], which was confirmed by a dummy experiment in our case too. However, the reaction of amino acid and a *stoichiometric* amount of pyridine is feasible only in aqueous medium leading to the desired mode of grafting by facilitating the elimination of HCl as the pyridine-hydrochloride salt. Under these conditions, quaternization does not take place. In another set of control experiment pyridine was allowed to react with the polymeric support in absence of amino acid under identical conditions. After the usual workup analysis of the resin treated with pyridine did not show any nitrogen. This indicates that there is no side reaction taking place in presence of pyridine and the observed nitrogen percent in the valine grafted resin entirely comes from the anchored amino acid fragment. This was further confirmed by estimation of the free carboxylic groups on the resin which was found to be equivalent to the amino acid loaded. These details are given in the experimental section.

In a related experiment efforts for N-functionalization of L-valine using K_2CO_3 in aqueous methanolic solution as described in a previous report was not effective in our case [25]. Further, indirect verification of mode of linkage was arrived at by reacting benzyl chloride with valine giving *N*-benzyl valine (mp 255 °C) [25,26] which supports that ligand attachment on polymer occur from the amine end. The probability of C-alkylation [27] of L-valine under these conditions is thus overruled. The synthetic protocol is depicted in Scheme 1.

3.2. Complex formation

Reaction of copper acetate with polymer anchored L-valine was conducted in the pH range of 3.5–3.6. A maximum Cu loading of up to 3.59% was obtained (Table 2).

Amino acids in general undergo two reversible proton ionization steps, viz.

$$\underset{HO_2C\text{-}CH\text{-}NH_3}{\overset{R}{|}}{}^{+} \;\underset{\text{pH 2-3}}{\rightleftharpoons}\; {}^{-}\underset{O_2C\text{-}CH\text{-}NH_3}{\overset{R}{|}}{}^{+} \;\underset{\text{pH} \sim 9}{\rightleftharpoons}\; {}^{-}\underset{O_2C\text{-}CH\text{-}NH_2}{\overset{R}{|}}$$

Consequently depending on the solution pH, L-valine is expected to coordinate to Cu ion through either or both of amino (NH_2) or carboxyl (CO_2^-) groups. Moreover, the order of stability constants for transition metal ions follows the Irving–Williams series [28]. For the bivalent Cu^{2+} ion, the formation of [Cu(L-val)$_2$] or [Cu(L-val)$_2$(OAc)$_2$] type of chelate may be favored [29]. Based on pK_a values Gillard et al. reported similar (N, O) chelation for different amino acid complexes at lower pH range [30]. The two polymer anchored Cu complexes used in the present work for catalytic oxidation of alcohols and olefinic compounds are designated as:

- Cu A: 8% poly(S-DVB)L-val Cu(II) complex;
- Cu B: 6% poly(S-DVB)L-val Cu(II) complex.
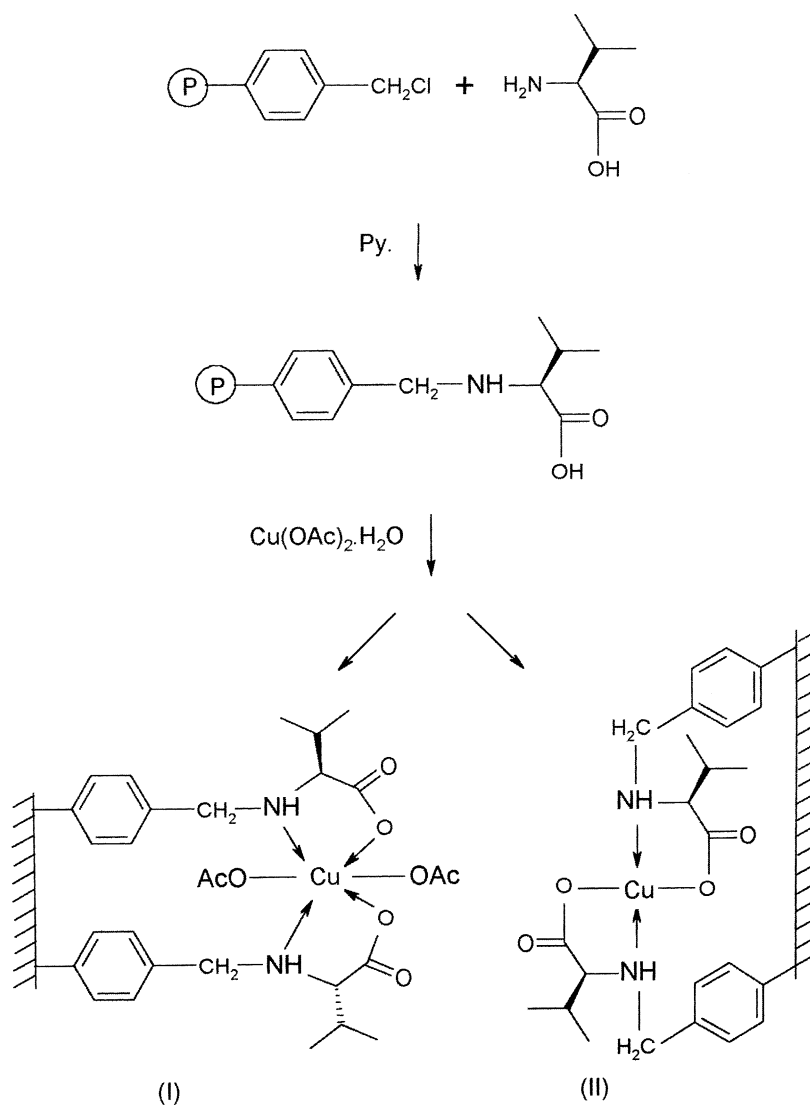
Scheme 1. Synthesis of poly(S-DVB)-supported Cu(II)–amino acid complex.

3.3. Characterization of supported catalysis

Some of the key physical properties of these catalysts have been compiled in Table 1. Cu B has a slightly higher surface area and larger pore volume than Cu A. The metal loading on Cu A with 8% cross-link (Cu 3.50%) was marginally lower than Cu B with 6% cross-link (Cu 3.59%) (Table 2). There is a noticeable decrease in surface area of the supports by 19–33% after metal loading indicating possible blocking of

pores on the external surface of polymer after complexation. Similar results have been reported for other surface modified polymeric catalysts [31,32]. The results of swelling behavior indicate that swellability increased in polar solvents than in non-polar aliphatic and aromatic hydrocarbon solvents. Both Cu A and Cu B show lower swelling in polar as well as non-polar solvents compared to the support (Table 3).

Table 1
Physical properties of poly(S-DVB)-supported Cu catalysts

Sample	Surface area ($m^2\,g^{-1}$)	Bulk density ($g\,cm^{-3}$)	Pore volume ($cm^3\,g^{-1}$)
8% Poly(S-DVB)CH$_2$Cl	32.7	0.44	0.20
6% Poly(S-DVB)CH$_2$Cl	38.3	0.38	0.29
Cu A	21.3	0.51	0.16
Cu B	30.6	0.45	0.19

Table 2
Analytical data of polymer support, ligand and Cu-anchored catalysts

Compound	C (%)	H (%)	Cl (%)	N (%)	Cu (%)
8% Poly(S-DVB)CH$_2$Cl	70.38	5.77	17.56	–	–
6% Poly(S-DVB)CH$_2$Cl	76.26	6.36	16.14	–	–
8% Poly(S-DVB)L-val	60.15	5.00	9.47	2.56	–
6% Poly(S-DVB)L-val	63.28	5.44	9.48	2.47	–
Cu A	58.46	5.06	n.d.	2.46	3.50
Cu B	60.48	5.16	n.d.	2.41	3.59

n.d.: not determined.

Table 3
Swelling study (mol%)

Solvent	8% Poly(S-DVB)CH₂Cl	6% Poly(S-DVB)CH₂Cl	Cu A	Cu B
Acetonitrile	1.99	2.02	1.42	1.53
Benzene	1.07	1.11	0.80	0.85
Dichloromethane	1.48	1.77	1.23	1.45
Ethanol	1.70	1.90	1.51	1.62
n-Heptane	0.58	0.59	0.41	0.51
Methanol	2.73	2.82	2.20	2.52
Tetrahydrofuran	1.44	1.53	0.97	1.03
Toluene	1.08	1.13	0.76	0.89

In order to ascertain the attachment of amino acid and the metal on the polymer support, IR spectra were recorded separately in mid (4000–400 cm^{-1}) and far-IR (600–30 cm^{-1}) regions at different stages of synthesis. The sharp C–Cl peak (due to –CH$_2$Cl group) at 1261 cm^{-1} in the starting polymer was practically absent or seen as a weak band after introduction of valine on the support. A strong band at 3423 cm^{-1} in poly (S–DVB)-valine is assigned to –NH (secodary amine) vibration. Medium intensity band due to C–N stretching appears at 1082 cm^{-1} both in the supported ligand and the catalysts. A slight shift in the –NH stretching band in Cu A and Cu B indicates the coordination of 'N' of amino acid to the metal [33]. Representative IR spectra of polymer supports and catalysts are shown in Fig. 1. The characteristic absorptions due to ν_{asym}(COO$^-$) and ν_{sym}(COO$^-$) stretchings of carboxylic group are seen at 1639 and 147 cm^{-1}, respectively, in the ligand as well as in Cu A and Cu B. Since the acetate ion (OAc) bands also appear in the same region (1600–1450 cm^{-1}) there is a possibility of some overlap of these bands.
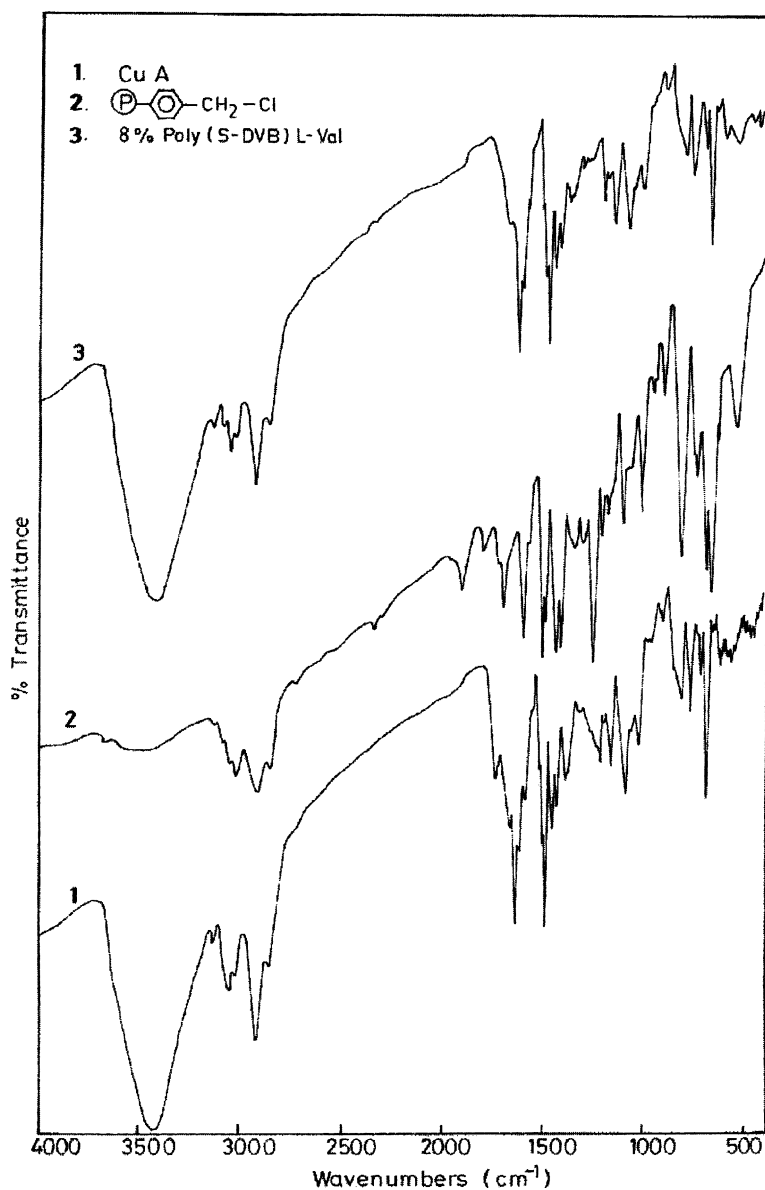

Fig. 1. FT-IR spectra of: (1) Cu A; (2) poly(S-DVB)CH₂Cl; (3) 8% poly(S-DVB)L-val.
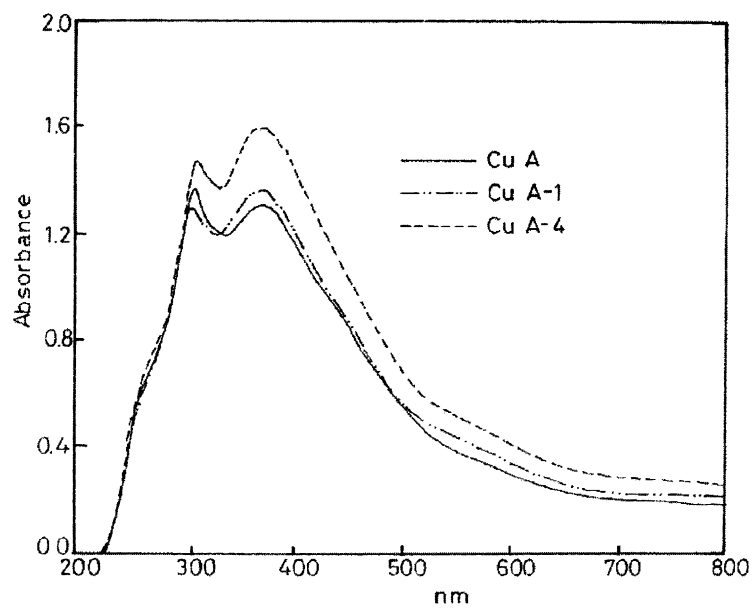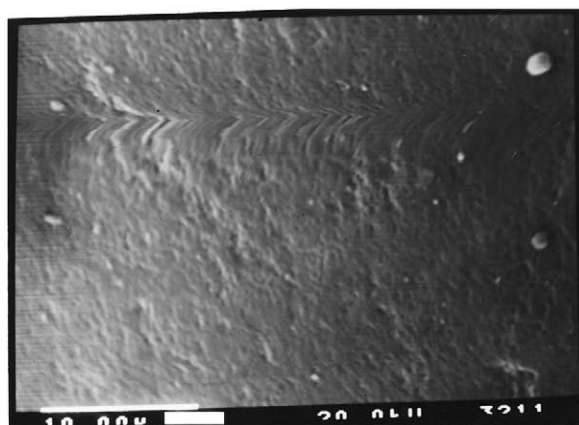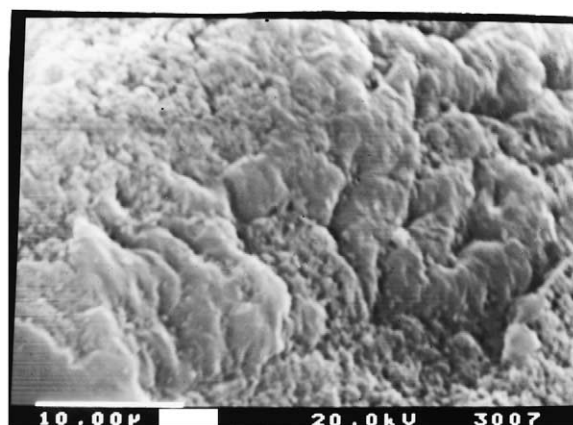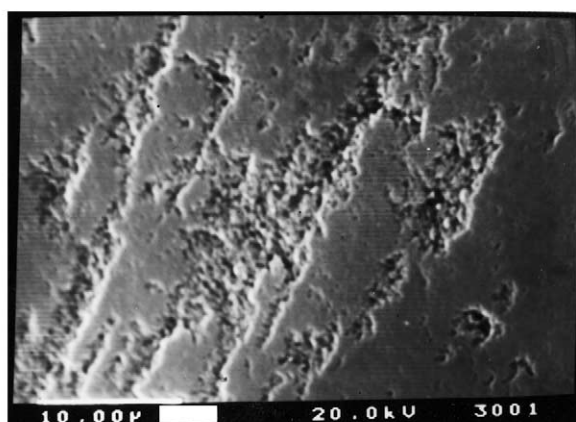
Fig. 2. Diffuse reflectance spectra of catalysts.

(a)

(b)

(c)

Fig. 3. Scanning electron micrographs of: (a) P(S-DVB)CH$_2$Cl; (b) 8% poly(S-DVB)L-val; (c) Cu A.

Weak bands in the far-IR region ($\sim$410–350 cm^{-1}) can be assigned to ν(Cu–N) and ν(Cu–O) vibrations [34].

The diffuse reflectance spectra (200–800 nm) of Cu A and Cu B display nearly identical features with two strong absorption bands in the UV region at $\sim$310 and 370 nm (ligand to metal charge transfer bands) and very weak and broad band in the visible region at 570 nm with reference to the BaSO$_4$ standard (Fig. 2). Absorption spectrum of Cu-proteins show characteristic LMCT bands in the region of 250 nm and a relatively broad band around 620 nm [12,13]. These values are consistent with a N$_2$O$_2$ co-ordination (square planar) environment around the central Cu^{2+} ion. The possibility of octahedral co-ordination though remote, can be visualized by assuming monodentate co-ordination of acetate ions to yield [Cu(L-val)$_2$(OAc)$_2$] type complex. The current evidence, however, appears to favor a predominantly planar configuration. Both these structural possibilities (I and II) are illustrated in Scheme 1.

Scanning electron micrographs (SEM) at various stages of preparation of the polymer-supported L-valine and the copper complexes were recorded to understand morphological changes occurring on the surface of the polymer. Scanning was done at 50–100 μm range across the length of the polymer beads. Comparison of images taken at a magnification of $\sim 3 \times 10^3$ indicate that the smooth and flat surface of the starting poly(S-DVB) (Fig. 3a) is distinctly altered upon anchoring of the ligand (Fig. 3b). After metal incorporation, irregularly oriented dark depositions on the external surface of the resin were observed (Fig. 3c).

TG analysis revealed a single step degradation peak for the chloromethylated poly(styrene–divinyl benzene) co-polymer in the 410–440 °C temperature range. On the other hand, both the copper-supported catalysts degrade at considerably lower temperatures as shown in Table 4. The variation in cross-linking in Cu A and Cu B does not, however, show much deviation in their thermal stabilities as seen from the weight loss which was between 20 and 22% at 360 and 372 °C. From the decomposition profile, it appears that either the dissociation of covalently bound amino acid ligand moieties or a partial scission of polymeric chain might be occurring at this temperature. Some weight loss ($\sim$2%) was also observed at $\sim$110 °C due to loosely bound surface moisture or volatiles on the surface of catalysts. These features are depicted in Fig. 4.

Table 4
TG data of polymeric supports and anchored Cu(II) catalyst

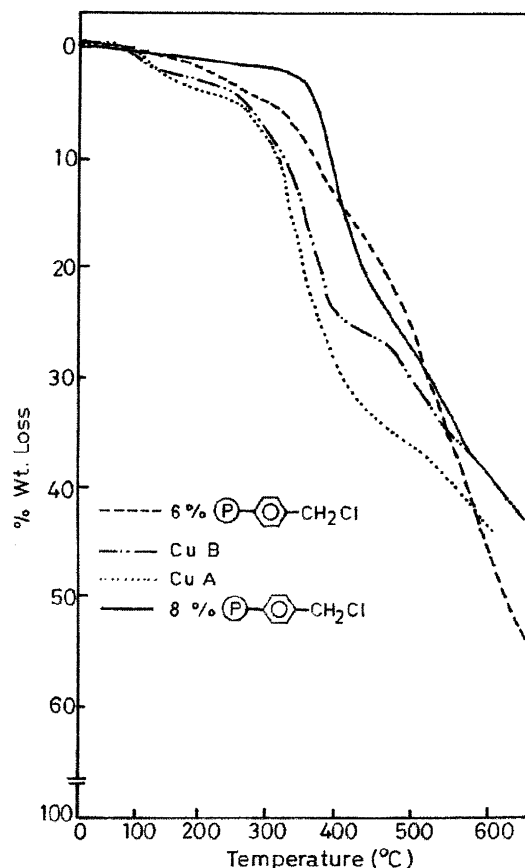| Compound	Degradation temperature (°C)	Weight loss (%)
8% Poly(S-DVB)CH$_2$Cl	440	21.0
6% Poly(S-DVB)CH$_2$Cl	410	21.0
Cu A	111	2.2
	370	23.0
Cu B	112	1.8
	372	20.0

Fig. 4. TG of chloromethylated 6 and 8% poly(styrene–divinyl benzene), Cu A and Cu B.

The X-band EPR spectrum of one of the catalyst Cu A recorded in the solid state at 297 K temperature showed signals characteristic of axial symmetry. Due to the irregular feature of resonance lines (Fig. 5) $A_{\parallel}$ value was computed by averaging over all three lines and is equal to $\sim$167 G. The experimentally calculated $g_{\perp}$ and $g_{\parallel}$ values correspond to 2.10 and 2.31 which are of the same order as found in mononuclear Cu^{2+} amino acid complexes [12,35].

3.4. Catalytic evaluation

The ability of the newly synthesized polymer-bound Cu(II)–L-valine complexes to catalyze the oxidation of alcohols and olefins was explored by conducting a systematic study with catalysts Cu A and Cu B in presence of TBHP as the terminal oxidant. Blank experiments revealed that no reaction occurred in the absence of either the catalyst or the oxidant. The results of oxidation carried out at two different temperatures are compiled in Table 5. All substrates undergo oxidation in presence of the two Cu-supported catalysts and in reactions with alcohols high selectivities were obtained. In order to verify whether the catalysts operate in a truly *heterogeneous* manner, a simple experiment was performed by keeping the catalyst in contact with the solvent and stirred for 24 h reaction period. The catalyst was
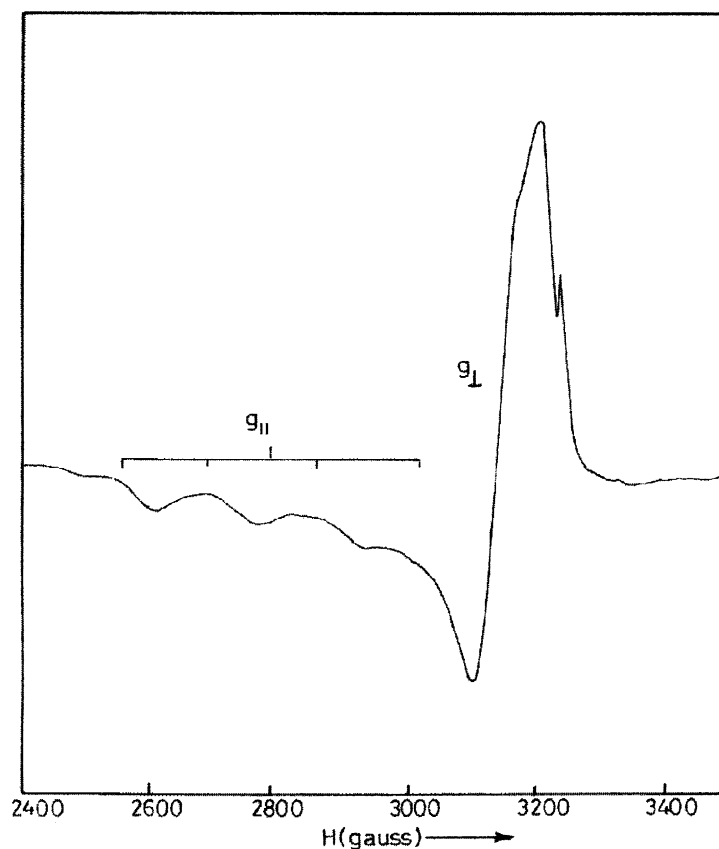
Fig. 5. ESR spectra of Cu A.

filtered off and the filtrate examined for any residual catalytic activity (room temperature, 24 h). Only trace amount of oxidation product (yield: ∼0.1–0.3%) was detected, indicating clearly that the observed reactivity was due to the metal complex bound to the polymer support. A second and

a more conclusive evidence for *heterogeneity* was arrived at by following a recent probe suggested by Sheldon [36]. The reaction of benzyl alcohol with Cu A was carried out at 45 °C as described earlier. After 3 h, the reaction was deliberately intercepted and the catalyst quickly separated

Table 5
Catalytic oxidation with Cu A and Cu B

Catalyst[a]	Substrate[b]	Temperature (°C)	Yield (%)[c]	selectivity (wt.%)		
				Epoxide	PhCHO	PhCOMe
Cu A	Styrene	28	28.6	9.6	81.1	9.3
Cu A		45	60.6	22.8	56.4	20.8
Cu B		28	19.2	16.0	56.4	27.1
Cu B		45	51.2	20.5	56.2	23.2
Cu A	Benzyl alcohol	28	30.8		94.7	
Cu A		45	72.0		93.8	
Cu B		28	30.0		94.4	
Cu B		45	70.0		93.6	
					Cyclohexanone	
Cu A	Cyclohexanol	28	12.8		100.0	
Cu A		45	24.6		100.0	
Cu B		28	11.2		100.0	
Cu B		45	25.4		100.0	

[a] 0.10 g.
[b] 5.0 mmol.
[c] Yield based on starting material.

by filtering at the same temperature. Analysis of the reaction mixture *at this point* showed a conversion of 13.1%. Stirring was continued for a total of 24 h and analysis at the end of this period (*without the catalyst*) showed only a marginal increase in conversion (16%). On the contrary, the result of reaction performed for 24 h in *presence* of the catalyst indicated around 70% overall conversion (Table 5).

As a further extension of this probe, another set of reaction was performed for 3 h *without* the substrate at 45 °C, the catalyst quickly filtered off and *then* the substrate added to the filtrate. Stirring was continued for 24 h and analysis of reaction mixture showed only ∼4.8% conversion. All the earlier diagnostic tests unambiguously point to the fact that the catalyst behave in a truly *heterogeneous* manner. Though our results show minor leaching, more importantly, the metal species leached into the filtrate *is not responsible* for the observed catalytic activity.

Styrene oxidation results in multiple product formation namely epoxide, benzaldehyde and acetophenone. In this reaction, interestingly aldehyde is the major product rather than the epoxide regardless of the variation in reaction conditions. Expectedly, overall yields are higher at 45 °C than at 28 °C. Formation of benzaldehyde as the major product suggests that the reaction with hydroperoxide proceeds beyond the epoxide stage resulting in the oxidative cleavage of styrene [37]. To eliminate the possibility whether Cu(II) itself takes part in the rearrangement of intermediate epoxide to PhCHO, a blank experiment was conducted using styrene oxide as the substrate. No PhCHO was found thus corroborating our conclusion that the primary product of styrene oxidation is benzaldehyde. Benzyl alcohol and cyclohexanol are selectively converted to the corresponding aldehyde and ketone with either catalyst. Interestingly, Weckhuysen et al. [12] reported that the oxidation of benzyl alcohol with Cu(II)–bis(amino acid) loaded on zeolite support yielded benzoic acid *in addition* to PhCHO in roughly 1:2 ratio. This difference in reactivity is attributed to the dissimilar nature of the supports employed for anchoring of Cu(II)–amino acid complexes as also to the predominantly acidic character of zeolite structure. In our case the overall mass balance based on GC data indicate that >94% of the converted product corresponds to PhCHO. In all the examples discussed earlier, Cu A displays slightly better activity compared to Cu B. A detailed study was thus undertaken with both catalysts to understand the effect of reaction conditions on the oxidation of benzyl alcohol as a model substrate. The extent of oxidation observed at different temperatures and catalyst concentrations are presented in Table 6. As can be inferred from Table 6, increase in reaction temperature is accompanied by marked improvement in yields at similar levels of catalyst concentrations. For instance, raising the reaction temperature from ambient (28 °C) to 45 °C, results in more than two-fold increase in yields with all substrates. Amongst the different solvents studied activity is maximum for acetonitrile followed by methylene chloride and methanol. With regard to the nature of oxidants, it was found that TBHP and

Table 6
Oxidation of benzyl alcohol using Cu A and Cu B under different reaction conditions

Parameter	Benzyl alcohol (mmol)	Catalyst weight (g)	Oxidant	Solvent	Yield (%)[a]
Catalyst concentration	5.0	0.05	TBHP	CH_3CN	22.0 (22.4)[b]
	5.0	0.10	TBHP	CH_3CN	30.8 (30.0)
	5.0	0.15	TBHP	CH_3CN	38.8 (39.6)
Oxidant	5.0	0.10	TBHP	CH_3CN	30.8 (30.0)
	5.0	0.10	H_2O_2	CH_3CN	10.8 (5.8)
	5.0	0.10	O_2	CH_3CN	6.8 (6.4)
	5.0	0.10	CHP	CH_3CN	37.0 (37.6)
Solvent	5.0	0.10	TBHP	CH_3CN	30.8 (30.0)
	5.0	0.10	TBHP	CH_2Cl_2	18.8 (19.6)
	5.0	0.10	TBHP	CH_3OH	15.6 (9.4)

At room temperature for 24 h; $c = 200$ psi O_2.
[a] Yield based on starting material.
[b] Values in parentheses are for Cu B.

CHP were most effective. Low activity was observed with molecular oxygen and hydrogen peroxide.

For a proper understanding of the efficacy of the present polymer-supported Cu catalysts vis-a-vis its homogeneous counterpart namely Cu(L-valine)$_2$ complex, direct comparison of catalytic activities under optimized reaction conditions is desirable. In the absence of relevant data on oxidation of olefins using homogeneous amino acid–metal catalysts, an attempt was made to generate in situ (without isolation) a simple L-valine complex of Cu(II) by mixing the ligand and the metal acetate in 1:2 and 1:1 molar ratios in an aqueous solution at a pH of ∼3.2. After a reaction period of 24 h an aliquot of the solution having Cu concentration equal to that employed in the supported catalysts was taken up for subsequent reaction with benzyl alcohol in presence of TBHP under identical conditions. The overall yields for *homogenous* complex (for 1:2 = 24% and for 1:1 = 26%) were generally lower than our supported catalyst (30%, Table 5). The UV-Vis solution spectra of both 1:1 and 1:2 in situ generated Cu(II)–L-valine complexes are blue in color and exhibit a single d–d absorption band in the visible region at ∼735 nm (Fig. 6). The spectral features are distinctly different compared to the DRS of the polymer-supported catalysts Cu A
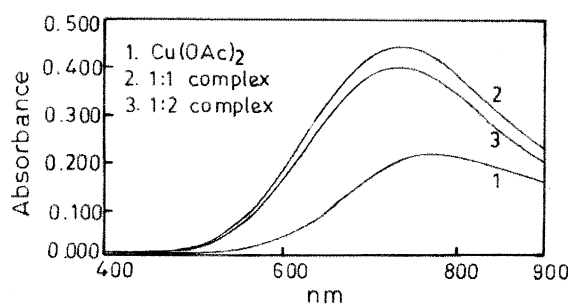

Fig. 6. UV-Vis spectra of: (1) Cu(OAc)$_2$; (2) 1:1 complex; (3) 1:2 complex.
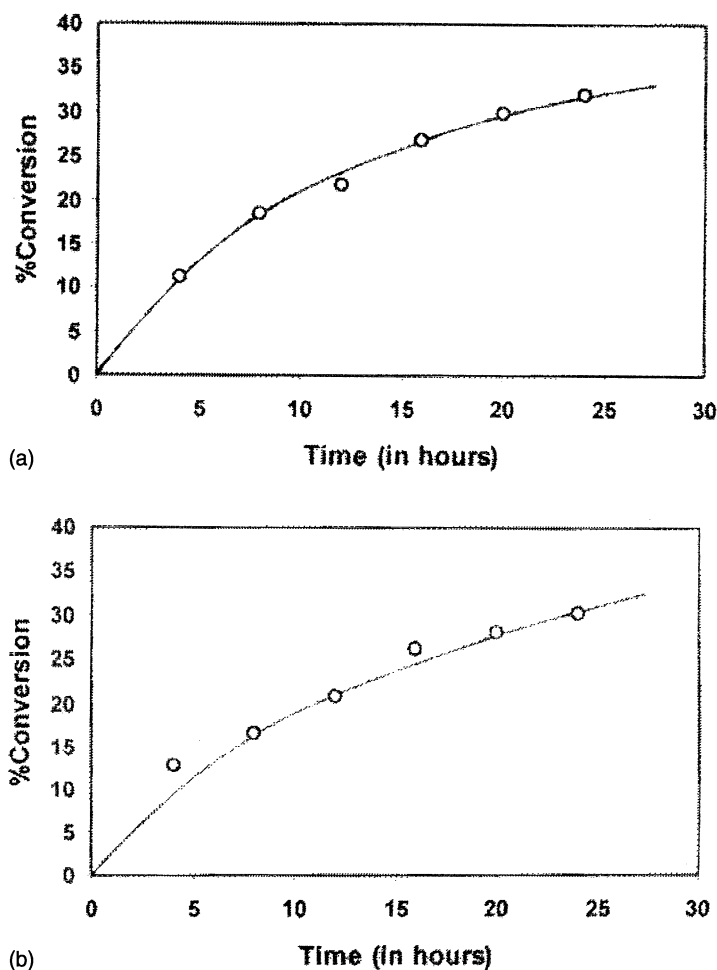
Fig. 7. Plot of conversion vs. time for benzyl alcohol using: (a) Cu A; (b) Cu B.

and Cu B. LMCT bands are not observed in the spectra of the homogeneous catalysts.

A preliminary kinetic study on the oxidation of benzyl alcohol in presence of TBHP at 28 °C was investigated with Cu A and Cu B up to 24 h by analyzing aliquots of reaction mixture at regular intervals of time. In Fig. 7 is shown a plot of alcohol conversion versus reaction time under a fixed oxidant concentration. With both the catalysts the conversions increase almost linearly up to about 16 h. The reaction becomes sluggish thereafter but continues even after 24 h.

3.5. Catalyst recycling

One of the main objectives of supporting a homogeneous metal complex on to a polymer support is to enhance the life of the resulting catalyst. We have made a preliminary study of the recycling efficiency of Cu A and Cu B using benzyl alcohol as model substrate. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with solvent and dried carefully before using it in the subsequent run. These results are shown in Table 7. The catalyst as recycled four times without noticeable loss

in activity (∼10%). The activity profile for four successive cycles is depicted in Fig. 8. The DRS of recycled catalysts after the first cycle (Cu A-l) and fourth cycle (Cu A-4) were similar (Fig. 2).

3.6. Mechanism

The metal catalyzed epoxidation of olefins by TBHP may proceed either by heterolytic or homolytic decomposition of

Table 7
Catalyst recycling in the oxidation of benzyl alcohol using TBHP[a]

Cycle no.	Yield (%)[b]	
	Cu A	Cu B
1	71.6	70.4
2	66.8	65.3
3	62.6	62.0
4	60.7	60.2

[a] Reaction conditions: 100 mg catalyst; 7.5 mmol TBHP; solvent, acetonitrile (20 ml); 45 °C; 24 h; substrate, 5.0 mmol.
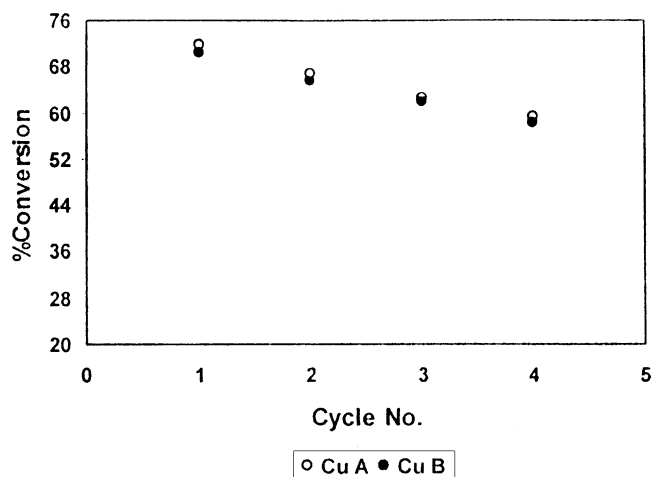
[b] Yield based on benzyl alcohol.

Fig. 8. Profile of catalyst recycle.

the alkyl hydroperoxide [38,39]. In order to probe the mechanism of epoxidation in the present system, 50 equivalents of BHT (2,6-di-*t*-butyl-4-methyl phenol) were added as a free radical trap in the oxidation of benzyl alcohol with Cu A and Cu B. BHT is known to scavenge free peroxy radicals and thus suppress the reaction proceeding *via* free radical pathway. From the results compiled in Table 8, it is evident that there is no substantial drop in the yields of oxidation products. Based on this mechanistic probe, it is possible to envisage that the major route for the formation of different products is *via* a heterolytic cleavage of peroxide bond. Nevertheless, further insight is essential to unambiguously establish the nature of active intermediates in these systems.

4. Conclusions

Copper(II) anchored on L-valine bound poly(styrene–divinyl benzene) co-polymer has been shown to catalyze the oxidation of alcohols and alkenes in presence of alkyl hydroperoxide under mild conditions. The catalysts behave in a truly *heterogeneous* manner and can be *recycled* without any loss in selectivity. In addition to the reaction conditions, the nature of amino acid and the stability of its metal complex on the surface of polymer support will determine the formation of active species responsible for product selectivity in oxidation reactions.

Table 8
Effect of free radical trap on oxidation[a] using Cu A and Cu B

Substrate	Additive	Catalyst:additive (mole ratio)	Yield (%)
Benzyl alcohol	BHT	50	26.4 (26.4)[b]
Cyclohexane	BHT	50	12.8 (10.8)

[a] Temperature, 28 °C.
[b] Values in parentheses are for Cu B; solvent, CH$_3$CN (20 ml); oxidant, TBHP (7.5 mmol); time, 24 h; catalyst amount, 0.10 g; substrate, 5 mmol.

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