

Preparation Physicochemical Characterization and Catalytic Applications of Polystyrene Ethylenediamine Tetra Acetic Acid Cu(II) Metal Complex

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Abstract

Chloromethylated styrene-divinylbenzene copolymer beads with 8% crosslink were chemically modified by reaction with Ethylenediaminetetraacetic acid leading to the incorporation of nitrogen as ligating site on the surface of the polymer. The polymeric ligand on treatment with a solution of Copper chloride gave the corresponding metal complex. The polymer supported Cu(II) complex was characterized by elemental analyses, IR, GC-MS, scanning electron micrographs (SEM). The oxidation of various alcohols such as benzyl alcohol, 2-butanol, and 2-propanol was investigated using the supported metal complexes in presence of molecular oxygen as the oxidant. The swelling studies were done by using different solvents. Kinetic data indicate that the catalysts could be recycled without significant degradation of polymer matrix.

Keywords

Synthesis, Polymer Supported Metal Complexes, Oxidation of Alcohols, Molecular Oxygen

1. Introduction

The field of polymer metal complexes as catalysts in organic synthesis has remained active ever, since the first example of catalysis by a polymer linked transition metal compound were reported in 1952 by Sherrington and others have reviewed in detail the various applications of supported catalysts in organic transformations [1]-[3]. It is now well recognized that the advantages derived from the use of functionalized macromolecules are gener-

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ally associated with a simplification of the work-up, easy separation of products from the reaction mixture, recovery and recycling of the catalyst, and the possibility of these catalysts being used in continuous flow systems or in automated synthesis [4] [5]. Polymer supported metal complexes are extensively used as oxidizing agents, reducing agents, photosensitizers, agriculturally and pharmacologically active reagents [6]-[8]. The applications of polymer-metal complexes in the field of catalysis have been widely investigated. Polymer-metal complexes are marked by their use as immobilized reagents which are useful for industrial purposes. Among organic polymer Chloromethylated polystyrene cross linked with divinyl benzene has been the polymer of choice with a wide range of functional groups incorporated in it to bind the metal into the polymer. The basic polymer backbone being chemically inert the polar properties can be modified by controlled functionalization. Polystyrene can be functionalized easily, because it incorporates aryl groups. In polystyrene based system the ability to control the pore size, either through the amount of cross-linking agent or by the choice of a solvent allows some steric selectivity which is not possible in homogeneous system. Oxidation with molecular oxygen catalyzed by transition metal complexes provides an attractive route for the preparation of synthetic intermediates and other oxygen containing organic substrates without the use of environmentally hazardous oxidants [9].

Catalytic oxidation of alcohols by immobilized transition metal complexes continues to remain an area of active research as it offers many opportunities for the design of novel catalysts for the production of fine and specialty chemicals [10]-[12]. The present work reports on the synthesis and characterization of divalent Copper ethylenediaminetetraacetic acid complex which is bound to a moderately cross linked styrene-divinyl benzene polymer. The Complex was found efficient catalyst in the oxidation of various alcohols using molecular oxygen as oxidant [13]-[15]. The effect of Solvent Substrate Temperature and Catalyst Concentration on the rate of reaction was reported. In addition, the effect of various oxidants (Iodosobenzene (PhIO), Tert-Butylhydroperoxide (TBHP), Hydrogen peroxide and Molecular oxygen) on the yield and product selectivity was compared with the present work.

2. Experimental

2.1. Materials

Chloromethylated poly(styrene-divinylbenzene) spherical beads with 8% crosslink were received from Ion-Exchange India Ltd. (Mumbai, India). The commercial resin were pretreated with aqueous dioxane (50:50 v/v) and finally washed with methanol and dried under vacuum at 90°C for 8 hr. Ethylenediaminetetraacetic acid were received from Merck and is used for chemical functionalization. $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ (Merck) benzyl alcohol, 2-propanol, 2-butanol (Merck) were used A.R. grade, dioxane, methanol, acetonitrile, and ethanol were freshly distilled using standard methods Commercial oxygen were purified by passing through copper gauze maintained at 250°C and dried over molecular sieve were used.

2.2. Measurements

Elemental analyses of polymer metal complexes were carried out using a Carlo-Erba Strumentazione micro analyzer. The total Cu content on the polymeric support after loading was estimated using an Optima 4300 DV inductively coupled plasma emission spectrometer (Perkin-Elmer). The chlorine content was estimated gravimetrically by precipitation of chloride as AgCl. The surface area of supports and the Cu-anchored polymer were determined on a Carlo-Erba surface analyzer employing the BET relationship. IR spectra of polymer supported ethylene diamine tetra acetic acid and its metal complexes were recorded on a KBr pellet using Perkin-Elmer 1600 IR Spectrophotometer. Scanning electron micrographs (SEM) of catalysts and supports were taken on a CAMICA SU30 instrument with SE electrode at 20 kV·X-band (9.5 MHz) The analyses of various liquid products obtained in the catalytic oxidation reactions were carried out by Hewlett-Packard gas chromatography (HP 6890) having FID detector, a capillary column (HP-5), with a programmed oven temperature from 50°C to 200°C and a $0.5 \text{ cm}^3 \cdot \text{min}^{-1}$ flow rate of N_2 as a carrier gas. Product identification was also carried on a Finnigan MAT 9001 GCQ-GC/MS system operated in the full scan mode and a quadruple ion trap mass analyzer. The swelling behavior of supported catalysts in representative polar and non-polar solvents were carried out at $30^\circ\text{C} \pm 1^\circ\text{C}$.

2.3. Synthesis of Polymeric Supports

Pre-washed chloromethylated styrene-divinyl benzene copolymer beads (6 g) were allowed to swell in 25 mL

Dioxane for 1hr. An aqueous solution of EDTA (6 g) in 25 mL distilled Methanol was separately prepared. The swollen polymer and the ethylenediamine tetracetic acid solution were refluxed for 24 hr at 80°C. The contents were cooled and kept aside for 3 days with occasional shaking. The color of the beads changed from off-green to pale yellow indicating the attachment of the EDTA. Finally, the EDTA linked polymer beads were filtered, washed with hot water followed by ethanol, and dried under vacuum at 90°C for 8 hr to yield 8 g of product.

2.4. Synthesis of Polymer Supported Metal Complex

The loading of metal on the polymer were carried out as follow: loaded polymer beads (6 g) were kept in contact with ethanol (25 mL) for 45 min. To this add an ethanolic solution (25 mL) of $\text{Cu}(\text{Cl})_2 \cdot 4\text{H}_2\text{O}$ (4 g) the contents were gently agitated on a shaker at constant speed for 24 hr at 80°C (**Figure 1**) [16]. The color of the beads changed from pale yellow to light brown during this period indicating the formation of the metal complex on the polymer matrix at the end of this period, the light brown colored polymer was filtered, washed thoroughly with ethanol, and methanol to ensure the removal of any unreacted metal salt and dried in vacuum for 6 hr at 90°C.

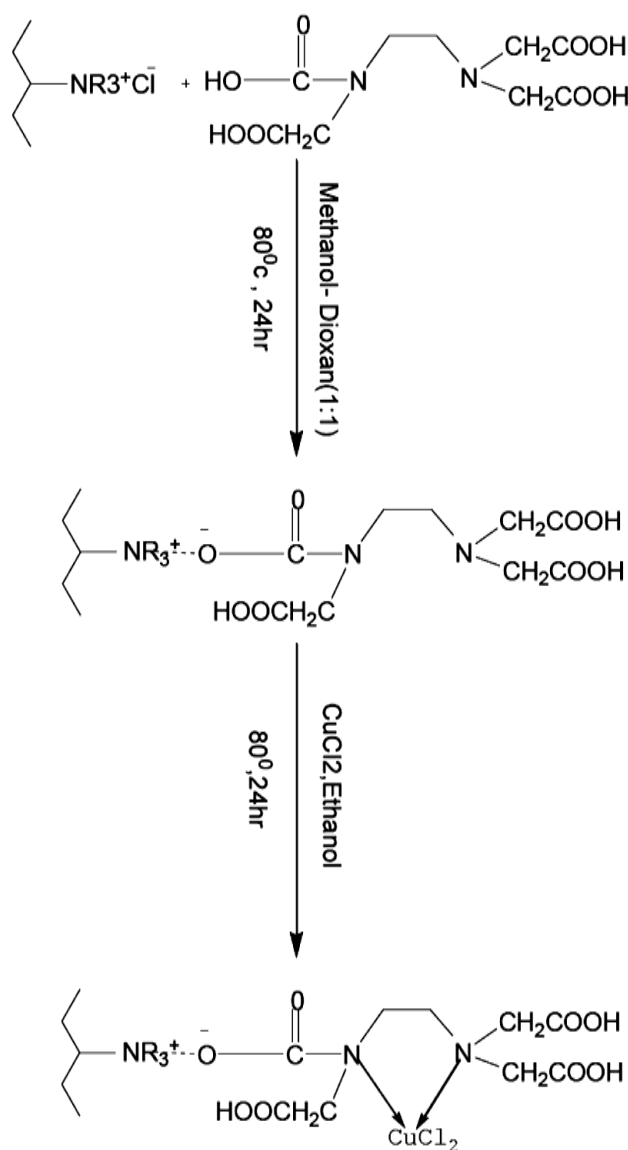


Figure 1. Scheme for the synthesis of polymer EDTA Cu (II) complex.

2.5. Catalytic Oxidation Reaction.

To evaluate the catalytic activity of Polymer Supported Metal catalyst, the oxidation of Propanol, 2Butanol, Benzyl alcohol was conducted in the Presence of oxidant. The oxidation was studied by varying the reaction conditions which included the type of Solvent type of oxidant (H_2O_2 , O_2 , t -BuOOH, Iodosylbenzene (PhO), the temperature ($30^\circ C$ - $90^\circ C$), the reaction time, and the catalyst amount (90 - 150 mg). The catalyst was allowed to swell in the solvent substrate (10 ml) for 20 min. in a round bottom flask. to this was added 10 ml benzyl alcohol, followed by 1atm. of molecular oxidant. The reaction mixture was stirred at the desired temperature. At the end of specific time, the content was analyzed by gas chromatography (GC). The conversion of Alcohols and selectivity for aldehydes and/or ketones was calculated as follows [17].

Conversion% of alcohols = $100 \times [\text{initial}\% - \text{Final}\%] / \text{Initial}\%$

Selectivity% = $100 \times [\text{GC Peak area \% of aldehydes or/Ketones}] \times \text{Peak area of the product}$

A blank experiment was conducted by taking the solvent and the catalyst without the substrate and another without the catalyst.

2.6. Test of Catalyst Leaching from Polymer Support

To Study the metal leaching in the polymer supported catalyst, it was refluxed in a methanol for few hours, then it was filtered and filtrate was treated with substrate and oxidant under the aforementioned reaction conditions.

3. Result and Discussion

3.1. Physical Property of Polymer Supported Metal Complexes

Some of the important physical properties of these polymer-supported catalysts have been measured and the data compiled shows a slightly lower surface area and lower pore volume shown in **Table 1** This result can partly be explained taking into account the fact that with a higher degree of cross linking of poly(S-DVB-EDTA-Cu) The polymer network consists of dense and a relatively larger number of inaccessible domains leading to lower capacity for metal uptake.

3.2. Elemental Analysis of Polymer Supported Catalyst

Elemental analysis of polymer poly (S-DVB-EDTA) shows decreases in the amount of C H and N after introduction of metal The Metal loading on Cu with 8% Cross linking was marginally lower. There is noticeable decrease in the Surface area of polymer 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 modified polymeric Catalysts [18] (**Table 2**).

3.3. High Resolution Scanning Electron Micrograph

SEM at various stages of preparation of the polymer supported EDTA and the Copper complexes were recorded

Table 1. Physical properties of poly(S-DVB) CH_2Cl Cu.

Sample	Surface area ($m^2 \cdot g^{-1}$)	Bulk density ($g \cdot cm^{-3}$)	Pore volume ($cm^3 \cdot g^{-1}$)
8% Poly(S-DVB) CH_2Cl	30.8	0.35	0.16
Cu	20.2	0.44	0.12

Table 2. Analytical data of polymer support ligand and Cu anchored catalyst.

	C%	H%	N%	Cu%
8% Poly(S-DVB) CH_2Cl oxidant yield (%)	68.38	4.62	-	-
8% Poly(S-DVB)EDTA	62.22	4.50	2.23	
Cu	60.5	5.20	2.05	3.40

to understand morphological changes occurring on the surface of the polymer. Scanning was done at a 50 - 100 μ range across the length of the polymer beads. The SEM images of polymer anchored EDTA ligand and immobilized metal complex on modified polystyrene are shown the pure polymer beads have a smooth and flat surface. The introduction of ligand on the surface causes roughening on the surface and the introduction of metal complex causes further roughening on the top of the surface. This may be due to the interaction of metal atoms with the ligands to accommodate the fixed geometry (**Figure 2**).

3.4. IR-Spectroscopy

In order to ascertain the attachment of EDTA and the metal on the polymer support, IR spectra were recorded separately in mid ($400 - 4000 \text{ cm}^{-1}$) the sharp C-Cl peak (due to $-\text{CH}_2\text{Cl}$ group) at 1220 cm^{-1} . In the starting polymer was practically absent or seen as a weak band after introduction of EDTA on the Support. Asymmetric band at 1643 cm^{-1} corresponds COO^- of EDTA Medium intensity band at 1086 cm^{-1} Corresponds to C-N and C-O shows both in support of ligand and the Catalyst. Very weak band in the far IR region ($600 - 650 \text{ cm}^{-1}$) may be due to $\nu \text{ Cu-N}$ vibrations [19]. The intensities of these bands are considerably affected due to lower metal loadings on the support (**Figure 3**).

4. Catalytic Activity for Oxidation

A suitable oxidant is used for catalytic oxidation. Three types of oxidants were tested: *t*-BOOH, H_2O_2 , and PhIO as show in **Table 3**. The oxidation reaction of benzyl alcohol was conducted using a polymer-supported Cu Catalyst. Molecular oxygen is not found more efficient in oxidation reaction as Compared to tert-butyl hydro peroxide (*t*-BuOOH) [20]. This is found to be best in oxidation reactions. The main aim of using Molecular oxygen as oxidant is its better availability, non toxic nature and high catalytic activity in environmentally friendly

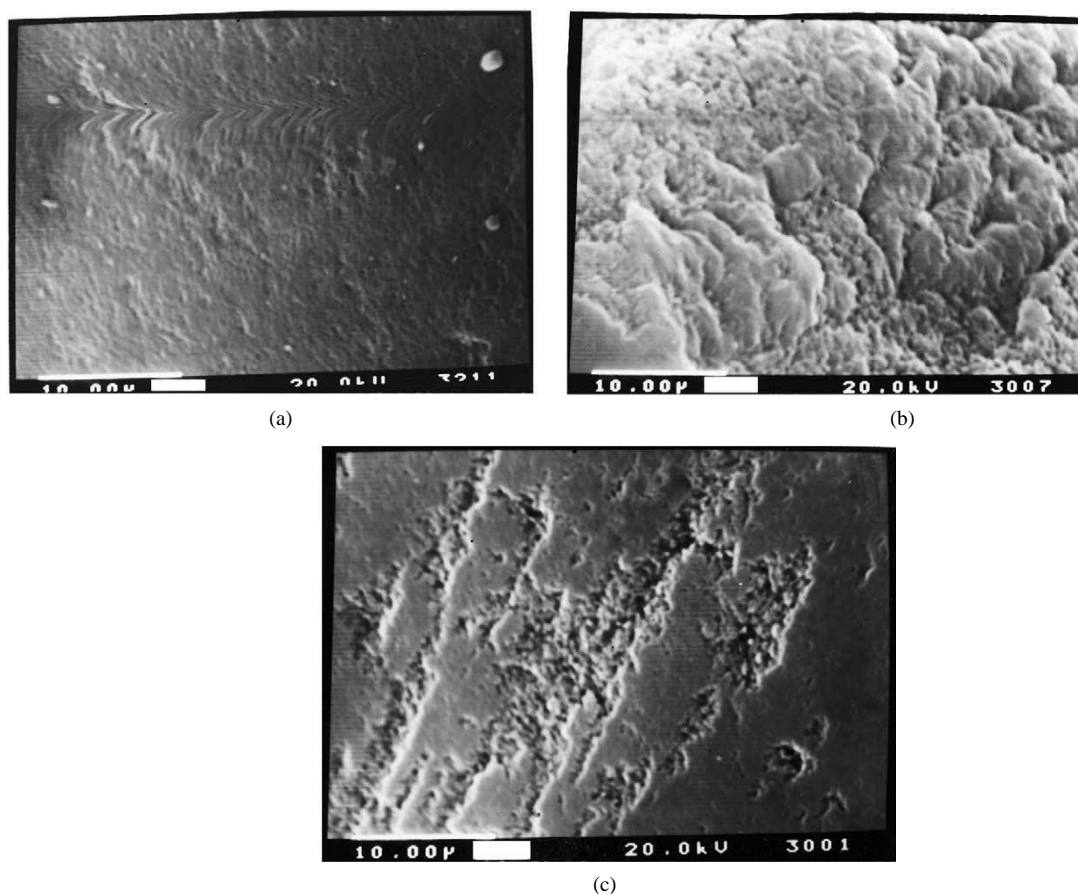


Figure 2. SEM Images of (a) P(S-DVB) CH_2Cl ; (b) P(S-DVB)-EDTA; (c) P(S-DVB)-EDTA Cu complex.

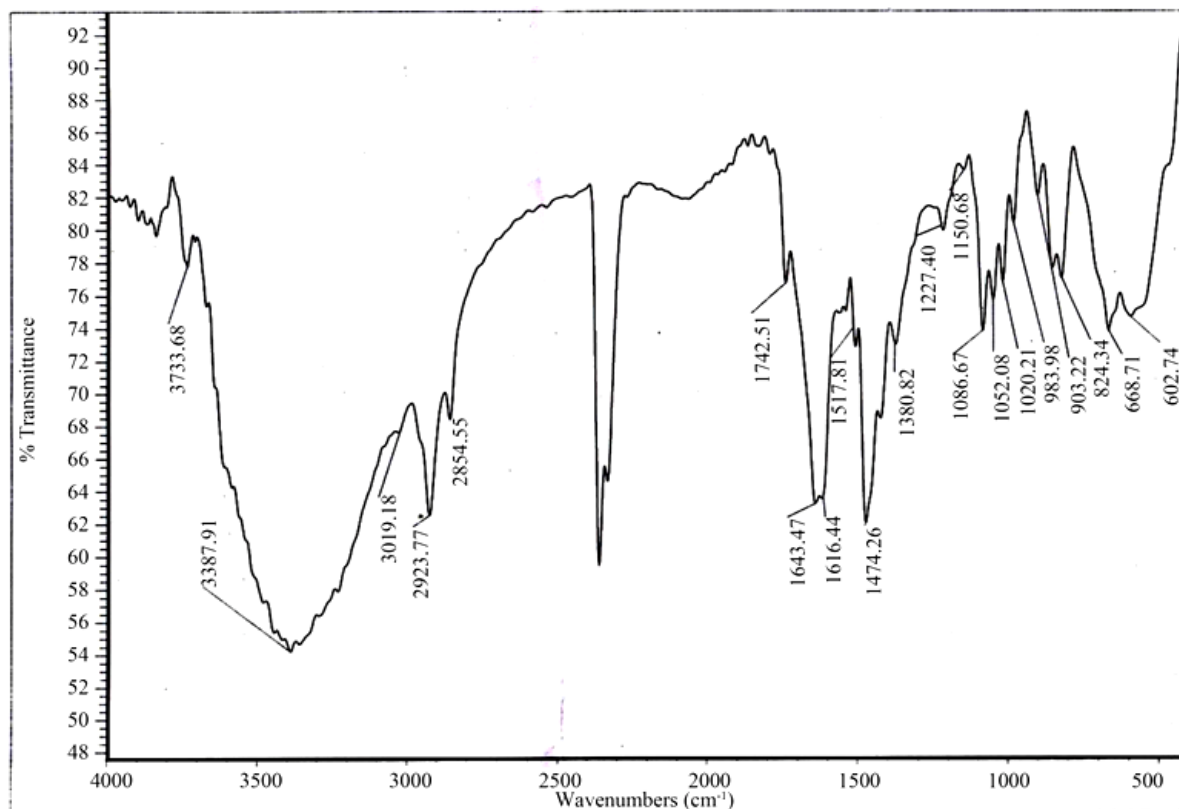


Figure 3. IR spectra of polymer Edta Cu(II) complex.

Table 3. Oxidation of deferent oxidants.

Oxidant	Yield (%)
H ₂ O ₂	15
PhIO	17
t-BuOOH	42

polar medium (Water). The catalytic activity depends upon the type of oxidant and O–O bond strength. The trends are similar to that which was reported previously [21]. To understand the effect of various reaction parameters on catalytic oxidation, a systematic study was performed on the oxidation of propanol, 2-Butanol, Benzyl alcohol as the substrate, using polymer supported Cu(II) Catalyst and molecular oxygen as oxidant. The blank experiment reveals no reaction occurred in the absence of oxidant.

4.1. Effect of Solvent

When oxidation of Propanol, 2-Butanol, and benzaldehyde was performed in different Solvents, the results show that the catalytic activity of Polymer supported Cu catalyst is highest in the presence of polar solvent [22]. This is explained by the fact, that the polymer supported catalyst was highly swelled in polar solvent. So that the substrate and the oxidant can approach easily the active sites of catalyst. Further this may be due to the high dielectric constant and better and better solubility of Substrate (Table 4).

4.2. Effect of Temperature

In regard to the effect of temperature, the experiments showed that product yield increases with increase in the temperature. At 50°C the product yield is 42%. Further increase in the temperature to 90°C the oxidation of

benzyl alcohol decreased, which was due to the decomposition of molecular oxygen (**Table 5**).

4.3. Effect of Catalyst

The Catalytic activity of Cu catalyst was compared using different amounts of catalyst (100 - 180 mg) at 50°C and 6 h. in the absence of solvent. The product yield increased with increase in the amount of catalyst and was maximum at a catalyst amount 150 mg (**Table 6**). Further increase in the amount of catalyst results lowering of yield similar results have been reported [23]. The main reason of this is that the excess of catalyst causes too-rapid decomposition of oxidant before oxidizing the substrate or the mass transfer limitation: It was observed that stirring is difficult when a large amount of catalyst is used.

The Catalytic oxidation of butanol, 2-Propanol and benzyl alcohol was carried out by using Molecular oxygen as oxidant. The oxidation of benzyl alcohol in to Benzylaldehyde occurs in the early stage 6 h. with 42% selectivity where as the oxidation of butanol and Propanol occurs slowly and with less selectivity (**Table 7**). When a reaction is carried out for long time then formation of carboxylic acid occurs. Similar results have been reported on the Catalytic oxidation of olefin and alcohol [24] (**Table 8**).

4.4. Catalyst Recycling

A preliminary study of recycling efficiency of Copper using various alcoholic substrates was done. 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. It can be inferred that the catalyst can be recycled at least about four times. However, there is a progressive loss of activity accompanied by diminished yields this may be due to the leaching of metal in the catalyst [25] Estimation of Cu present in the recycled catalyst after four cycles revealed a lowering in Cu content by about 10% - 20% than that present at the start of the first cycle This partial lowering of Cu values can be due to a minor loss of catalyst during recovery after every run. The activity profile for four successive cycles is shown in **Table 9**.

5. Conclusion

Copper(II) anchored on EDTA bound poly(styrene-divinylbenzene) has been successfully prepared and used

Table 4. Swelling data of Cu in different solvents (mol %).

Solvents	8% poly(S-DVB)CH ₂ Cl	Cu
Acetonitrile	2.99	2.40
Benzene	1.04	0.65
Dichloromethane	1.46	1.00
Ethanol	1.68	1.35
Methanol	2.70	2.37
Toluene	1.05	0.70
THF	1.40	0.99

Table 5. Effect of temperature.

Catalyst (mg)	Temperature (°C)	Time (h)	Solvent	Yield (%)
150	30	6		33
150	50	6		42
150	70	6		35
150	90	6		40

Reaction Conditions: 5 ml Acetonitrile, 1 atm. O₂, Yield based on the Substrate that is taken.

Table 6. Effect of catalyst amount.

Catalyst (mg)	Temperature (°C)	Time (h)	Solvent	Yield (%)
90	50	6		33
120	50	6		36
150	50	6		42
180	50	6		39

Reaction Conditions: 5 ml Acetonitrile 1 Atm. O₂, Yield based upon Substrate that is taken.

Table 7. Catalytic oxidation of deferent alcoholic substrates.

Time (h.)	Substrate	Product	Yield	Selectivity
6	Propanol	Propanone	13	25
6	Butanol	Butanal	14	35
6	Benzylalcohol	Benzaldehyde	42	42

Reaction Conditions: Catalyst 150 mg, Solvent Methanol: Acetonitrile (1:1) Temperature 50°C.

Table 8. Effect of various oxidants on the rate of conversion and product selectivity.

Entry	Substrate	Conversion	Product(Selectivity)	Reference	Catalyst/oxidant
1	Styrene ^a	95	Benzaldehyde (93) Acetophenone (7)	20	PolymeranchoredNi(II)/TBHP
2	Styrene ^b	14	Benzaldehyde (23)	20	Polymer anchored NI(II)/Mol. O ₂
3	Benzylalcohol ^c	21 63	Benzaldehyde (25) Benzoicacid (75)	25	Ru Catalyst/TBHP
4	Benzylalcohol ^d	50	Benzaldehyde (100)	25	Co Catalyst/TBHP
5	Benzylalcohol ^e	14	Benzaldehyde (42)	This Work	Cu(II)/Mol.O ₂

Reaction Conndtions: Catalyst 150 mg, Substrate 10 mmol, 1 Atm. O₂, Temperature 50°C. Entry5.

Table 9. Recycling study of polymer supported Cu(II) complex (Benzyl alcohol) substrate.

Cycle no	Aldehyde (Conversion %)
1	42
2	37.50
3	34.6
4	31.1
5	33.8

Conditions: Catalyst 150 mg, Temperature 50°C, Solvent Methanol 10 ml, Substrate 10 ml Benzylalcohol. Pressure 1 Atm. O₂, Time 20 min.

to catalyze the oxidation of alcohols in presence of molecular oxygen under mild conditions. The activity and selectivity of the catalyst were dependent on the experimental conditions, solvent, reaction time, and reaction temperature. The catalysts can be recycled without any loss in selectivity. Slow deactivation of the catalysts was observed over extended reuse.

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