

Preparation Physico-Chemical Characterization and Catalytic applications of Polymer anchored Dimethylglyoxime Copper (II) Metal Complex

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ABSTRACT

Oxidation of 1-Propanol, 1-butanol 1-Hexanol and benzyl alcohol using chloromethylated polystyrene (6% Cross link) DMG (Dimethylglyoxime) copper complex or Poly(S-DVB)-DMG-M Where M= Cu) as catalyst and tert.butylhydroperoxide(TBHP) as oxidant, was studied. The polymer supported Cu Complex was characterized by some physicochemical and spectroscopic methods like elemental analysis IR Scanning electron micrographs (SEM). In the oxidation of 1-propanol, 1-butanol, 1-hexanol and benzyl alcohol. It was found that Product yield of these alcohols corresponding the order 1-Butanol >1-hexanol >Benzylaldehyde > 1-Propanone. Kinetic data indicates that catalyst could be recycled without significant degradation of polymer matrix

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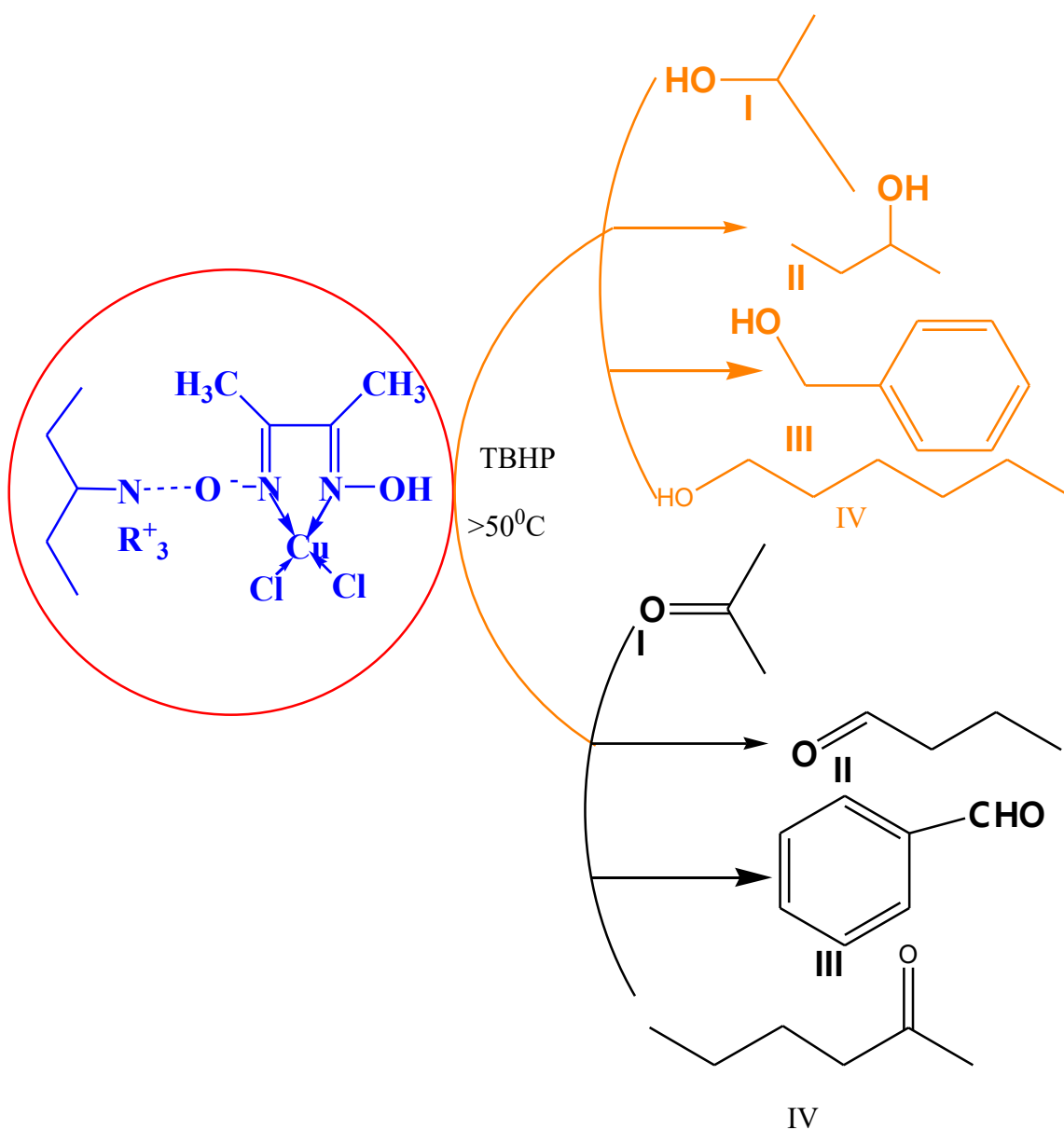
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Graphical abstract



Introduction :

Oxidation of alcohols in to aldehydes is a pivotal reaction in the organic synthesis both for fundamental research and industrial manufacturing. ¹⁻³ The oxidation of alcohols in to adehydes is an important and useful reaction in both chemical and pharmaceutical industries now, from both economic and environmental points of view, much attention has recently been focused on the aerobic catalytic oxidation of alcohols to oxygenic compounds using metal catalysts.

Transition metal complexes are widely used in homogeneous and heterogeneous catalytic oxidations of different alkenes, alkynes, alcohols, halides, phenols etc in the recent past; there has been an increasing interest in developing environmental friendly greener processes, which are also economically viable. ⁴⁻⁶ Homogeneous transition metal catalyst systems suffer from a major drawback of the catalyst recovery and/or reuse affecting the overall economics of the process in the past few decades; there have been significant developments in the application of heterogeneous catalysts for the industrial production of organic chemicals. Heterogeneous catalysts, which are widely used in industry, have good thermal stability, can be easily separated from the reaction mixture and can be often regenerated and reused. Therefore, heterogenizing of a homogeneous metal complex by supporting it on an insoluble support has attracted a lot of interest as a suitable method for solving many practical problems including recovery of the catalyst from reaction mixture and recycling. of the catalyst, and the possibility of these catalysts being used in continuous flow systems or in automated synthesis. ⁷⁻⁹

Among organic polymers polystyrene has been extensively used as a support with a wide range of functional groups incorporated in it to bind the metal into the polymer. ¹⁰ 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 Stericselectivity which is not possible in homogeneous system. ¹¹⁻¹³ Oxidation with tert-butylhydroperoxide catalyzed by transition metal

complexes provides an attractive route for the preparation of synthetic intermediates and other oxygen containing organic substrates. ¹⁴ 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. The present work reports on the synthesis and characterization of divalent Copper complexes with DMG bound to a moderately cross linked styrene-divinyl benzene polymer (6%). In addition, a preliminary study of Catalytic activity of the newly synthesized polymer supported DMG Cu complexes towards oxidation of alcohols was undertaken. The effect of various physical parameters like Temperature, Catalyst amount, effect of Solvent and Substrate was also investigated.

Experimental:

Materials:

Chloromethylated polies (styrene divinylbenzene) as spherical beads with 6% crosslink were received from Ion-Exchange India Ltd. (Mumbai, India). The commercial resin was pretreated with aqueous dioxane (50:50 v/v) and finally washed with methanol and dried under vacuum at 60°C for 8 hr before using for chemical functionalization. All the solvents like methanol, ethanol, dioxane, were supplied by Aldrich and purified by standard methods. The substrates 1-butanol, 1-propanol, 1-Hexanol, benzyl alcohol and TBHP (70% aqueous solution) were supplied by Aldrich and purified by standard methods. CuCl₂.3H₂O supplied by Fischer was used as such. DMG the analar grade sample supplied by Merck were used as such.

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 4300DV inductively coupled plasma emission spectrometer (Perkin-Elmer). The surface area of supports and the Cu-anchored polymer was determined on a Carlo-Erba surface analyzer employing the BET relationship. IR spectra of polymer supported Cu-complexes was recorded on Perkin Elmer. The surface morphology of

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polystyrene DMG and the complexes were observed using a scanning electron microscope of model SEM-JSM 6390 at an accelerating voltage of 18kV with a magnification range of 5KX at liquid nitrogen temperature. 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 to 200 °C and a 0.5cm³min⁻¹ low rate of N₂ as a carrier gas.

Synthesis of Polymeric Support:

Pre-washed chloromethylated styrene-divinyl benzene copolymer beads (4g) were allowed to swell in 25mL methanol for 1hr. An aqueous solution of DMG (4g) in 25mL dioxane was separately prepared. The swollen polymer in methanol and the DMG in dioxane were refluxed for 24hr. The contents were cooled and kept aside for 5hr with occasional shaking. The color of the beads changed from off-light orange to pale yellow indicating the attachment of the DMG. Finally, the DMG linked polymer beads were filtered, washed with hot water followed by ethanol, and dried under vacuum at 80°C for 24 hr to yield 6g of product.

Synthesis of polymer support metal complex:

The loading of metal on the polymer was carried out as follows: liganded polymer beads (12.5g) were kept in contact with ethanol (50mL) for 45min. To this was added an ethanol solution (50mL) of CuCl₂.5H₂O gently agitated on a shaker at constant speed for 24hr at 80°C. 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. The interaction between Metal and polymer is electrostatic¹⁵ at the end of this period, the light brown colored polymer were filtered, washed thoroughly with ethanol, and methanol to ensure the removal of any unreacted metal Chloride and dried in vacuum for 6 hr at 60°C. Fig 1.

Oxidation Procedure and Products Analysis:

The catalytic activity of Polymer Supported Metal catalyst, for the oxidation of 1-Propanol, 1-Hexano, 1-Butanol and Benzyl alcohol was conducted in the presence of oxidant tert-butylhydroperoxide (TBHP). The oxidation was studied by varying the reaction conditions which included the type of Solvent, temperature (30-

90°C), the reaction time, and the catalyst amount (0.01 - 90mg). The catalyst was allowed to swell in the solvent substrate (10ml) for 20min. in a round bottom flask. To this was added 10ml 1-butanol, followed by 1mmol of 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 blank experiments were also run individually without catalyst and oxidant in both the cases no oxidized product was formed which means reaction did not take place.

Result and discussion:

Physical property of polymer metal complex:

Some of the important physical properties of these polymer-supported catalysts have been measured and the data compiled in Table 1. Cu 6% crosslink has high surface area and pore volume. Thus higher metal loading on Cu 6% crosslink (Cu 0.9%) were observed. This result can partly be explained taking into account the fact that with a lower degree of cross linking the polymer network consists of clear and a relatively high number of accessible domains leading to higher capacity for metal uptake.

Elemental analysis of polymer metal complexes:

Elemental analysis of polymer metal catalyst shows decreases in the amount of C, H and Cl but increase amount of N by the incorporation of ligand DMG. The introduction of metal results in the decrease in the amount of C and decrease in the amount of H. Table 2

IR Spectra of polymer metal complex:

In order to ascertain the attachment of ligand and the metal on the polymer support, IR spectra were recorded separately in mid (4000–400cm⁻¹) and far IR (600–30cm⁻¹) regions at different stages of synthesis. The sharp C–Cl peak (due to –CH₂Cl group) at 1220–1240cm⁻¹ in the starting polymer was practically absent or seen as a weak band after introduction of ligand on the support. A strong band at 3420cm⁻¹ in poly (S-DVB). Medium intensity band due to C–N stretching appears at 1090cm⁻¹ both in the supported ligand and the catalysts¹⁶. The N–Cu band occurs at around 450cm⁻¹. A slight shift in the –NOH stretching of

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Figure 1

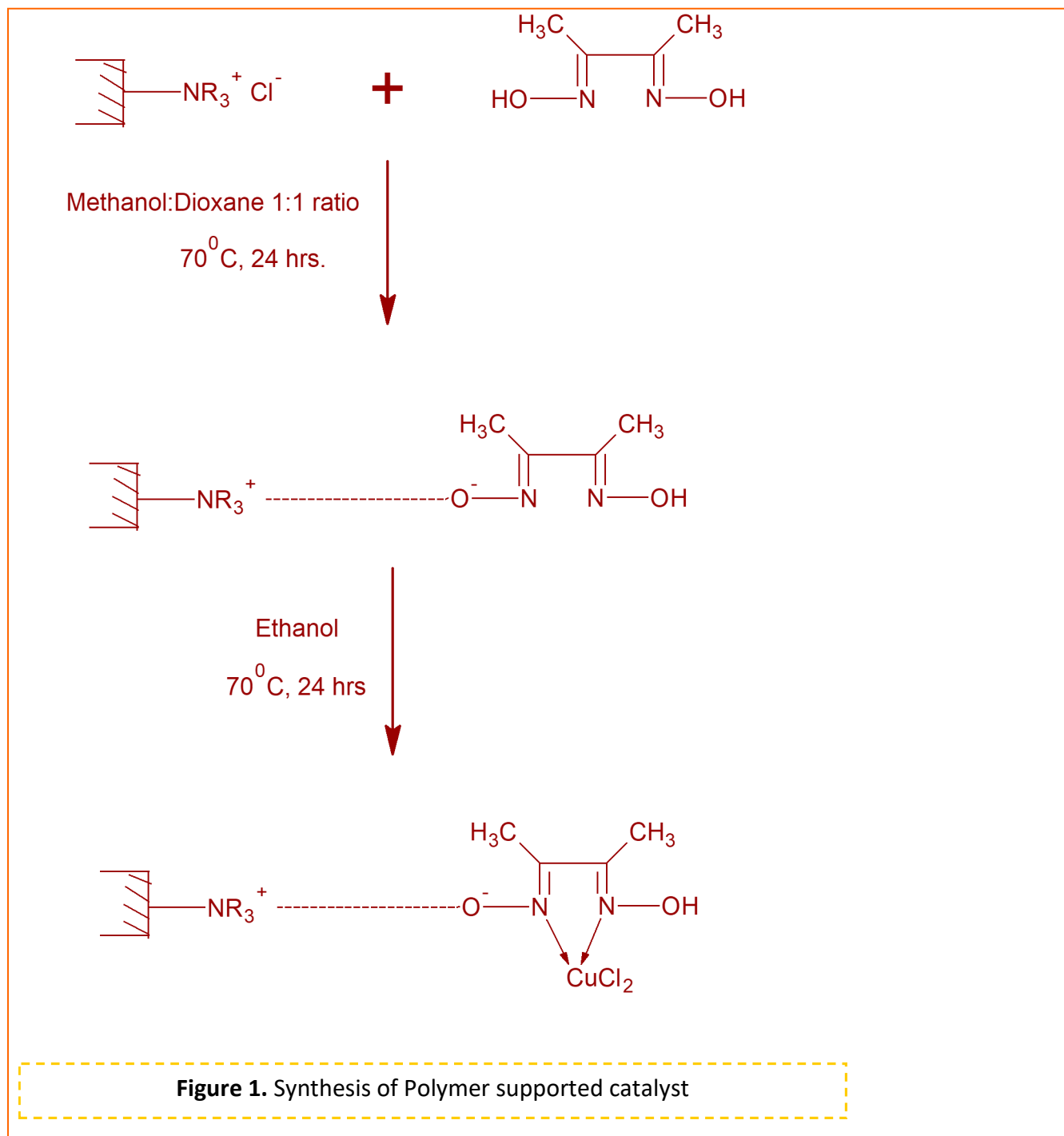


Table 1. Physical properties of Cu -supported poly (S-DVB) catalysts

Sample	Surface area (m ² g ⁻¹)	Bulk Density (gcm ⁻³)	Pore volume (cm ³ g ⁻¹)
6%Poly(S-DVB)CH ₂ Cl	40.00	0.39	0.30
Cu	35.2	0.44	0.21

Dimethylglyoxime Band occurs which is due to the coordination of "N" of DMG to the metal. IR spectra of polymer supports catalyst are shown in fig. 2.

High resolution Scanning Microscope:

HR SEM at various stages of preparation of the polymer supported ligand and the copper complexes were recorded to understand morphological changes occurring on the surface of the polymer. Scanning was done at a 50–500 μ range across the length of the polymer beads. Comparison of images taken at $\sim 2 \times 10^2$ magnification showed that the smooth spherical surface of the starting poly (S-DVB) is distinctly altered, exhibiting three dimensional uneven roughing on the top layer upon anchoring of the DMG. After metal incorporation, more randomly oriented rough depositions occurs on the outer

TBHP as an oxidant. The results clearly show the effect of temperature catalyst amount and the choice of solvent effects the product yield. The blank experiment shows no reaction occurs in the absence of oxidant

Effect of Solvent:

Solvent plays an important role in the yield and product distribution of oxidation reactions. In order to study the effect of solvent, various solvents were employed. The oxidation reactions of alcohols (1mmol) TBHP as oxidant at 50^oC Keeping other parameters constant. The oxidation was carried out with some polar and non polar solvents.¹⁷The selected solvent should possess the Property like stability and solubility in substrate and solvent. The quantitative yield is shown by polar solvents as compared to non polar solvents .The

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

	C%	H%	N%	Cu%
6%Poly(S-DVB)CH ₂ Cl	78.38	8.62	n.d	n.d
6%Poly(S-DVB)DMG	70.22	6.80	3.33	0.93
Cu	65.5	5.80	n.d	1.75

surface of the resin were seen. Fig 3.

Catalytic activity for oxidation:

Catalytic oxidation of Polymer supported Cu(II) was performed using TBHP as oxidant the results are shown below in table.3 Using the TBHP as oxidant gives highest yield as compared to Molecular oxygen, Hydrogen peroxide and PhIO. This is due to the reason that in TBHP the O-O bond strength is weak This trend is similar to that which was reported early.¹⁸

To understand the effect of various reaction parameters on catalytic oxidation. A systematic study on oxidation of 1-butanol, 1-propanol, 1-hexanol, benzylalcohol as the substrates using polymer supported Cu (II) complex and

efficiency of catalyst for oxidation of alcohols in different solvents decreases from more polar solvent to less polar solvent. The higher yield of polar solvents is because of their high dielectric constant and better solubility of substrate. Table 4

Effect of temperature:

The experiment shows that with increase in the temperature the product yield increases and it is maximum for 1-Butanol at 50^oC and after that it decreases. This is due to the decomposition of oxidant. 1-butanol gives 100% product yield. Table 5

Effect of Catalyst:

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Fig.2. FT-IR Spectra of Polymer anchored metal complexes

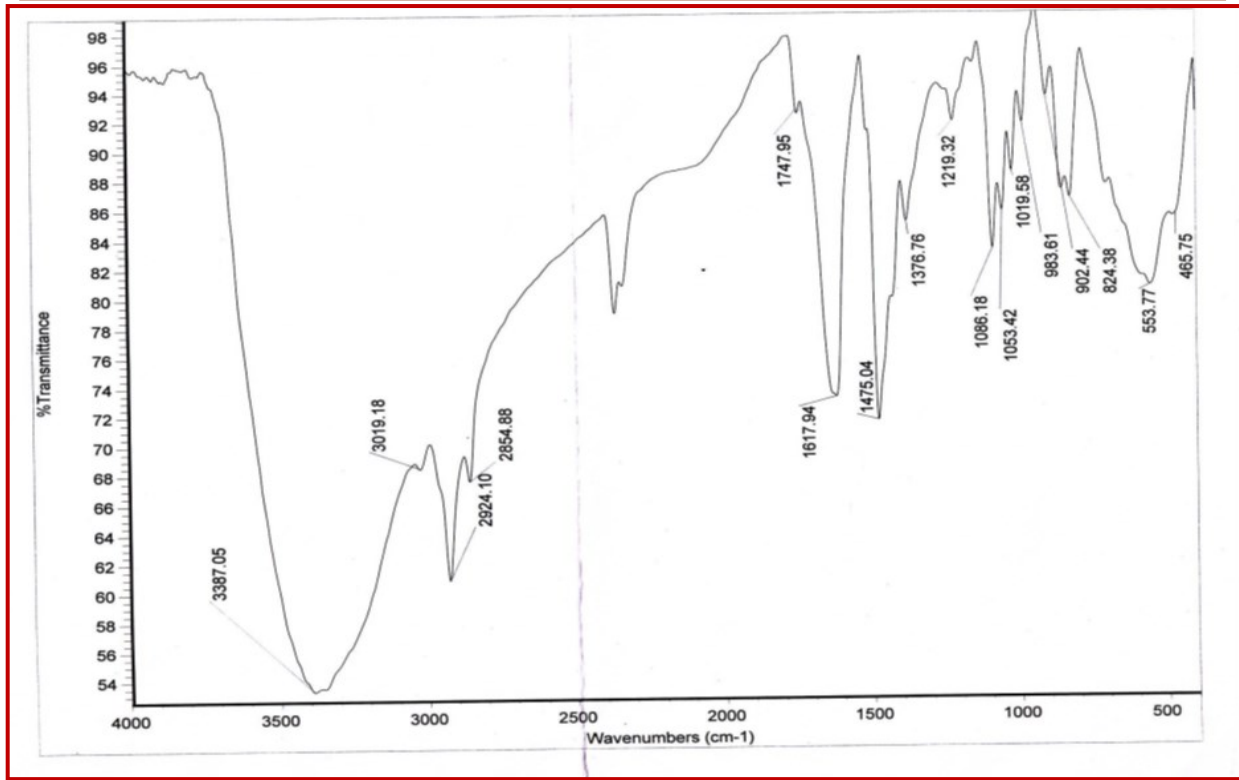


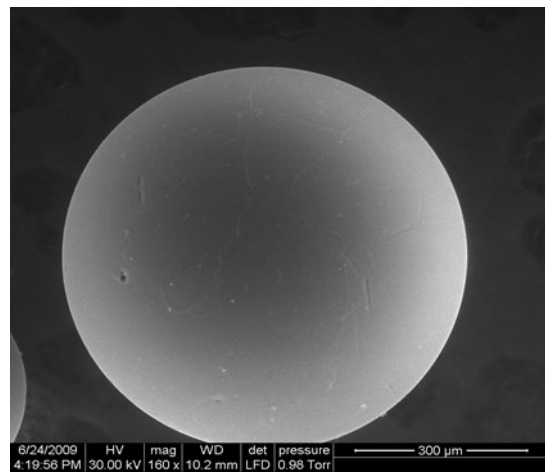
Fig.3. SEM images of

(a) Poly(S-DVB-)

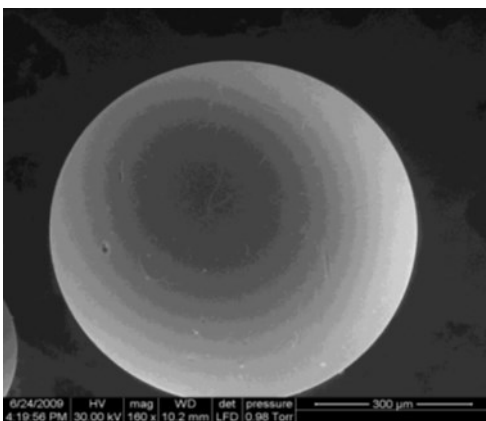
(b) Poly(S-DVB-DMG)

(c) Poly(S-DVB-DMG-Cu) Complex

(b)



(a)



(c)

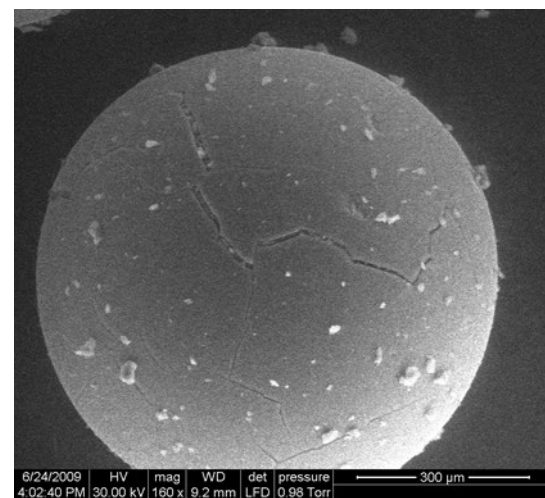


Table 3. Conversion percentage of alcoholic substrates in the metal complexes catalyzed oxidation reaction

Catalyst	Substrate	Time (hr)	Conversion (%) Alcohols into aldehyde	Yield
Poly[S-DVB-DMG Cu]	1-Propanol	3/6	65/85	80
	1-Butanol	3/6	70/100	100
	1-Hexanol	3/6	68//82	90
	Benzyl alcohol	3/6	70/90	88

Conditions: Where 70/100 represents 3 and 6 hr ; 90mg catalyst, 5mmol substrate, 1mmol. TBHP , 10ml methanol, $\geq 50^{\circ}\text{C}$.

Table 5. Effect of Temperature

Catalyst (mg)	Temperature ($^{\circ}\text{C}$)	Time (h)	Solvent	Yield (%)
90	30	6		78
90	50	6		100
90	70	6		92
90	90	6		87

Reaction Conditions: 10Methanol, 1mmol TBHP , Yield based on the Substrate that is taken

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

Solvents	6%poly(S-DVB)CH ₂ Cl	Cu
DMF	2.00	2.20
Acetic acid	1.20	1.30
Dichloromethane	1.16	1.10
Diethyl ether	1.10	1.25
Chloroform,	1.0319	1.05
Water	1.30	1.80
Pentane	0.88	0.99

The catalytic activity of polymer supported Cu(II) was compared using different amounts of catalyst (30mg-120mg) at 50°C and 6hr in the absence of solvent. The product yield increases with increases in the amount of catalyst and it was maximum at a catalyst amount of 90mg. Further increase in the amount of catalyst results in the decrease in the product yield. Similar results have also been reported.¹⁹⁻²⁰ One explanation might be the excess amount of catalyst causing a 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 was used. Table 6

Reusability of Poly [S-DMG -Cu] complex.

An important advantage of polymer supported metal catalysts is its reusability. The complex can be removed by simple filtration upon completion of the reaction and can be used several times without loss of its catalytic activity.²⁰ The same catalyst was re-used for seven subsequent catalytic oxidation of various alcoholic substrates the conversion of different alcoholic substrates was illustrated in table.7

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Table 6. Effect of Catalyst amount

Catalyst (mg)	Temperature (°C)	Time (h)	Solvent	Yield (%)
30	50	6		90
60	50	6		88
90	50	6		100
120	50	6		85

Reaction Conditions: 10ml methanol 1mmolTBHP₂, Yield based upon Substrate that is taken

(TBHP) as an oxidant resulted in higher product yield, in comparison to using H₂O₂ and iodobenzene under the same reaction conditions. It is found that catalyst is recyclable up to four cycles. After that decreases in rate was observed which may be due to leaching of the metal ion. The activity and selectivity of the catalysts was dependent on the experimental conditions, solvent, reaction time, and reaction temperature.

The conversion of alcoholic substrates is not much affected until fourth catalytic run without affecting the selectivity of the corresponding products. But when we extend the reaction cycle (from the fifth to seventh) further, the activity of the complex decreases and reaches the lowest value for the seventh run. This significant change in the catalytic activity of the [PS-DMG-Cu] complex may be due to the poor chemical resistance and mechanical strength of polystyrene

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Table 7. Recycling study of Cu (1-Butanol)

Conditions: 90mg, 5mmol1-butanol,

Cycle no	Aldehyde (yield %)
1	100
2	92
3	86
4	77

1mmolTBHP, 10ml methanol (Solvent), Time 6hr. Temperature 50°C.

polymeric backbone which provides the heterogeneity to the complex. Therefore, we can use this studied complex for alcoholic substrate oxidation reaction till four cycles without major loss of its catalytic activity.

Conclusion:

Copper (II) anchored on DMG bound poly (styrene-divinylbenzene) has been shown to catalyze the oxidation of various alcohols in the presence of tert-butylhydroperoxide as oxidant The catalytic activity of the polymer-supported metal catalysts was tested for oxidation of alcohols (1-Propanol, 1-Butanol, 1-hexanol and benzyl alcohol). The use of tert-butylhydroperoxide

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