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Synthesis, Surface Morphological Studies and Biological Application of Polymer Supported Metal Complex

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ABSTRACT

The polymer supported Cu metal Complex was characterized by some physicochemical and spectroscopic methods like elemental analysis Scanning electron micrographs (SEM) and Energy dispersion spectra (EDS). The complex was tested for their antimicrobial activity against bacteria and fungi. The anti- microbial activity was determined in Mueller Hinton media (M H Media).

Keywords: Chloromethylated polystyrene, energy dispersion spectra, Antimicrobial activity.

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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 aldehydes 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**3**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 [11-13]. 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]

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%). [14-16] In addition,

a preliminary study of Catalytic activity of the newly synthesized polymer supported DMG Cu complexes towards oxidation of alcohols was undertaken.

MATERIALS AND METHOD

Materials

Chloromethylated poly (styrene divinylbenzene) as spherical beads with 6% crosslink was 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 2-butanol, 2-propanol and benzyl alcohol 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 CarloErba Strumentazione micro analyzer. The total Cu content on the polymeric support after loading was estimated using Optima 4300DV 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 was determined on a Carlo-Erba surface analyzer employing the BET relationship.IR spectra of polymer supported Cu-complexes at various stages of synthesis were 5recorded on Perkin Elmer. The surface morphology of 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−1low rate of N2 as a carrier gas. The swelling behavior of supported catalysts in representative polar and non-polar solvents was carried out at 25C±1C

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 at800C.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 Yellowish colored polymer were filtered, washed thoroughly with ethanol, and methanol to ensure the removal of any unreached metal Chloride and dried in vacuum for 6hr at 60C.

RESULTS 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%) was 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

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 50–500µ range across the length of the polymer beads. Comparison of images taken at 2×102 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 surface of the resin were seen. Figure 1

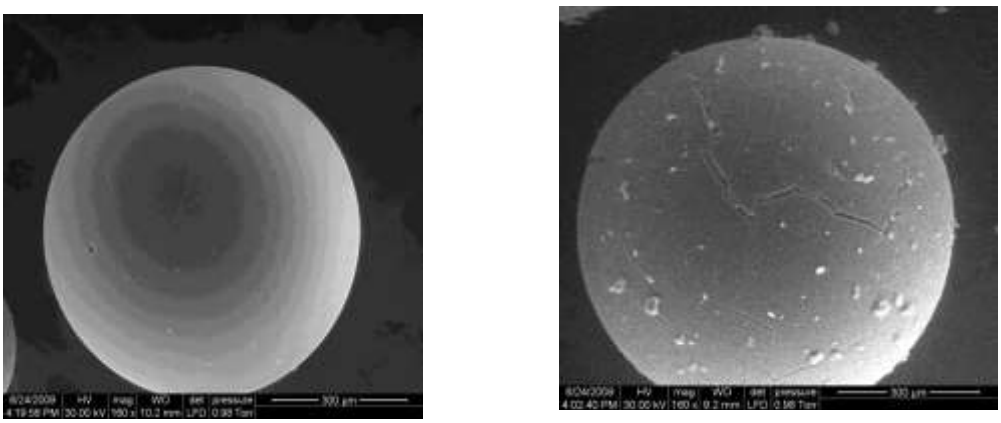

Figure 1: SEM images of polymer supported metal complexes before and after the interaction

Energy dispersion x-rays

Energy Dispersive X-ray Spectroscopy (EDS) is a qualitative and quantitative X-ray technique that can provide information on the chemical composition of a sample. An electron beam is focused on the sample in either a scanning electron microscope (SEM)The electrons from the primary beam penetrate the sample and interact with the atoms from which it is made [18] .The X-rays are detected by an Energy Dispersive detector which displays the signal as a Energies of the Characteristic X-rays allow the elements making up the sample to be identified, while the intensities of the Characteristic X-ray peaks allow the concentrations of the elements to be quantified. EDS is considered a non-destructive analytical technique, that is, the sample can be re-analyzed many times. The range of EDS0.1-0.5 wt%.Energy dispersion x rays shows metal content along C and O suggesting formation of metal complex with the anchored ligand at various sites. Figure 3 the attachment on the polymer matrix is conformed from these SEM images and EDX data. Figure 1.

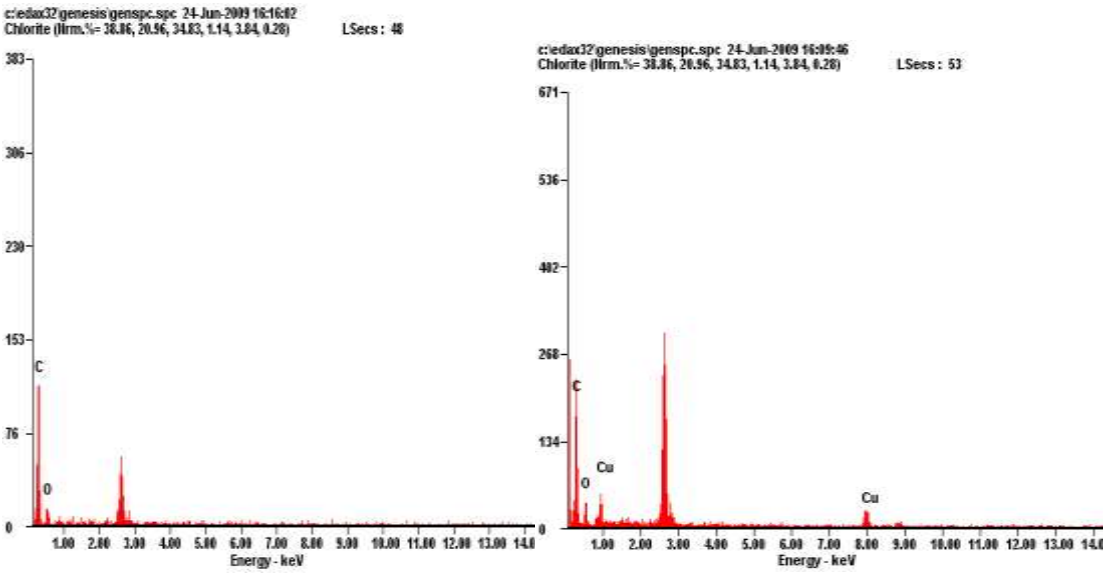

Figure 2: EDX images of polymer supported metal complexes before and after complexation

Antimicrobial Studies:

The complexes had been tested for their antibacterial activity against Pseudomonas aeruginosa, Proteus vulgaris, Proteus mirabilis, Klebsiella pneumonia and Staphylococcus aureus. Cu (II)complexes with base ligands. The complex were screened for antimicrobial activities against the bacteria Staphylococcus aureus, Escherichia coli and fungi Candida albicans . The in vitro biological screening effects of the investigated compounds were tested against the bacteria, Klebsiella pneumonie and salmonella typhi and fungi. Stock solutions of 2 mg of the complexes were dissolved in 1ml distilled water while 2 mg of the compound Cu-complex was dissolved in1ml DMSO. Serial dilution of the compounds were prepared in sterile distilled water to determine the minimum inhibitory concentration (MIC) .Different dilution of the stock solution were applied on the 10mm diameter sterile disc .The discs were placed on a incubator for 3 days .Antibacterial and antifungal potential of the complexes were assessed in terms of zone of inhibition of bacterial and fungal growth in Table 1-3.

Table 1: Determination of MIC for antibacterial and antifungal activity of the Co-complex

Micro-organism	2.0 mg/ml	1.7 mg/ml	1.5 mg/ml	1.2 mg/ml	1.0 mg/ml	0.7 mg/ml	0.5 mg/ml	0.1 mg/ml
S. typhi	-	-	-	-	+	+	+	+
K. pneu- monie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

Table 2: Determination of MIC for antibacterial and antifungal activity of the Cu-complex

Micro-organism	2.0 mg/ml	1.7 mg/ml	1.5 mg/ml	1.2 mg/ml	1.0 mg/ml	0.7 mg/ml	0.5 mg/ml	0.1 mg/ml
S. typhi	-	-	-	-	-	+	+	+
K. pneu-monie	-	-	-	-	-	+	+	+
Fungi	-	-	-	-	-	+	+	+

Table 3.Antibacterial and antifungal activity of the complexes: MIC values

Micro-organism	Complex	MIC value
Bacteria	Cu-complex	1.0mg/ml
Fungi	Do	1.0mg/ml

CONCLUSION

In this paper we synthesized the polymer ligand metal complex. The complex was characterized by different spectra chemical processes like SEM, EDX and some surface physical properties.. The antimicrobial studies carried out with the complex confirm that they are good antibacterial and antifungal agents with their MIC values.

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