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Short Communication

Preparation Characterisation and Catalytic Oxidation of Alcohols using Polymer Supported Cu (II) Metal Complex

Imtiyaz Rasool Parrey, Athar adil Hashmi*
Department of chemistry,
Jamia Millia Islamia (A Central university)
New Delhi-110025, INDIA

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**: Correspondence: dr.ahashmi@yahoo.co.in.: Tel: 0091-11-26981717 Ext.3269*

Abstract

A new polymeric ligand (L) was synthesized by the Michael addition of ethylenediamine to methyl methacrylate. The prepared ligand was complexed with Cu (II) ions, The ligand and its complex were characterized by elemental analysis and spectroscopic studies (FT-IR, UV-Vis, 1H NMR and ESI-MS). Square pyramidal geometry was proposed for copper complexes, on the basis of UV-Vis spectroscopic data and molar conductance measurements. The catalytic application of ligand metal complex was recorded for the oxidation of cyclohexanol, benzyl alcohol, 1-phenyethanol, propanol, respectively andeco-friendly, nontoxic hydrogen peroxide.

Keywords: Polymeric ligand, copper complexes, Catalytic oxidation, Hydrogen peroxide, Oxidant.

Introduction:

Ideally, dendrites are perfect mono disperse macromolecules with a regular and highly branched three-dimensional architecture. Dendrites are produced in an iterative sequence of reaction steps, in which each additionalitelation leads to a higher generation material. The divergent method, first reported by Vögtle is based on the successive attachment of branching units to the core molecule [5]. As a result of this growth, each subsequent reaction is characterized by the generation of an exponentially increasing number of functional groups on the periphery, so that a large spherical molecule is formed. This is analogous to the burst of exploding firework. In contrast, the convergent approach involves the synthesis of dendrimeric fragments followed by their subsequent addition to the core. This method was initially described by Hawker and Frechet [6]. The synthesis of dendrimers offers the opportunity to generate monodisperse, structure controlled macromolecular architectures [7-9]. Phosphorus containing dendrimers benefit from the global interest in dendrimers, but they have also their own specificities and properties [10]. Recently, a synthesis has been developed and the properties of phosphorus containing dendrimers has been investigated

There are some reports regarding the diverse applications of polymeric ligands they include encapsulation and solubilisation, medicinal and bio mimetic applications, novel materials, and catalysis [10].

2. Experimental

2.1 Materials and Methods

All the chemicals were of AR Grades and used without further purification. Ethylenediamine and methylmethacrylate were purchased from S.D. Fine Chem. Ltd., Mumbai, India. Metal chlorides ($CuCl_2.2H_2O$ and $CoCl_2.6H_2O$) and methanol were procured from E. Merck, Mumbai, India.

The percentages of C, H and N were determined by a Vario EL elemental analyzer. Electronic spectra were recorded on a Perkin Elmer Lambda- 40, double-beam UV-Visible spectrophotometer. FTIR spectra of the compounds were recorded on Perkin Elmer 1750 FTIR spectrophotometer (CT 06859 USA) using KBr pellets in the range of 4000-400 cm-1. 1H NMR Spectra were achieved with a Bruker (DRX-400) spectrometer. Mass spectra were recorded using Model-Q-TOF Micro mass ESI source. Molar conductance measurements were carried out on Decibel conductivity meter at room temperature (DB-1038). Melting points were determined on Veego instrument (Model REC-2203882). In the case of benzyl alcohol, the formation of benzyl aldehyde was detected using GC-MS/MS [Varian GC-MS-Saturn 2200, Thermo capillary column – VF5MS (5% phenyl-95% methyl polysiloxane), 30m length, 0.25 mm internal diameter, 0.25 μm film thickness, temperature of column ranges from 50 to 280°C (10°C/min) and injector temperature 250°C.

2.2 Synthesis of Ligand (L)

Ethylenediamine (0.1 mol) and methylmethacrylate (0.4 mol) in methanol were mixed together in a round bottom flask and stirred for 24 h at room temperature. Further, ethylenediamine (0.04 mol) was added and refluxed for further 24 h at 40-50 ºC. The golden yellow oily liquid obtained. Mol. wt. 572.78 g mol-1, golden yellow oily liquid, anal. calc. for $C_{26}H_{56}N_{10}O_4$(%): found (calculated): C. 54.1% (54.52%); H, 9.2% (9.9%); N, 24.5% (24.45%); I.R. (KBr pellets, cm-1):

CuL:

Yield: 62.3%, mol. Wt.: 841.67 g mol-1, m.p. >300 ºC, green colour, anal. Calc. for[Cu2($C_{26}H_{56}N_{10}O_4$)]Cl_4: found(calculated): C, 37.5% (37.1%); H, 6.31% (6.71%); N, 15.9%(16.64%); IR (KBr pellets, cm-1): 3420 (NH2)str., 1590 (C=O)str., 3090 (N-H)str., 1220 (CN)str., 450, 430, 475 (Cu-N) ; UV-Vis. (H2O, nm): 219 (n→σ*), 262 (π→π*), 324 (n→π*), 709(2B1g→2B2g); Molar conductance: 600.9 Ω-1cm2M-1; ESI-MS (m/z): 701.8 [M-4Cl+2H+], 350.3[(M-4Cl/2)+1H+], 288.2 [{(M-4Cl)/2}-Cu+2H+], 257.3 [{(M-4Cl)/2}-Cu-2O+3H+], 220.1 [{(M-4Cl)/2}-Cu-C2H6O2-4H+],161.2[{(M-4Cl)/2}-Cu-$C_4H_{13}N_2O_2$-4H+],104[{(M-4Cl)/2}-Cu-$C_6H_{20}N_4O_2$-2H+].

3. Result and discussion

3.1 Catalytic oxidation reaction:

A typical reaction for carrying out the oxidation of alcohols using polymer Cu (II) complex as catalyst is described as follow. The required catalyst was taken into two necked round bottom flask equipped with nitrogen inlet and condenser. To this was added hydrogen peroxide (5mmol) catalyst(0.05mg) and acetonitrile (5mmol). The flask was stopped and the above mixture was magnetically starred at different temperatures. At the end of specific time the contents were analysed by GC.

The rate of product yield in oxidation depends upon many factors like stability of catalyst, type of oxidant, temperature, Catalyst amount etc. The oxidation with t-BuOOH gave a higher yield (expressed as a percentage) than H_2O_2, because t-BuOOH is a more-efficient oxidant, due to weaker O-O bonds, with respect to H_2O_2 [10]. When the oxidation of 1-phenylethanol as the substrate, using a polymeric copper metal complex and hydrogen peroxide as an oxidant was performed the product is highest in the solvent (acetonitrilte) due to the higher swelling of polymer copper metal complex in polar solvents[10].It is because the substrate and the oxidant can easily approaches the active sites of catalyst. The results are shown in Table 1. The blank (control) experiment revealed that no reaction occurred in the absence of the oxidant [10].

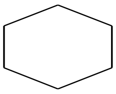
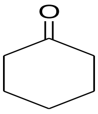
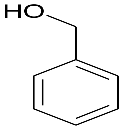
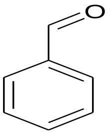
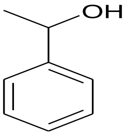
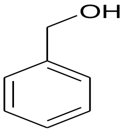
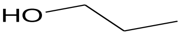
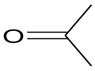
Temperature also affects the rate of reaction with increase in temperature the rate of reaction increases but not smoothly. This may be due to the decomposition of peroxide with higher temperature. The optimum temperature for oxidation of alcohols is 70°C.

The amount of catalyst also influences the product yield. With increase in the amount of catalyst the rate of product yield decreases. This is due to the reason that the excess of catalyst causes too decomposition of oxidant before oxidising the substrate, another reason is that the large amount of catalyst is difficult to stirrer.

3.2 Product analysis

The chromatogram and the corresponding mass spectra were recorded for the substrate as well as the final product of the oxidation reaction. The chromatogram and the mass spectra recorded before the oxidation reaction are shown in fig. 13. The chromatogram for the reaction mixture shows only a single peak of benzyl alcohol. The sample recorded after the oxidation showed two peaks, one for the unreacted benzyl alcohol and the other for the oxidation product benzyl aldehyde Fig.1. The mass fragmentation peak for the reaction mixture and the oxidation product are given in tables 2 and 3.

Table 1 Catalytic oxidation of alcohols

Substrate	Product	Yield	Selectivity	Time(hr)
		65	52	3
		63	49	3
		100	100	3
		52	15	3

Reaction conditions: temperature 70°C, H_2O_2(5mmol), Catalyst (0.05mg), acetonitrile(5mmol)

Table 1 Mass fragmentation for the Reaction mixture

Mass Fragments	m/z
M	108
M-17	91 (base peak)

Table2 Mass fragmentation for the Oxidation product

Mass Fragments	m/z
M	106
M+1	107 (base peak)

4. Conclusion

1. The synthesis of polymeric ligand copper metal complex was successfully done.
2. The complex was used as catalyst for the oxidation of various alcohols.
3. The nature of O-O bond influences the product yield.
4. Hydrogen peroxide was used as oxidant it oxidized the alcohols into their respective oxides.
5. The effect of various reaction parameters was also recorded.

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