Studies on polymer-anchored thiosemicarbazone transition metal complexes as catalysts for oxidation

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Abstract

Polymer-anchored transition metal complexes were synthesized by supporting cobalt (II), iron (III) and copper (II) on anion exchange resin (polystyrene) through the ligand thiosemicarbazone. The resulting catalysts were characterised by elemental analysis, SEM, IR spectroscopy, ESR and thermal studies. The catalysts were found to be active for oxidation of some alcoholic substrates under ambient conditions of temperature and pressure. The influence of solvent polarity on the rate of reaction was studied. Kinetic studies were done by varying the parameters like concentration of catalyst and substrate. The catalysts were found to have recycling efficiency for 5-6 cycles.

Key words: Polymer-anchored catalysts, oxidation, recycling efficiency

Introduction

The use of polymer supports in organic reactions has emerged as an attractive approach in both fundamental and technological field. In the solvent swollen polymeric reagents, the micro environment of the reactive site is essentially the same as that encountered by the reactants in the solution. Thus the polymer-anchored catalysts retain their homogeneous character when examined on molecular basis, but are heterogeneous when considered on functional basis [1-4]. The simple work-up procedure, facile access to the active site by soluble reagents and the reusability of the catalyst are some of the significant advantages that these system can offer [5]. Polymer-supported materials are extensively used as oxidising agents, reducing agents, photosensitizers and 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 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. The basic polymer backbone being chemically inert the polar properties can be modified by controlled functionalization. Poly-styrene can be functionalised easily, because it incorporates aryl groups. In polystyrene based system the ability

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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 catalysed by transition metal complexes provides an attractive route for the preparation of synthetic intermediates and other oxygen containing organic subtrates without the use of environmentally hazardous oxidants [9].

In this paper we report catalytic oxidation of some alcohols using cobalt (II), iron (III) and copper (II) anchored on ion exchange resin (polystyrene) through thiosemicarbazone with molecular oxygen as the oxidant.

Experimental

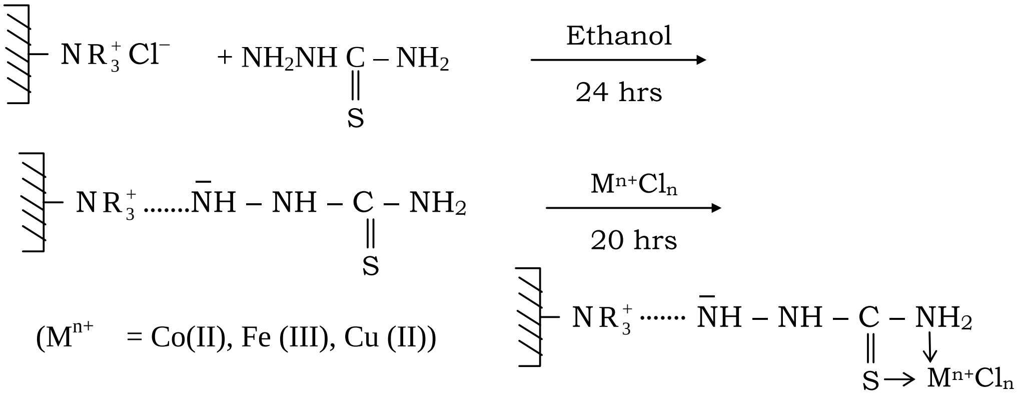
All the solvents and substrates were purified by standard methods. $CoCl_2.6H_2O$, Analar $FeCl_3$ and $CuCl_2.5H_2O$ supplied by Fischer were used as such. Analar grade sample of thiosemicarbazide was used as such. Crosslinked polystyrene (N-IP resin) was supplied by Ion Exchange India Ltd. Commercial oxygen was purified by passing through copper guaze maintained at 250°C and dried over molecular sieve.

Preparation of the catalysts: Thiosemicarbazide was anchored to polystyrene N-IP resin by stirring with excess of thiosemicarbazide in absolute ethanol at room temperature for 20 hrs. The resin was filtered and washed with water and absolute ethanol for several times and dried under vacuum.

Preparation of polystyrene-anchored thiosemicarbazone Cobalt (II) [Catalyst I]: The functionalised polymer was stirred with $CoCl_2.6H_2O$ in absolute ethanol for 24 hrs. The resulting resin was filtered and washed thoroughly with ethanol to get rid of the unanchored $CoCl_2$ and it was dried under vacuum.

Preparation of polystyrene-anchored thiosemicarbazone Iron (III) [Catalyst II]: A mixture of functionalised polymer and $FeCl_3$ were stirred in absolute ethanol for 24 hrs. After filtration the resin was washed thoroughly with absolute ethanol and the resin was dried under vacuum.

Preparation of polystyrene-anchored thiosemicarbazone Copper (II) [Catalyst III]: A mixture of functionalised polymer and $CuCl_2$ were stirred in absolute ethanol for 24 hrs. After filtration the resin was washed thoroughly with absolute ethanol and dried under vacuum.



(M^{n+} = Co(II), Fe (III), Cu (II))

n = 2, 3, 2

The results of elemental analysis of the polymer support, supported ligand and the catalysts are given in the table 1.

Table 1. Elemental Analysis of Catalysts I , II and III (in wt%)

Catalyst	Polymer support			After ligand introduction			After complexation		
	C	**H**	**N**	**C**	**H**	**N**	**C**	**H**	**N**
I	72.95	5.93	2.96	83.17	7.19	4.56	81.98	6.96	4.31
II	72.95	5.93	2.96	83.17	7.19	4.56	81.92	6.92	4.26
III	72.95	5.93	2.96	83.17	7.19	4.56	81.91	6.91	4.24

The metal contents in the catalysts were 6.1, 5.6 & 5.5 mg of Cobalt, Iron and Copper per gram of the catalyst as determined spectrophotometrically by standard method. A change in morphology of the catalyst from the support has been observed by the use of SEM, indicating the attachment of metal ions into the support.

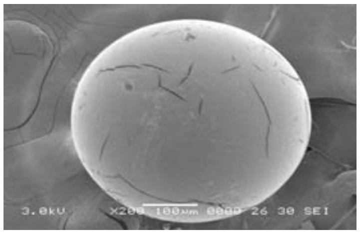


Fig. 1a. Polymer support

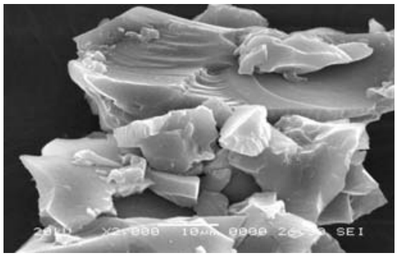


Fig.1b.After ligand introduction

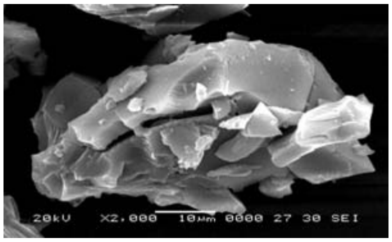


Fig.1c. After complexation with Co(II)

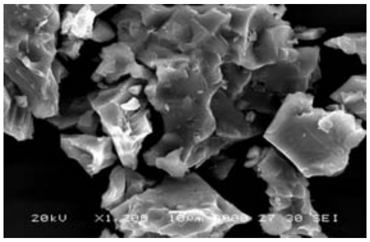


Fig. 1d. After complexation with Fe(III)

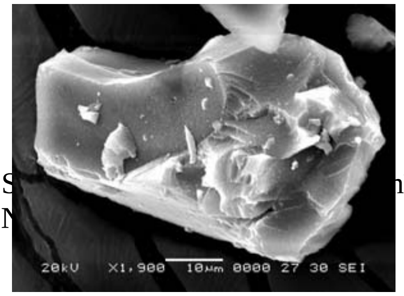


Fig.1e.After complexation with Cu(II)

IR spectra of the catalysts showed the following bands at 3384 (N-H), 1086 (C=S n^{-1} (M-N

Table 2 IR bands of the catalysts I, II, and III

Band (Cm^{-1})	Assignment
3384	N-H
1086	C=S
293-300	M-Cl
570	M-N
550	Out of plane deformation of benzene ring

From the EPR spectra of the catalysts the g_{ll} & $g_{\perp}$ values were 2.15 and 2.05 at LNT for the catalyst with Fe(III) and 2.09 and 2.01 for the catalyst with Cu (II). Since the g_{11} values are <2.34 a covalent character of the metal-ligand bond in the catalysts can be predicted [10]. For the catalyst with Co(II) no EPR signal was observed because of the rapid spin-lattice relaxation.

Table 3. EPR parameters for catalysts II and III

catalysts	Temperature	$g_{\|\|}$	$g_{\perp}$
Fe(III)	LNT	2.15	2.05
Cu(III)	LNT	2.09	2.01

The catalysts were found to be stable upto 300°C from thermal studies.

Oxidation set-up

The oxidation reactions were carried out at room temperature in a static rector using molecular oxygen as the oxidant at one atmospheric pressure. The required amount of the catalyst was taken inside the reaction vessel in the set-up. The system was evacuated before filling up with the gas. The substrates along with the solvent were introduced into the system by a syringe through a rubber septum. Uniform rate of stirring was maintained. The kinetics of the reaction was followed by the uptake of oxygen using a gas burette as a function of time. All the reactions were carried out in 1:1 methanol – toluene mixture (by volume). Blank experiments were carried out in the absence of substrate as well as the catalyst. In both cases there was no uptake of oxygen which means that the reaction did not proceed.

For some selected substrates, product analysis was carried out using GLC with FFAP column. The products formed were only the corresponding aldehydes. Identification of the products were done by comparing the retention times of the authentic samples. No other side products were found to be formed.

Results and discussion

The catalysts are found to be active for oxidation of various alcohols. The rates and relative rates are given in the tables II , III and IV.

Table 3. Rates and Relative rates for various substrates

[Catalyst I] x 10^3 = 0.240 M 35°C : [80 mg of catalyst / 20 ml of reaction mixture]		
Substrate (0.02 M)	Rate x 10^3 (M min^{-1})	Relative rate
n-butanol	0.72	2.32
n-hexanol	0.60	1.94
Benzyl alcohol	0.58	1.87
2-propanol	0.42	1.35
2-butanol	0.31	1

Table 4. Rates and Relative rates for various substrates

[Catalyst II] x 10^3 = 0.220 M 35°C; [80 mg of catalyst/20 ml of reaction mixture]		
Substrate , (0.2 M)	Rate x 10^3 , (M m^{-1})	Relative rate
n-butanol	0.68	2.43
n-hexanol	0.56	2.00
Benzyl alcohol	0.53	1.89
2-propanol	0.39	1.39
2-butanol	0.28	1

Table 5. Rates and relative rates for various substrates

[Catalyst III] = 0.220 M 35°C; [80 mg of catalyst /20 ml of reaction mixture]		
Substrate (0.2 M)	Rate x 10^3 , (M m^{-1})	Relative rate
n-butanol	0.64	2.56
n-hexanol	0.54	2.16
Benzyl alcohol	0.53	2.12
2-propanol	0.37	1.48
2-butanol	0.25	1.00

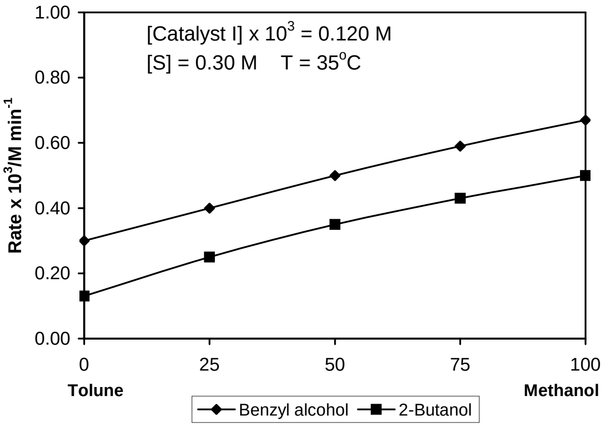
The rate of reaction increases on increasing the concentration of the catalyst. The plots of rate vs [catalyst] are linear indicating the rate to be the first power on catalyst concentration. But above a certain limit the reaction is independent of the catalyst concentration. This is explained as the saturation of the catalytic sites by the substrate. So further increase in the amount of catalyst cannot increase the rate due to the unavailability of the substrate. Similarly the rate of reaction increases linearly on increasing the amount of substrate within a limited range of concentration. Upon this limit the plot of reciprocal of rate against 1/substrate is linear with a positive intercept. At high concentration of substrate the oxygen absorption becomes rate-limiting.

The rate of reaction α [catalyst][substrate]

Effect of polarity of solvent on the rate

Benzyl alcohol and 2-butanol were oxygenated in methanol-toluene mixture of various composition (by volume). In all the cases the concentration of the catalyst and substrate were kept constant. For both the substrates the rate of reaction increased on increasing the percentage of methanol i.e. on increasing the polarity of the medium. Toluene can swell the polymer beads and thus increase the porosity of the catalyst. Methanol imparts polarity for the medium. Thus from the results the rate of reaction is more influenced by the polarity of the medium.

Fig.I EFFECT OF SOLVENT POLARITY ON THE INITIAL RATE OF OXIDATION FOR BENZYL ALCOHOL AND 2-BUTANOL



Recycling efficiency

It is found that the catalysts are recyclable upto five runs. After five cycles the rate of reaction decreased gradually. The loss of catalytic activity may be due to loss of mechanical strength of the polymer and also due to metal leaching.

Conclusion

The polymer anchored transition metal complexes are found to be efficient catalysts for oxidation reactions under mild conditions of temperature and pressure.

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