Crosslinked Isoxazole Functionalized Resin Transition Metal Complexes – Use as Polymeric Catalysts for Epoxidation of Olefins

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ABSTRACT

Transition metal complexes on polymers were found to be highly efficient in many catalysis reactions. The activity of Fe(III), Co(II), Ni(II) and Cu(II) complexes of polystyrene bound Isoxazole resin have been tested towards the epoxidation of alkenes by the decomposition of hydrogen peroxide. The reactions show a first order dependence on the concentration of both the substrates and the catalyst. The metal complexes having less cross linking at the backbone and ring-activating group near the active site showed high catalytic efficiency.

Key Words: Metal Complexes, Polymer Supported Ligands, Poly-styrene Supported Ligands, Isoxazole Ligands, Hydrogen Peroxide, Epoxidation, Olefins.

INTRODUCTION

Polymer supported catalysts have found important applications in the field of laboratory and industrial oxidation reactions and are of substantial scientific interest[1-3]. Synthetic polymers have the capacity to mimic the role of enzymes in bioorganic reactions. With the aim to combine the function of low molecular chelate with the advantage of polymer immobilization, several attempts have been made to synthesize polymeric transition metal complexes[4,5]. Neutral transition-metal catalysts have got considerable attention because of their special characteristics resulting from the reduced charge at the catalytic center[6,7].

Transition metal complexes have been receiving more attention as models for enzyme-catalyzed oxidation reactions, for example, as catalysts for selective epoxidation of alkenes[8-10]. Epoxides serve as versatile intermediates in synthetic organic chemistry. Their importance lies in the fact that they can be readily converted to various useful functional groups in regio- and stereo selective manners. Henbest *et al* first reported the epoxidation of styrene with peroxycamphoric acid[11].

Olefin epoxidation stands as one of the useful functional manipulations in organic synthesis.

Some of the important oxygen sources for epoxidation reactions are dioxygen(O_2), hydrogen peroxide(H_2O_2), alkyl hydroperixides, hyperchlorite anion,(ClO^-) iodosobenzene,(PhIO) etc. The most common method of converrtion of alkenes to epoxides involves the use of peroxides. Peroxides are a source of electrophilic oxygen and react with nucleophilic p bond of an alkene. H_2O_2 is cheap and is available from auto-oxidation of 2-ethyl anthroquinol where H_2/palladium is used to recycle the quinone formed. H_2O_2 is a powerful oxidizing agent with a reduction potential of 1.77 V[12]. While most of the peroxide reactions involve hemolytic cleavage of O-O bond generating free radicals, hydrogen peroxide and its monosubstituted derivatives reacts with alkenes in an concerted or ionic manner[13].

Jacobsen epoxidation has emerged as a powerful method for the asymmetric oxidation of unfunctionalized olefins[24]. Jacobsen has described a number of different oxidation systems that are effective for carrying out the epoxidation[14]. This study is an extension of the investigation by the authors regarding the suitability of the Isoxazole functionalized resin bounded transition metal complexes as catalysts for Hydrogen peroxide decomposition[15].

A loss of specific activity is very often noticed in the case of catalysts with active sites directly bound to the support. This drawback can be overcome by adopting systems whose active sites are separated from the macromolecular backbone by a spacer group. Introduction of flexible spacer arm between the polymer matrix and the reactive sites makes the active function protrude into the continuous phase. Thus the reactive group is made available to low molecular weight reagents and substrates. Porosity of the resin and a long spacer chain that allows the catalytic site to protrude into the reaction medium are significant in catalysis by polymer bound complexes. Improvement in the Merrifield synthesis of polypeptide was observed by placing a chain of about 30 atoms between the polystyrene support and the point of attachment of the first amino acid. Reger *et al* [16] anticipated that the five carbon spacer provided by the linking group would place the catalyst away from the polymer backbone to allow impeded access of the olefinic substrate to the metal center.

EXPERIMENTAL

Preparation of the polymer bound Isoxazole metal complexes

The synthesis of the polystyrene bound Isoxazole complexes involves a reported method by the same authors[17].

Reagents and materials

The materials used for the study were of reagent grade. H_2O_2 (NICE chemicals), substrates (FLUKA) were used as such. Methanol was purified by distillation.

Epoxidation of alkenes

To a definite amount of the metal complex catalyst in methanol (20 ml) was added an aqueous solution of H_2O_2 (0.4 V, 100 ml). After maintaining the temperature at 30°C, olefins to be epoxidised (0.01 moles) were added to it drop by drop with constant stirring. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the reaction mixture was

Scheme of Reaction
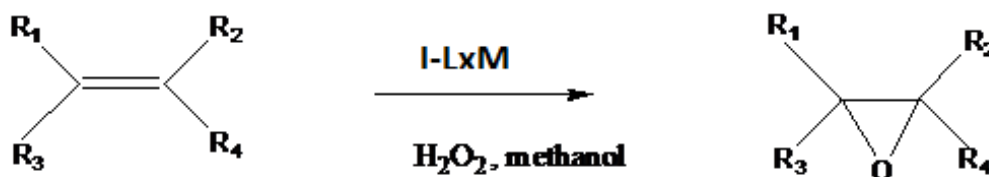
cooled to 0°C and the polymer metal complex catalyst settled at the bottom was separated. The reaction mixture was washed several times with chloroform and the combined organic extract was concentrated, dried and weighed. The product obtained was identified by FTIR and ^{1}H NMR. Influence of various factors such as degree of cross-linking of the polymeric backbone and structural environments of polymer metal complexes on the epoxidation reaction were studied by carrying out similar experiments.

RESULTS AND DISCUSSION

Alkenes such as styrene, a-methyl styrene, cyclohexene, cyclopentene and cholesterol were subjected to epoxidation reaction by stirring of the corresponding olefins at 30°C with aqueous H_2O_2 solution in presence of supported metal catalysts using methanol solvent. The rate and percentage yield of the reaction in the absence and presence of the polymer supported catalyst were studied and the results tabulated in Tables 1 and 2.

Influence of nature and degree of cross-linking

Reactivity of the immobilized functional groups is governed by their distribution and accessibility on the polymer backbone. Linear polymers can provide their functional groups free in solution because they form homogeneous macromolecular solutions. Due to their insolubility, for the cross-linked polymers, the accessibility of the functional group is diffusion controlled. This diffusion controlled penetrant transport causes some sort of molecular relaxation making the functional groups deeply buried in the polymer matrix as available to low-molecular weight species[18-19]. The mechanical stability of the network also depends on cross-link density. The effect of cross-link density on the reactivity of polymer-supported reagents has been the subject of a many investigations[20-22].

Table.1: Percentage yield of epoxides of uncatalyzed reaction

	Substrate	Product	% Yield
No catalyst	Styrene	Phenyl oxirane	10.13
	a- methyl styrene	a- methyl phenyl oxirane	13.36
	Cyclohexene	Cyclohexane oxide	8.40
	Cyclopentene	Cyclopentane oxide	6.42
	Cholesterol	Cholestan- 5,6- oxo- 3- ol	4.45

Conditions:[H_2O_2]=0.4 V, [alkene] = 0.01 moles, Temperature = 303 K, Time = 10 h, MeOH = 20mL

Table.2: Influence of polystyrene supported Isoxazole catalysts in epoxidation reactions

Substrate	Product	% Yield			
		Fe (III)	Co (II)	Ni (II)	Cu (II)
Styrene	Phenyl oxirane	75.21	74.30	40.22	79.10
a- methyl styrene	a- methyl phenyl oxirane	78.13	76.40	45.53	82.20
Cyclohexene	Cyclohexane oxide	67.35	69.20	35.71	70.11
Cyclopentene	Cyclopentane oxide	60.42	52.00	32.20	63.32
Cholesterol	Cholestan- 5,6- oxo- 3- ol	50.52	52.44	24.71	52.45

Conditions: [H_2O_2]=0.4 V, [alkene]=0.01 moles, 2% DVB cross-linked resin=100 mg, R =OCH_3, Temperature = 303 K, Time = 10 h, MeOH = 20mL

Epoxidation reactions were carried out using polymeric catalysts of varying cross-linking agents and densities and percentage yield in each case is calculated. The results are given in Tables 3 and 4.

EGDMA cross-linked resins possess high catalytic efficiency than the DVB cross-linked ones. The catalytic efficiency of the complexes was found to decrease with increase in cross-linking density. Eventhough better stability is achieved with increased cross-linking, the accessibility of the reactive groups are considerably diminished leading to decreased reactivity. For large molecules like cholesterol this influence is much more pronounced with very less efficiency.

Influence of structural environment of the ligand

The epoxidation reaction of various olefins were carried out using Isoxazole metal complexes having different substituents groups to study the effect of role of varying structural environment of the polymer supports. The pH of the solution was kept at 8.5 at low temperature during the slow addition of the substrates. The results are tabulated in Tables 5. Maximum efficiency was noticed for the catalyst with methoxy phenyl substituents, possibly due to the basicity of the coordinating atoms are

Table.3: Influence of nature of cross-linking of catalysts in epoxidation reactions

Catalyst	DVB cross linked resin		EGDMA cross linked resin	
	Fe (III)	Cu (II)	Fe (III)	Cu (II)
Isoxazole complex	78.13	82.80	81.4	84.6

Conditions: $[H_2O_2]$=0.4 V, [a-methyl styrene] = 0.01 moles, 2% cross-linked resin=100 mg, R =OCH_3,Temperature = 303 K, Time = 10 h, MeOH = 20mL

Table. 4: Influence of degree of cross-linking of catalysts in epoxidation reactions

Catalyst	Metal	% of Cross linking				
		2	5	10	15	20
Isoxazole complex	Fe (III)	78.13	73.5	68.3	63.4	59.6
	Cu (II)	82.8	78.6	72.9	67.4	63.3

Conditions: $[H_2O_2]$=0.4 V, [a-methyl styrene] = 0.01 moles, DVB cross-linked resin =100 mg, R =OCH_3, Temperature = 303 K, Time = 10 h, MeOH = 20mL

Table.5: Influence of structural environment of the Isoxazole catalyst in epoxidation reactions

Ligand Environment	% Yield			
	Fe (III)	Co (II)	Ni (II)	Cu (II)
H	67.3	64.6	36.4	72.8
Me	72.6	70.3	40.6	77.9
OMe	78.1	76.4	45.5	82.6
Cl	63.1	59.8	33.6	68.3
NO_2	61.9	58.3	32.4	67.6

Conditions: $[H_2O_2]$=0.4V, [a-methyl styrene]=0.01 moles, 2% DVB cross-linked resin=100 mg, Temperature=303 K, Time=10 h, MeOH = 20mL

increased by electron donating groups. Thus the interaction between the metal catalyst and the olefins is increased which enhance the electron transfer from the dp molecular orbital of the metal to p* anti bonding orbital of the olefin. On the other hand, the electron withdrawing groups such as chloro and nitro retards this electron transfer process leading to decreased catalytic efficiency.

Reusability

Reusability is a condition for supported catalysts to offer any technological advantage. For a truly effective polymer-supported catalyst, it is critical that the recovery should be simple and efficient and the recovered catalysts retain its activity through multiple cycles. To check this, successive reactions were carried out using the same catalyst in an identical manner. The same polymeric catalyst was used for four cycles of epoxidation reaction of a- methyl styrene and the yield was noticed in each case. The results of are entered in Table 6. There was no considerable difference in the reactivity after recycling and the catalysts retained their form and characteristics after each cycle.

DISCUSSION

The yield of the product was found to increase with the amount of catalyst. Based on

Table.6: Reusabilty of the catalysts in epoxidation reaction

Number of Cycles	% Yield Isoxazole complex
1	82.8
2	82.6
3	82.5
4	82.2

Conditions : $[H_2O_2] = 0.4$ V, [a-methyl styrene]=0.01moles Temperature = 303 K, Time = 10 h, MeOH = 20mL

percentage yield, comparable or better selectivity of these catalysts manifested specificity and defined structures of the catalytic sites in the polymer matrix. Also, micro environmental effects of the immobilized catalysts such as the site isolation in the polymer matrix are likely to contribute to this improved selectivity during epoxidation.   More highly substituted alkenes are found to react faster than the low substituted alkenes in the epoxidation reaction. When a coordinating group is present, a neighbouring group effect is possible.

Eventhough the structure of the metal center coordinated to the polymer is assumed to be the same as in monomeric analogs; there is a chance for large steric interactions by the polymer matrix leading to a slight reduction in catalytic activity. This can be overcome to a little extent by the pre swelling of the polymer catalyst in the solvent used for the reaction. Subsequent cooling of the oxidant before the reaction is very important, because a major part of H_2O_2 disproportionate to oxygen which highly dilutes the substrate[23]. Appropriate choosing of the reaction conditions is necessary such that the balance between epoxidation and peroxide disproportion is strongly shifted towards the former.

Good yield of epoxides are achievable with inexpensive reagents under mild conditions.

CONCLUSION

The study shows that Isoxazole functionalized transition metal complexes can act as efficient catalysts for epoxidation reactions of various substrate.   It was found that substituted alkenes are more susceptible to this catalysis reaction.

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REFERENCES

1. Li N.H., Frechet J.M.J., *React.Polym.,* **6**, 311 (1987).

2. Sherrington D.C., *Pure Appl.Chem.,* **60**, 401 (1988).

3. Sherrington D.C.,Tang,H.G., *J.Catal.*, **142**, 540 (1993).

4. Wohrle D. , Bohen H., Meyer G., *Polym.Bull.*, **11**, 143 (1984).

5. Akelah A., Masoud M.S., Kandil K.S., *Ind.J.Chem.*, **25A**, 918, (1986).

6. Safir A.L., Novak B.M., *Macromolecules,* **28**, 5396, (1995).

7. Safir A.L., Novak B.M., *J.Am.Chem.Soc.,* **120**, 643 (1998).

8. Nina Kann,, *Molecules* **15**, 6306 (2010).

9. B³a¿ E., Pielichowski , *Molecules*, **11**, 115 (2006).

10. Mannar R. Maurya, João Costa Pessoa , *J.Organometallic Chem*, **696(1)**, 244 (2011).

11. Ewins R.C., Henbest H.B., Mc Karbevev M.A., *J.Chem.Soc., Chem.Commun*., 1085 (1967).

12. Smith M.B., Organic Synthesis, Mc-Graw Hill, INC, New York, (1994).

13. Augustine R.L., Oxidation, Marcel Dekker, New York, (1969).

14. Jacobsen E.N., In Catalytic Asymmetric Synthesis, Ojima,I., Ed., VCH: New York, (1993).

15. Rathika Nath G., Rajesh K., *Orient. J. Chem*, **27(3)**,1215-1220 (2011).

16. Reger T.S., Janda K.D., *J.Am.Chem.Soc.*, **122**, 6929 (2000).

17. Rathika Nath G., Radhakrishnan T., Synthesis and Reactivity in Inorganic, *Metal-Organic and Nano-Metal Chemistry,* **35**, 491 (2005).

18. Ford W.T., *J.Polym.Sci.Polym.Chem.Edn.,* **22**, 509 (1984).

19. Warshawsky A., *Isr.J.Chem.,* **18**, 318 (1979).

20. Harrison C.R., Hodge P., *J.Chem.Soc., Perkin Trans.,* I 605 (1976).

21. Cantow H.J., Schuster R.H., *Polym.Bull.,* **8**, 225 (1982).

22. Vrentas J.S., Duda J.L., Han A.G., *J.Appl.Polym.Sci.,* **29**, 399 (1984).

23. Dirk D.V., Thomas B., *Chem.Commun*., **917** (1996).