

Transition Metal Complexed Crosslinked Pyrazole Functionalized Resin-Use as Polymeric Catalysts for Epoxidation of Olefins

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Functionalized polymers are found to be highly efficient in immobilizing transition metal ions. The activity of Fe(III), Co(II), Ni(II) and Cu(II) complexes of polystyrene bound pyrazole 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 show high catalytic efficiency.

Key Words: Metal complexes, Polymer supported ligands, Poly-styrene supported ligands, Pyrazole ligands, Hydrogen peroxide, Epoxidation, Olefins.

INTRODUCTION

The development of viable, polymer supported catalysts for laboratory and industrial oxidation reactions has received recent scientific interest¹⁻³. The major goal of providing synthetic polymers is 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 attracted 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 enzymecatalyzed oxidation reactions, for example, as catalysts for selective epoxidation of alkenes⁸⁻¹⁰.

Epoxides serve as versatile intermediates in synthetic organic chemistry, because they are readily converted to various useful functional groups in regio- and stereo selective manners. Ewins *et al.*¹¹ first reported the epoxidation of styrene with peroxy camphoric acid. Olefin epoxidation stands as one of the useful functional manipulations in organic synthesis.

Important oxygen sources for epoxidation reactions are dioxygen (O₂), hydrogen peroxide (H₂O₂), alkyl hydroperoxides, (ROOH) [for example *t*-butyl hydroperoxide, *t*BHP and cumene hydroperoxide, CHP], hyperchlorite anion, (ClO⁻) and iodosobenzene, (PhIO). The most common method of conversion of alkenes to epoxides involves the use of peroxides. Peroxides are a source of electrophilic oxygen and react with

nucleophilic π bond of an alkene. Hydrogen peroxide is cheap and is available from auto-oxidation of 2-ethyl anthroquinol where H₂/palladium is used to recycle the quinone formed. Hydrogen peroxide H₂O₂ is a powerful oxidizing agent with a reduction potential of 1.77 V¹². 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 manner¹³.

Jacobsen *et al.*¹⁴ epoxidation has emerged as a powerful method for the asymmetric oxidation of unfunctionalized olefins. They described a number of different oxidation systems that are effective for carrying out the epoxidation. This study is an extension of the investigation by the authors regarding the suitability of the pyrazole functionalized resin bounded transition metal complexes as catalysts for hydrogen peroxide decomposition¹⁵.

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. Improve-

TABLE-2
INFLUENCE OF POLYSTYRENE SUPPORTED PYRAZOLE CATALYSTS IN EPOXIDATION REACTION

Substrate	Product	Yield (%)			
		Fe(III)	Co(II)	Ni(II)	Cu(II)
Styrene	Phenyl oxirane	82.1	79.8	48.3	87.3
α -Methyl styrene	α -Methyl phenyl oxirane	86.4	83.5	53.6	91.9
Cyclohexene	Cyclohexane oxide	80.2	73.1	42.8	84.3
Cyclopentene	Cyclopentane oxide	77.37	68.4	36.6	80.6
Cholesterol	Cholestan-5,6-oxo-3-ol	69.3	58.6	28.6	78.2

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

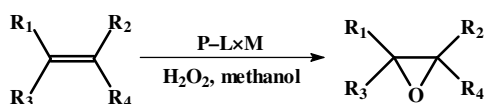
ment in the Merrifield synthesis of polypeptide was observed by placing a chain of *ca.* 30 atoms between the polystyrene support and the point of attachment of the first amino acid. Reger and Janda¹⁶ anticipated that the five carbon spacer provided by the linking group would place the catalyst away from the polymer backbone to allow impeded access of the olefinic substrate to the metal center.

EXPERIMENTAL

Preparation of the polymer bound pyrazole metal complexes: The synthesis of the polystyrene bound pyrazole complexes involves the reported method¹⁷.

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), aqueous H_2O_2 solution (0.4 V, 100 mL) was added. After maintaining the temperature at 30 °C, olefins to be epoxidized (0.01 mol) 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 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 1H 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.



Scheme-I

RESULTS AND DISCUSSION

The epoxidation reactions of alkenes such as styrene, α -methyl styrene, cyclohexene, cyclopentene and cholesterol were carried out by the 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: The chemical reactivity of immobilized functional groups is governed by their distribution and accessibility on the polymer backbone.

TABLE-1
PERCENTAGE YIELD OF EPOXIDES OF UNCATALYZED REACTION

	Substrate	Product	Yield (%)
No catalyst	Styrene	Phenyl oxirane	10.13
	α -Methyl styrene	α -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, $[\text{alkene}] = 0.01$ mol, Temp. = 303 K, Time = 10 h, MeOH = 20 mL

Linear polymers can provide their functional groups free in solution because they form homogeneous macromolecular solutions. Because of 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 species¹⁸⁻¹⁹. The mechanical stability of the network also depends on cross-link density. The effect of cross-link density on the reactivity of polymersupported reagents has been the subject of a few investigations²⁰⁻²².

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

TABLE-3
INFLUENCE OF NATURE OF CROSS-LINKING OF CATALYSTS IN EPOXIDATION REACTIONS

Catalyst	DVB cross linked resin		EGDMA cross linked resin	
	Fe(II)	Cu(II)	Fe(II)	Cu(II)
Pyrazole complex	86.40	91.9	89.3	94.1

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

TABLE-4
INFLUENCE OF DEGREE OF CROSS-LINKING CATALYSTS IN EPOXIDATION REACTIONS

Catalyst	Metal	% of cross linking				
		2	5	10	15	20
Pyrazole complex	Fe(II)	86.4	82.7	76.4	71.6	67.7
	Cu(II)	91.9	89.1	83.4	78.6	73.4

Conditions: $[H_2O_2] = 0.4$ V, $[\alpha\text{-methyl styrene}] = 0.01$ mol, DVB cross-linked resin = 100 mg, $R = OCH_3$, Temperature = 303 K, Time = 10 h, MeOH = 20 mL

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 crosslinking 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: To study the effect of role of varying structural environment of the polymer supports, the epoxidation reaction of various olefins were carried out using pyrazole metal complexes having different substituents groups. 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 Table-5.

Ligand environment	Yield (%)			
	Fe(III)	Co(II)	Ni(II)	Cu(II)
H	76.3	72.6	43.6	82.7
Me	80.4	77.4	48.6	86.4
OMe	86.4	83.5	53.6	91.9
Cl	70.1	69.6	41.7	78.3
NO ₂	68.3	67.1	39.6	76.1

Conditions: [H₂O₂] = 0.4V, [α -methyl styrene] = 0.01 mol, 2 % DVB cross-linked resin = 100 mg, Temperature = 303 K, Time = 10 h, MeOH = 20 mL

Maximum efficiency was noticed for the catalyst with the methoxy phenyl substituents, since the basicity of the coordinating atoms are increased by electron donating groups. Thus the interaction between the metal catalyst and the olefins is increased which enhance the electron transfer from the $d\pi$ molecular orbital of the metal to π^* antibonding 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: To offer any technological advantage, supported catalysts should be reusable. 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 α -methyl styrene and the yield was noticed in each case. The results of which are entered in Table-6.

Number of cycles	Yield (%) Pyrazole complex
1	91.9
2	91.7
3	91.4
4	91.2

Conditions: [H₂O₂] = 0.4 V, [α -methyl styrene] = 0.01 mol; Temperature = 303 K, Time = 10 h, MeOH = 20 mL

There was no considerable difference in the reactivity after recycling and the catalysts retained their form and characteristics after each cycle.

The yield of the product was found to increase with the amount of catalyst. It points out the fact that with increase in the amount of catalyst and the content of active units in the polymeric catalysts, the efficacy of the active sites decreases. Based on percentage yield, comparable or better selectivity of these catalysts manifested specificity and defined structures of the catalytic sites in the polymer matrix. In addition, 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 H₂O₂ disproportionate to oxygen which highly dilutes the substrate²³. Appropriate choosing of the reaction conditions is necessary such that the balance between epoxidation and peroxide disproportionation is strongly shifted towards the former. Good yield of epoxides are achievable with inexpensive reagents under mild conditions.

Conclusion

The study shows that pyrazole 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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