RESEARCH PUBLICATIONS

LIST OF PUBLICATIONS

1. "Olefin epoxidation catalysed by Mn(II) Schiff base complex in heterogenised-homogeneous systems"
   S. A. Patel, S. Sinha, A. N. Mishra, B V. Kamath and R. N. Ram,
   Journal of Molecular Catalysis A: Chemical 192 (2003) 53-61.

2. "Synthesis and catalytic activity of Ru(III) anchored to a polystyrene-Schiff base support"
   S. A. Patel, S. Sinha, A N. Mishra, B V Kamath and *Late* R. N Ram,
   (communicated)

3. "Hydrogenation of olefin using polymer supported Pd(II) catalyst"
   S. A. Patel, S Sinha, A N. Mishra, B. V Kamath and *Late* R. N Ram,
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Olefin epoxidation catalysed by Mn(II) Schiff base complex in heterogenised–homogeneous systems

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This paper is dedicated to Dr. R.N. Ram

Abstract

The polymer supported Mn(II) Schiff base complexes were prepared from crosslinked chloromethylated poly(styrene-divinyl benzene) copolymer beads by sequential modification into a Schiff base bearing ligand. These Schiff base bearing polymer on treatment with a solution of $MnCl_2 \cdot 2H_2O$ gave the corresponding metal complexes. The polymer supported Mn(II) complexes were characterised by elemental analysis, FT-IR, diffuse reflectance, SEM and thermogravimetric analysis. Physicochemical properties such as surface area, bulk density and swelling behaviour in different solvents were studied. The catalytic activity of the supported metal complexes were studied in the epoxidation of norbornene and *cis*-cyclooctene using *tert*-butylhydroperoxide (TBHP) as the terminal oxidant. The influence of various reaction parameters such as temperature, solvent, substrate and catalyst concentration, on conversion and selectivity has been studied.

Keywords: Styrene-divinylbenzene; Chloromethylation; Epoxidation; Polymer support; Catalysis; Norbornene; *cis*-Cyclooctene

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1. Introduction

Recent trends [1–7] in immobilisation of transition metal complexes on insoluble support (mainly organic polymer) appear to be a good way of heterogenising homogeneous catalysts. Such type of heterogenised–homogeneous catalytic systems not only offer the combined advantages of homogeneous (mild conditions) and heterogeneous (easy separation), but also impose extreme shape selectivity in catalytic process. The Schiff bases are one of the most versatile and thoroughly studied ligands, but very few reports are available on the polymer anchored Schiff bases and their application in catalysis [8–12]. These Schiff bases having multidentate coordination sites form complexes with transition metal ions readily. In the present paper, we report our results on the synthesis of new poly(styrene-divinyl benzene) bound Schiff base ligands and their manganese complexes. The polymer supported Mn(II) complexes were evaluated for their catalytic behaviour towards epoxidation of norbornene and *cis*-cyclooctene in the presence of *tert*-butylhydroperoxide (TBHP) as an oxidant.

2. Experimental

2.1. Material

Chloromethylated poly(styrene-divinyl benzene) copolymer spherical beads (0.3–1.2 mm bead size)

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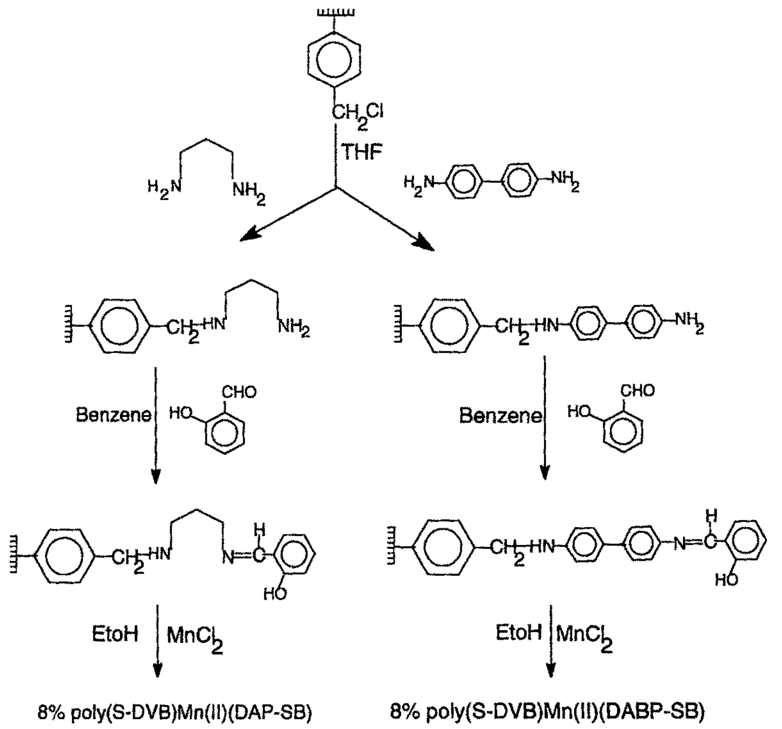


Scheme 1 Synthesis of Mn(II) supported poly(styrene-divinylbenzene) Schiff base complexes

norbornene and *cis*-cyclooctene. The different catalysts are designated as under

- Mn-A· 8% poly(S-DVB)Mn(II)(DAP-SB)
- Mn-B 8% poly(S-DVB)Mn(II)(DABP-SB)

3 1 *Catalyst characterisation*

The analytical data of the polymer supported complexes at a different stage of the preparation is presented in Table 1 The maximum loading of Mn in the prepared catalysts was found to be in the range of 8 1 × 10^{-5} to 3 19 × 10^{-4} mol g^{-1} resin Some of the important physical properties of the newly prepared catalysts are given in Table 2 The slightly higher surface area observed in catalysts Mn-B than Mn-A which may possibly be due to the relative difference in size of the Schiff base formed from 1,3-diaminopropane and 4,4′-diaminobiphenyl [17,18]

The choice of the suitable solvent is an important factor for studying the catalytic behaviour of polymer supported homogeneous catalysts Polar solvents were generally found to be better swelling agents than aliphatic or aromatic non-polar solvents (Table 3) Water exhibited higher percentage swelling. However, for practical purposes, methylene chloride and

Table 1
Physical properties of the polymer supported Mn(II) catalyst

Sample volume	Surface area ($m^2 g^{-1}$)	Moisture content (wt %)	Bulk density ($g cm^{-3}$)	Pore ($cm^3 g^{-1}$)
8% P(S-DVB) CH_2Cl	50 16	–	–	–
Catalyst-A	45 92	0 37	0 50	0 11
Catalyst-B	51 28	0 37	0 37	0 15

Table 2
Elemental analysis of polymer support, ligand and Mn-anchored catalyst

Sample	C (%)	H (%)	N (%)	Cl (%)	Mn (mol g^{-1} resin)
8% P(S-DVB) CH_2Cl	72.76	5.99	–	17.8	–
8% P(S-DVB)(DAP-SB)	78.1	6.19	4.74	–	–
8% P(S-DVB)(DABP-SB)	75.6	6.09	2.44	–	–
Catalyst-A	71.9	6.06	4.01	–	3.19×10^{-4}
Catalyst-B	69.96	5.96	1.91	–	8.1×10^{-5}

Table 3
Swelling studies of catalysts at 27 °C (mol%)

Solvent	Catalyst-A	Catalyst-B
Water	6.71	6.68
Methanol	4.62	5.17
Ethanol	3.41	3.60
Acetonitrile	2.79	3.79
Dichloromethane	2.80	3.50
THF	1.82	1.82
Benzene	1.37	1.36
n-Heptane	0.87	0.74

acetonitrile were used as the solvents of choice for carrying out catalytic reactions to overcome miscibility problem with the reactions. The thermal stability of the Mn supported catalysts reveal that they are not stable above 300 °C (Fig. 1). Initial weight loss might be due to moisture content, whereas the weight loss observed above 400 °C in all the catalysts may be due to the dissociation of attached ligand moieties as well as scission of polymeric chain. From the present study it was concluded that the catalyst could be used safely up to 100 °C.

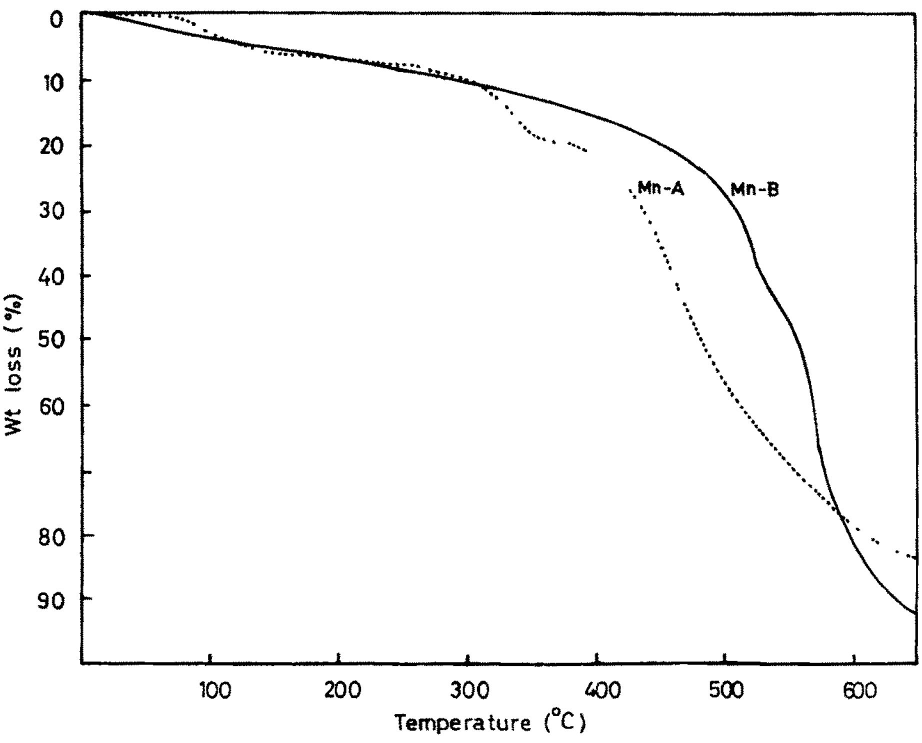


Fig. 1. TGA curves for catalyst-A and -B.

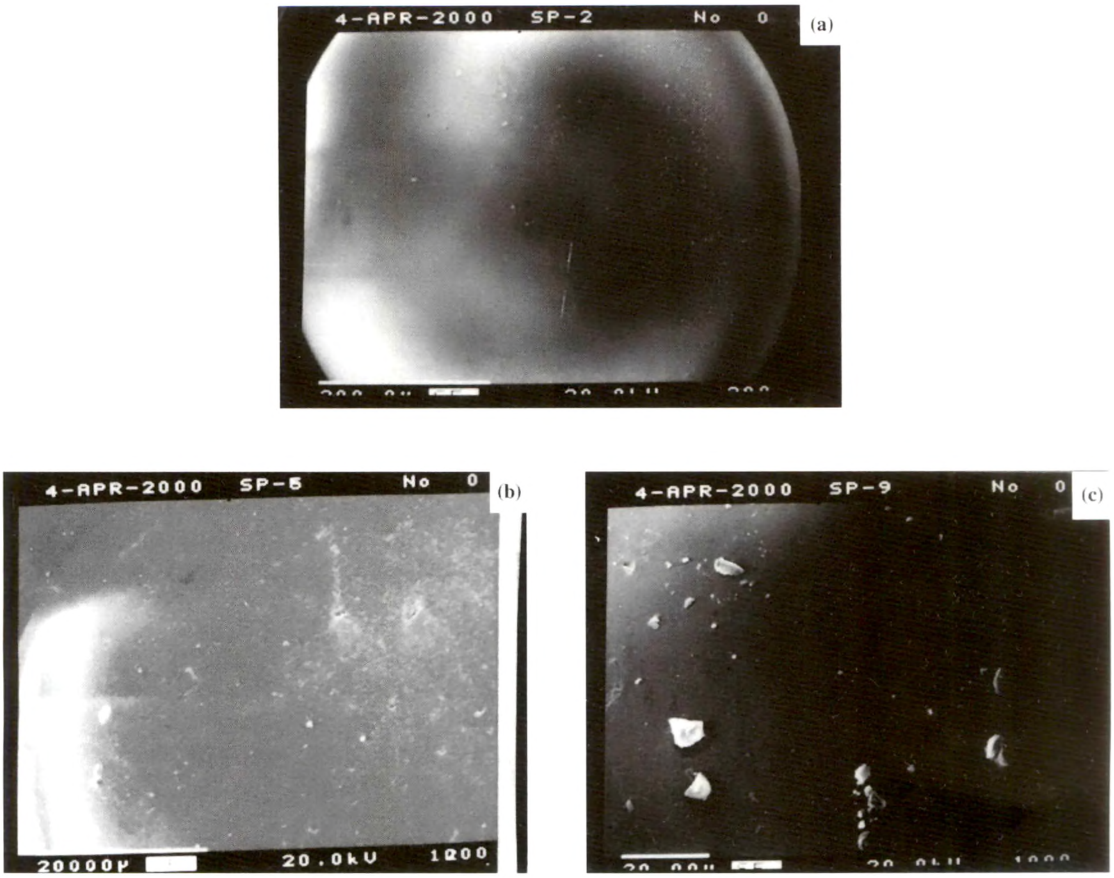


Fig. 2. Scanning electron micrographs: (a) chloromethylated poly(S-DVB), (b) catalyst-A and (c) catalyst-B.

The morphological changes occurring on the surface of the polymeric matrix as well as newly synthesised catalysts were studied using a scanning electron microscope (Fig. 2). Initial examination of the SEMs reveal that the Mn(II) atoms are finely distributed across the smooth spherical surface of the beads. However, accurate information regarding the change in distribution profile of Mn on the surface of the matrix before and after the catalytic cycle cannot be provided due to the very low loading ($\approx 10^{-5}$) of the metal on the support.

The UV–VIS reflectance spectra of newly synthesised catalysts in the $BaSO_4$ matrix exhibit a broad peak at 395 nm which might be due to the d–d transition of Mn(II). Its homogeneous counterpart also shows a peak at 395 nm, which indicates the present of manganese in the same oxidation state.

The mid (4000–400 cm^{-1}) and far (500–50 cm^{-1}) of polymer supported manganese complexes at the different stages of the synthesis was used to understand the nature of coordination of the metal to the polymer. The spectra shows peaks in the region of 3400 cm^{-1} assigned to νNH stretching frequency. A medium intensity band in the region of 1660–1640 cm^{-1} assigned to νC=N (azomethine) indicating the formation of Schiff base on the support. Medium intensity band at 530 cm^{-1} (νMn–N), 754 cm^{-1} (νMn–O) and weak intensity band at 291 cm^{-1} (νMn–Cl) show the coordination of the metal with the ligand to form the complex on the polymer support.

Table 4
Catalytic epoxidation of *cis*-cyclooctene with supported Mn-catalysts[a]

Catalyst	Solvent	Temperature (°C)	Epoxide (%)[b]
Catalyst-A	CH_2Cl_2	25	10.1
	CH_2Cl_2	40	13.9
	CH_3CN	25	3.2
	CH_3CN	50	4.6
Catalyst-B	CH_2Cl_2	25	9.4
	CH_2Cl_2	40	12.2
	CH_3CN	25	2.3
	CH_3CN	50	3.8

[a] Reaction condition: solvent, 20 ml; oxidant, TBHP 2 mmol; reaction time, 24 h; catalysts, 0.25 g.
[b] Yield based on substrate taken.

Table 5
Catalytic epoxidation of norbornene with supported Mn-catalysts[a]

Catalyst	Solvent	Temperature (°C)	Epoxide (%)[b]
Catalyst-A	CH_2Cl_2	25	32.5
	CH_2Cl_2	40	45.1
	CH_3CN	25	8.8
	CH_3CN	50	23.4
Catalyst-B	CH_2Cl_2	25	29.4
	CH_2Cl_2	40	37.7
	CH_3CN	25	5.8
	CH_3CN	50	13.4

[a] Reaction condition: solvent, 20 ml; oxidant, TBHP 2 mmol; reaction time, 24 h; catalysts, 0.25 g.
[b] Yield based on substrate taken.

3.2. Catalytic epoxidation

Catalysts Mn-A and Mn-B were employed in the epoxidation of the electron rich olefins such as norbornene and *cis*-cyclooctene. These results are compiled in Tables 4 and 5. It is observed from the table that the epoxidation reactions at room temperature in the presence of TBHP and catalysts results into low yield of products. However, at slightly elevated temperature (40–50 °C) there is a marked increase in the corresponding yields of epoxides. This is observed for both norbornene and *cis*-cyclooctene. The catalytic activity is much more pronounced in methylene chloride medium than in acetonitrile. The polymeric Mn-bound catalyst-A showed marginally better catalytic activity than catalyst-B.

The rate of reaction exhibited by polymer bound catalysts is slower than their homogeneous counterparts. This is attributed mainly due to the slower diffusion of substrate olefins into the polymer matrix in which the active sites are located [19]. A profile on the progress of the reaction (% yield) with respect to time is shown in (Fig. 3). In order to determine the effect of various reaction parameters such as temperature, catalyst and substrate concentration on the catalytic performance, epoxidation of norbornene as a substrate was carried out using polymeric Mn-B (Table 6).

3.3. Catalyst recycle

One of the main reason of supporting a homogeneous metal complex on to the polymer is to enhance the life of the resulting catalyst. We have selected the catalyst Mn-B using norbornene as a model substrate for the recycling study. The catalyst was separated from the reaction mixture after

Table 6
Epoxidation of norbornene by catalyst-B under different reaction conditions[a]

	Norbornene (mmol)	Catalytic weight (g)	Temperature (°C)	Epoxide (%)[b]
Effect of temperature	5	0.25	25	29.4
	5	0.25	35	32.2
	5	0.25	40	37.7
Catalyst concentration effect	5	0.15	40	24.2
	5	0.25	40	37.7
	5	0.35	40	42.8
Substrate effect	5	0.25	40	37.7
	10	0.25	40	42.0
	15	0.25	40	45.2

[a] Solvent is CH_2CL_2, 20 ml; oxidant, TBHP 2 mmol; reaction time, 24 h.
[b] Yield based on substrate taken.

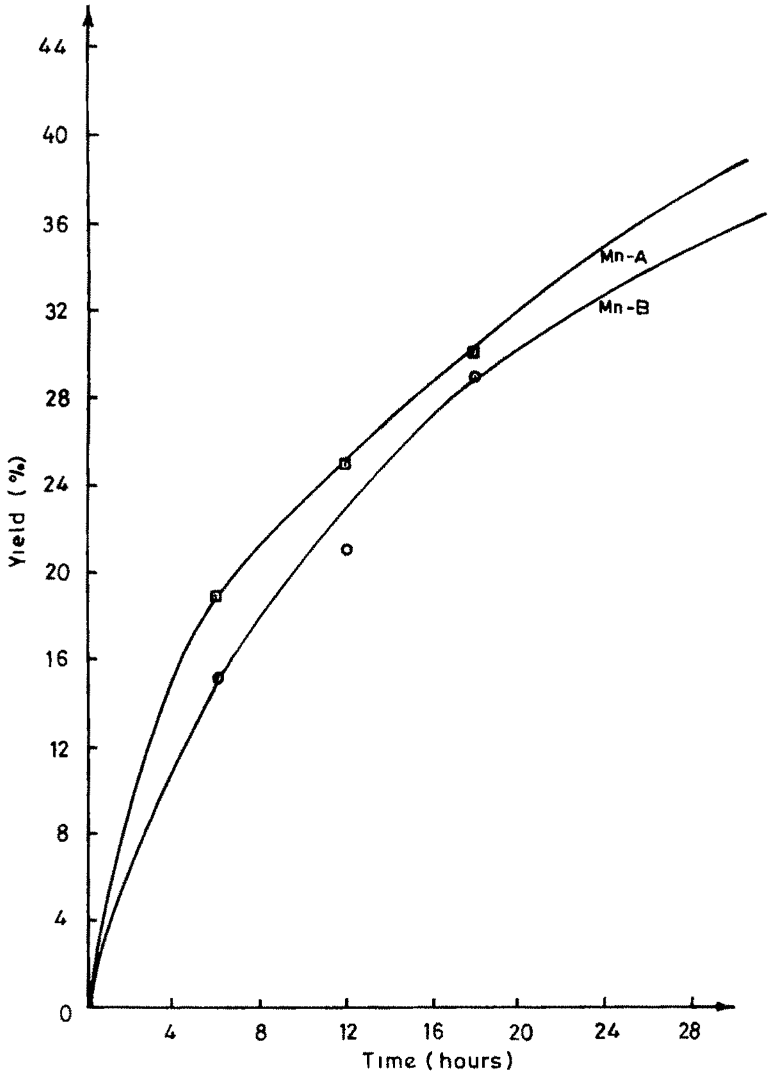


Fig 3 Plot of conversion (%) vs time for norbornene epoxidation using catalyst-A and -B

each experiment by filtration, washed with the solvent and dried carefully before using it in the subsequent run The catalyst may be recycled for five to six times, there is a progressive loss of activity with lowering in epoxide yields indicating leaching of Mn metal from the support [20], which was also confirmed by visible gradual change in colour of the catalyst surface with every recycle This is shown in Fig. 4

3 4. *Mechanism of olefin epoxidation*

The two major mechanistic pathways for metal catalysed oxygen transfer are known to involve either peroxometal or oxometal species as the active intermediate The peroxometal species are generally favoured with early transition metals, viz. Mo(VI), W(VI), V(V), etc. on the other hand, many first row transition metals including manganese follow that

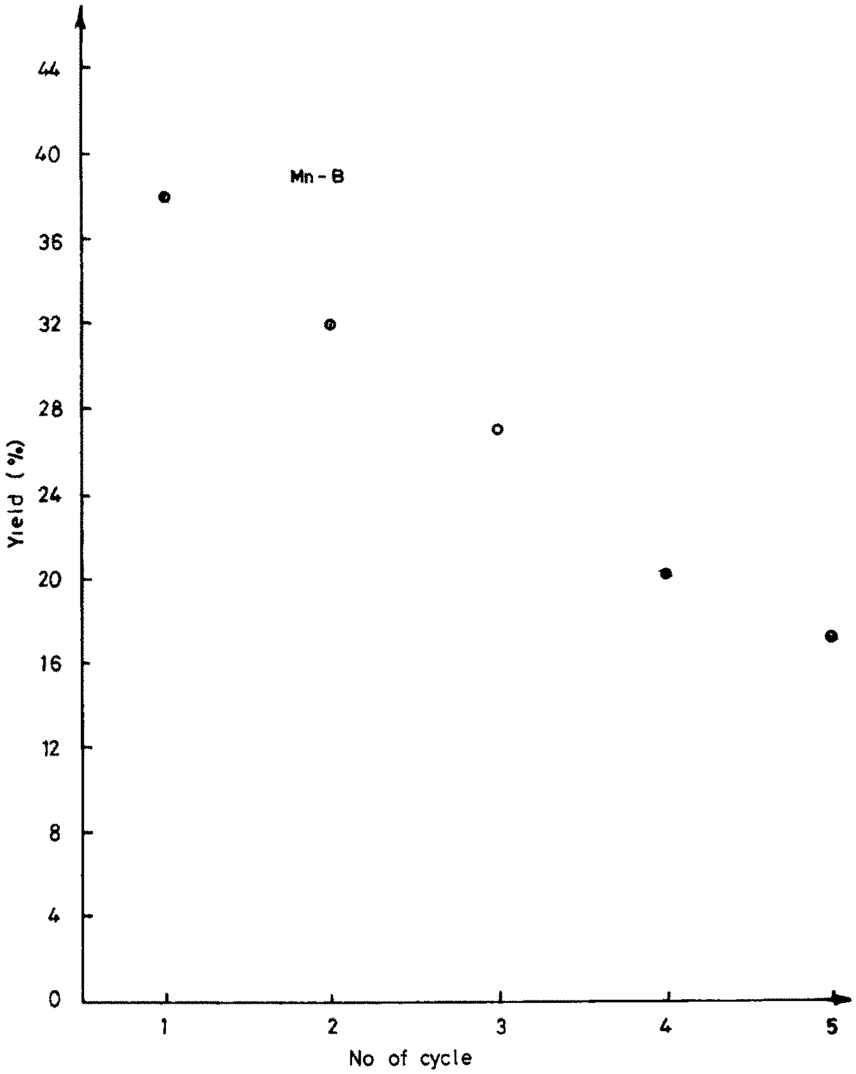
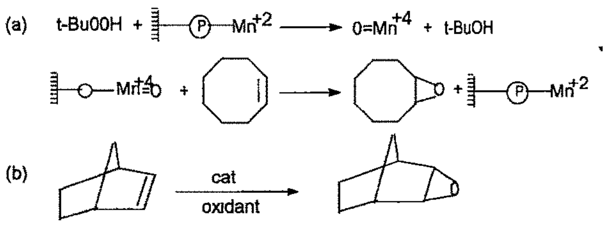


Fig 4 Profile of catalyst recycling

the metal oxocatalysed route These mechanistic processes observed in homogeneous complex catalysis may be applicable in the polymer supported metal complexes. For Mn(II) supported polymeric catalysts, the probable mechanism is shown in Scheme 2

Efforts are underway to examine the role of the coordination geometry of Mn(II) ions bound to the polymeric ligand on catalytic activity and to confirm the active species generated on the surface of the support during the oxidation.



Scheme 2 Mechanism of olefin epoxidation

4. Conclusion

Mn(II) on Schiff base bound poly(styrene-divinyl benzene) copolymer has shown to catalyze the epoxidation of norbornene and *cis*-cyclooctene in the presence of alkylhydroperoxide under mild conditions Kinetic experiments reveal that at elevated temperature the activity of the catalysts toward the epoxidation is enhanced The catalysts can be recycled several times without any loss in selectivity Slow leaching of metal was observed over reuse which can limit their application and needs further investigation

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