

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 $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ 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.

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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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with 8% crosslink were supplied by Ion-Exchange (India) Ltd., Mumbai, India, hydrated manganese chloride (Ranbaxy), TBHP (Lancaster, 70% in H₂O), 1,3-diaminopropane (Loba Chem.), *cis*-cyclooctene (Aldrich) and norbornene (Fluka) were used without further purification. All other chemicals and solvents were of analytical grade and were purified by standard methods [13].

2.2. Preparation of polymer containing Schiff base ligand

In order to functionalise the polymer support with Schiff base, chloromethylated poly(styrene-divinyl benzene) was treated with an appropriate quantity of 1,3-diaminopropane, using THF as solvent at room temperature for 48 h [14]. The beads were washed with deionised water, methanol and dry dioxane and dried at 60 °C under reduced pressure. It was then refluxed in a solution of salicylaldehyde prepared in benzene for 24 h [15]. The functionalised polymer was then purified with methanol using the soxhlet extraction method and dried under reduced pressure at 80 °C for 24 h. The formation of Schiff base of the resin was confirmed by analytical and infrared (IR) spectral data. The Schiff base from 4,4'-diaminobiphenyl were similarly prepared.

2.3. Loading of Mn(II) on to the support

Polymeric ligand (10 g) was kept in contact with 50 ml ethanol in round bottom flask for 1 h. In this (1% (w/v)) ethanolic solution (50 ml) of hydrated MnCl₂ was added over a period of 30 min with occasional shaking. The mixture was then agitated on shaker at room temperature. After 15 days brown coloured manganese loaded beads were filtered and carefully washed with ethanol. The polymer supported complex thus obtained was dried under reduced pressure for 24 h at 70 °C.

2.4. Analysis

Elemental analysis of the prepared novel catalysts were carried out using a Coleman analyser unit. Metal content on the polymer support was estimated using Zeeman ZL-4100, Perkin-Elmer AAS instrument, after digesting a known amount of catalyst

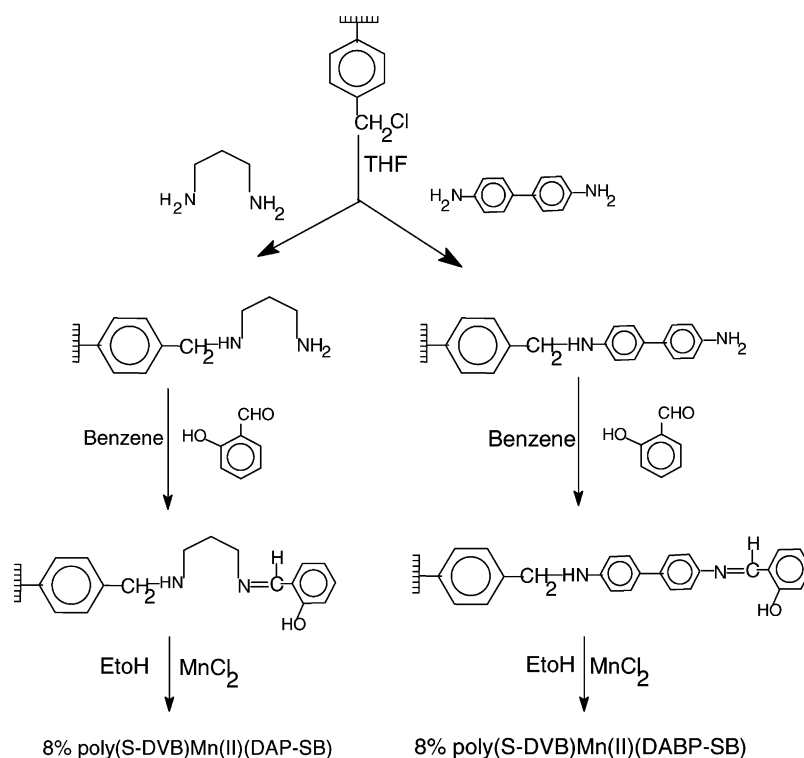
with conc. HCl (10 ml) and subsequent dilution in a volumetric flask with distilled water. Surface area of the polymer before and after complexation with metal was determined using the BET relationship with a Carlo-Erba surface analyser. IR spectra in the 50–4000 cm⁻¹ range was recorded on a Nicolet Manga-550 spectrophotometer. Thermogravimetric analysis of the catalysts were carried out on Shimadzu DT-30 analyser at a heating rate of 10 °C min⁻¹ up to 600 °C under the atmosphere of nitrogen. Diffuse reflectance spectra (200–400 nm) were recorded on a Shimadzu UV-240 instrument using optical grade BaSO₄ as the reference. Scanning electron micrographs of the catalysts and supports were taken on JEOL JSM-T 300 instrument. The analysis of various products of catalytic epoxidation were carried out on Shimadzu-15A gas chromatograph. Swelling behaviour of the freshly prepared catalysts in polar as well as non-polar solvents and their bulk densities at 27 °C were determined as previously described [16].

2.5. Procedure for catalytic epoxidation

In a typical experiment, 250 mg of polymer supported Schiff base Mn(II) complex was placed in a two-necked round bottom flask containing 20 ml methylene chloride. The catalyst beads were allowed to swell in solvent for about 30 min. To this was added norbornene (10 mmol) slowly. After brief agitation, TBHP (70% 5 mmol) was quickly added using graduated pipette. The solution was stirred for 24 h at 40 °C. Using an internal standard (PhCl) the progress of the oxidation was monitored by carefully withdrawing aliquots of the sample at specific intervals of time and estimating for the extent of product formation by GC analysis.

3. Results and discussion

The chemical modification of crosslinked chloromethylated poly(styrene-divinylbenzene) and the loading of manganese on this support was carried out as per the sequence shown in Scheme 1. The Mn(II) complexes supported on functionalised polymer were characterised by various physicochemical methods and evaluated for their activity in epoxidation of



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 ₂ Cl	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 ₂ Cl	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
<i>n</i> -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.

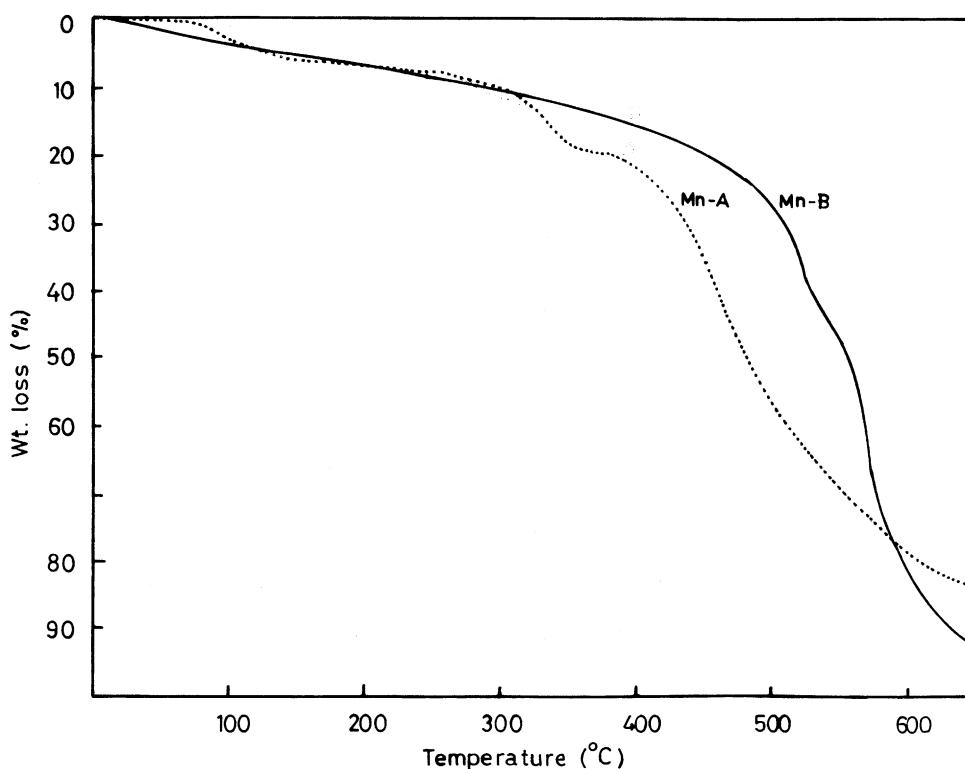


Fig. 1. TGA curves for catalyst-A and -B.

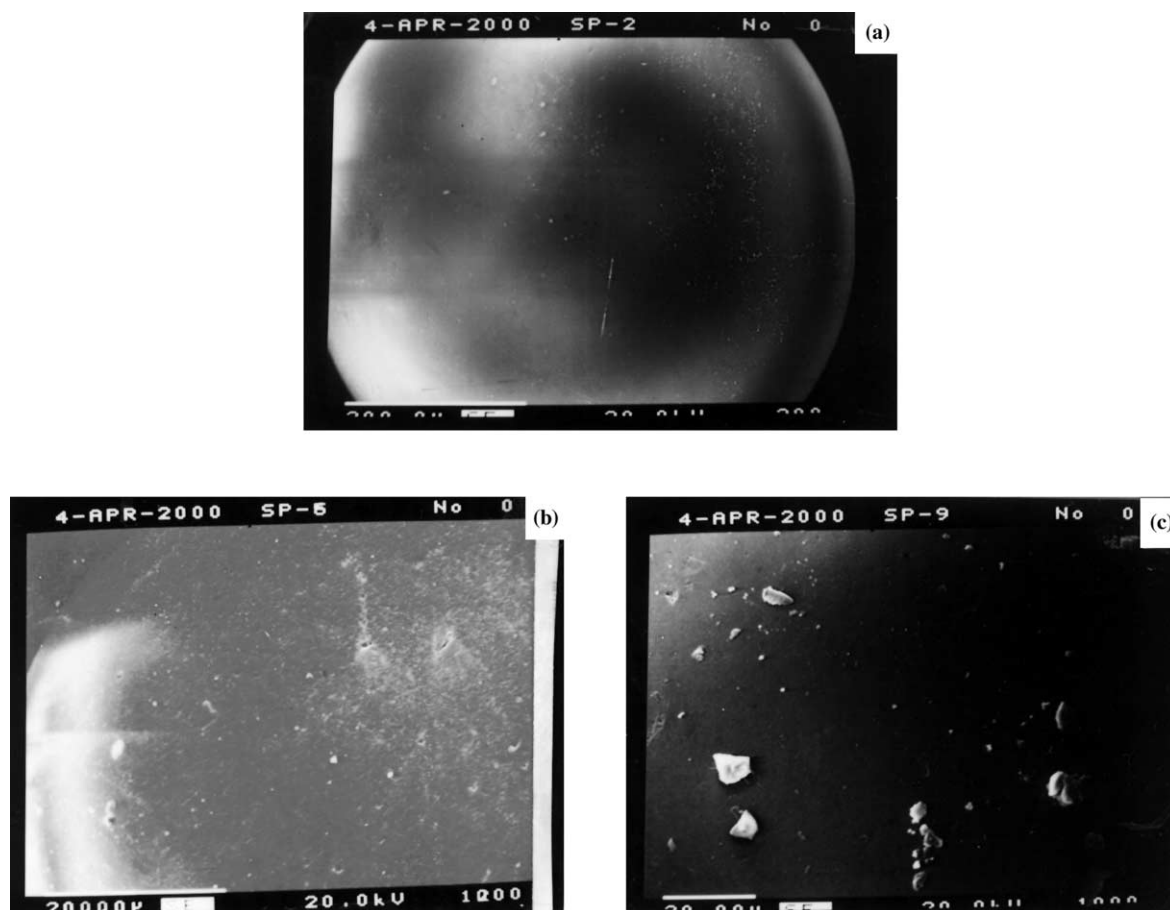


Fig. 2. Scanning electron micrographs: (a) chloromethylated poly(S-DVB), (b) catalyst-A and (c) catalyst-B.

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 BaSO₄ 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 ($4000\text{--}400\text{ cm}^{-1}$) and far ($500\text{--}50\text{ cm}^{-1}$) 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 $1660\text{--}1640\text{ cm}^{-1}$ assigned to $\nu\text{C=N}$ (azomethine) indicating the formation of Schiff base on the support. Medium intensity band at 530 cm^{-1} ($\nu\text{Mn-N}$), 754 cm^{-1} ($\nu\text{Mn-O}$) and weak intensity band at 291 cm^{-1} ($\nu\text{Mn-Cl}$) 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 ₂ Cl ₂	25	10.1
	CH ₂ Cl ₂	40	13.9
	CH ₃ CN	25	3.2
	CH ₃ CN	50	4.6
Catalyst-B	CH ₂ Cl ₂	25	9.4
	CH ₂ Cl ₂	40	12.2
	CH ₃ CN	25	2.3
	CH ₃ CN	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.

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.

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

Catalyst	Solvent	Temperature (°C)	Epoxide (%) ^b
Catalyst-A	CH ₂ Cl ₂	25	32.5
	CH ₂ Cl ₂	40	45.1
	CH ₃ CN	25	8.8
	CH ₃ CN	50	23.4
Catalyst-B	CH ₂ Cl ₂	25	29.4
	CH ₂ Cl ₂	40	37.7
	CH ₃ CN	25	5.8
	CH ₃ CN	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.

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 CH₂Cl₂, 20 ml; oxidant, TBHP 2 mmol; reaction time, 24 h.

^b Yield based on substrate taken.

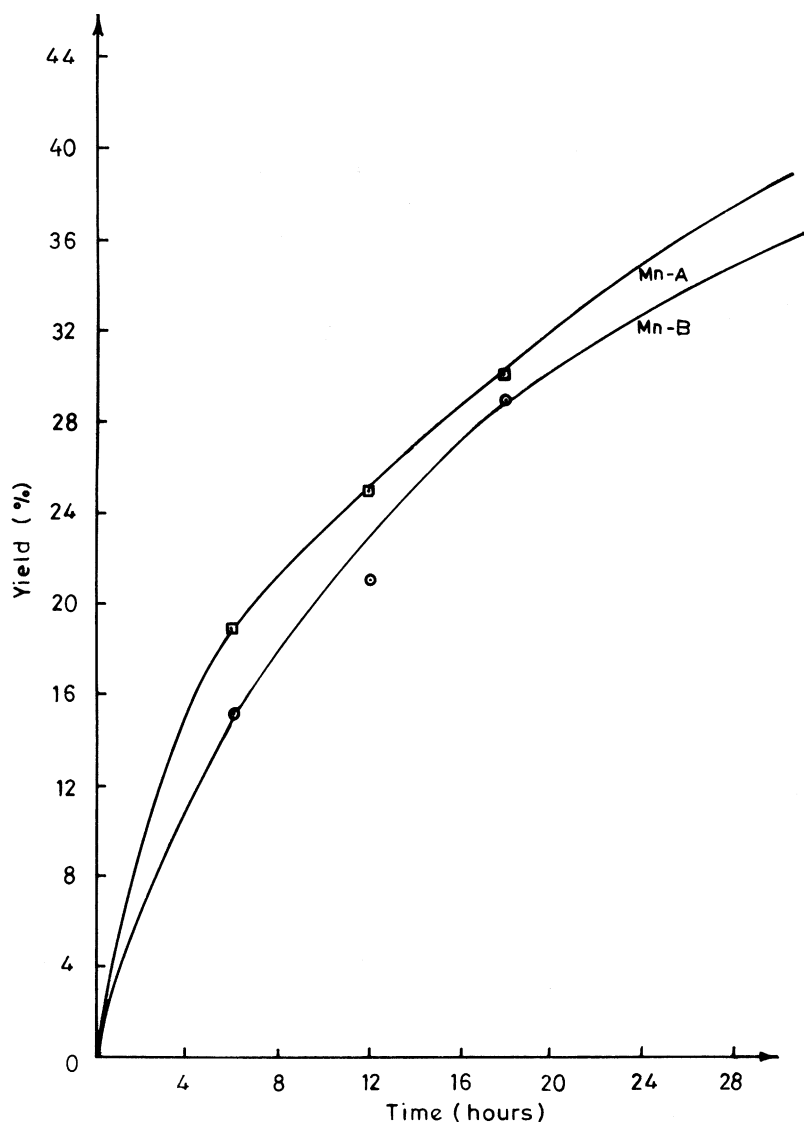


Fig. 3. Plot of conversion (%) vs. time for norbornene epoxidation using catalyst-A and -B.

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

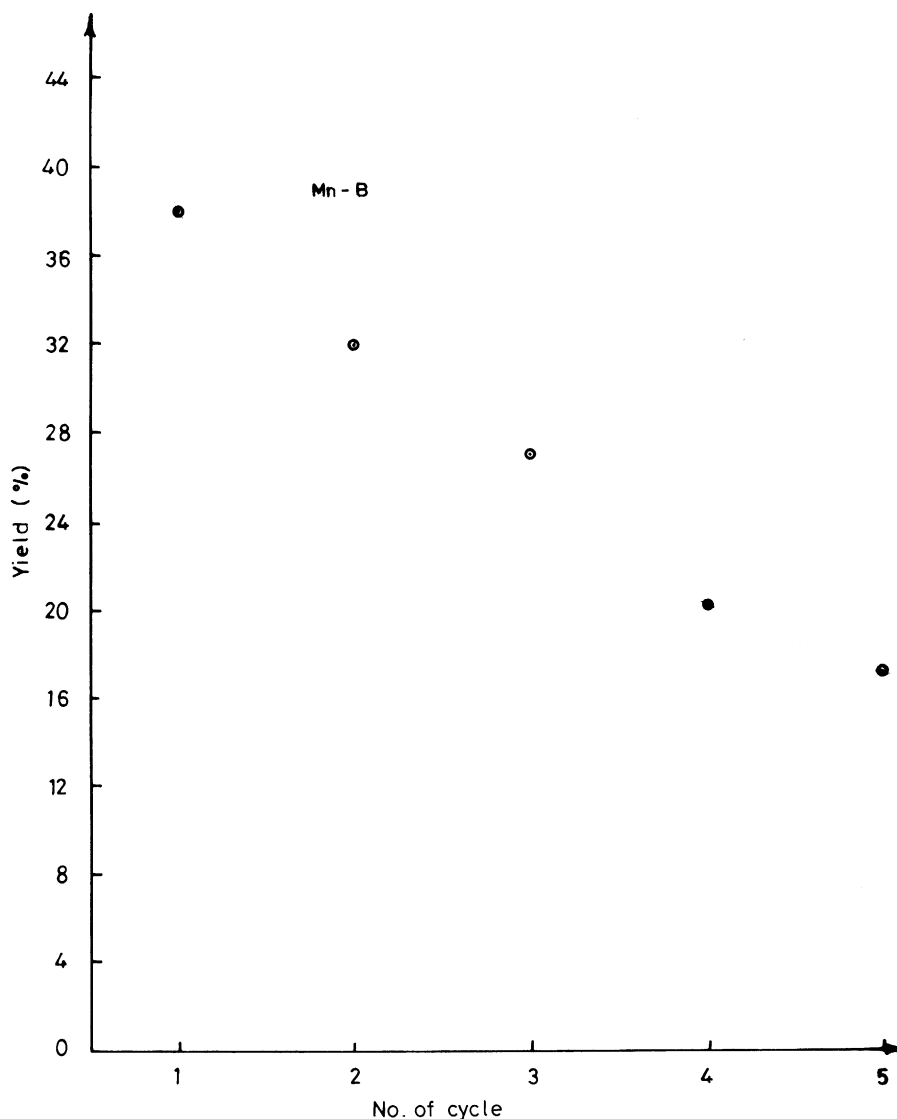
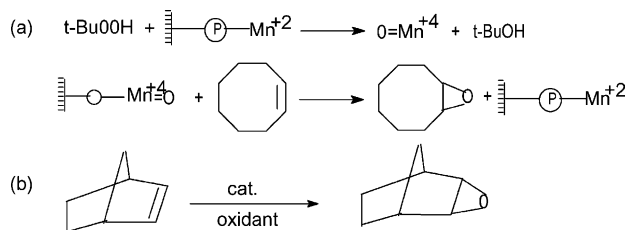


Fig. 4. Profile of catalyst recycling.

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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