CHAPTER - 4

EPOXIDATION OF OLEFINS

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4.0 INTRODUCTION

Epoxidation is one of the most useful oxidation transformation of olefins. Epoxidation functionalizes two adjacent carbon atoms to form three membered ring having one oxygen atom [1]. Polarity and the ring strain make the epoxide ring highly reactive. Often epoxides formed in an initial step react further to provide industrially important products, having variety of uses, such as surfactants or detergents, antistatic- or corrosion protection agents, additives to laundry detergents, lubricating oils, textiles and cosmetics [2].

Catalytic epoxidation requires an oxygen source i.e. electrophilic agent which may be either chemically bound oxygen such as iodosylbenzene, alkyl hydroperoxides, hydrogen peroxide, percarboxylic acid or molecular oxygen to carry out oxygen transfer to the molecule to be epoxidized.

The epoxides on the other hand are susceptible to attack by almost all known nucleophilic reagents. Ring opening which takes place by ionic mechanisms, involving the highly polar carbon-oxygen bond occurs upon reaction with haloacids, amines, water, carboxylic acids and anhydrides alcohols, hydrogen sulfides, sodium thiosulfates as well as essentially all other compounds having a labile hydrogen. Lewars [1] and Rao et al [3] have cited many of the earlier reviews on epoxides. Recent works on epoxides have been reviewed by Harvey [4], Sharpless and Verhoeven [5], Bartok and Lang [6], Plesnicar [7], Mimoun [8] and Jorgensen [9].

The ease of preparation of epoxides and their facile ring opening have made them important intermediates in organic synthesis for past several decades **c.f. Table 1**[1,10-14]. In the present decade the main objective in organic synthesis is to develop reactions which are enantio-, diastereo-, regio- and chemo- selective, for example, the enantioselective epoxidation of prochiral acyclic allyl alcohols by Katsuki and Sharpless [8] and observation of high and predictable diastereoselectivity during (i) the epoxidation of several types of cyclic unsaturated chiral alcohols with TBHP/Vo(acac)$_2$ and (ii) the preparation of epoxy alcohols via halolactonization, coupled with elegant routes for highly regioselective intermolecular ring opening of epoxides [15]. It is quite clear that epoxides are versatile intermediates for organic synthesis even in the present decade also. A number of complex compounds such as monensin [16], maytansine [17] and prostaglandins [18] have been synthesized using epoxides as intermediates.

By asymmetric epoxidation allylic alcohols are converted to optically active epoxides in better than 90% enantiomeric excess(ee), by treatment with tert-butyl hydroperoxide, titanium tetraisopropoxide and optically active diethyl tartarate [19-20] Ethylene oxide manufacturing by direct oxidation technology was invented and commercialized by Shell Oil Co. in 1958. The catalytic oxidation of ethylene with oxygen over a silver-based catalyst to yield ethylene oxide[21].

Molybdenum, Vanadium and Tungsten have been proposed as liquid-phase catalysts for the oxidation of ethylene by hydroperoxide to ethylene oxide [22], where tert-butyl hydroperoxide is the preferred oxidant.

One of the important developments in the epoxide chemistry during the past 25 years is the use of alkyl hydroperoxide for the preparation of epoxide from olefins, in the presence of high-valent d^0 transition metal complexes as shown in **Table 2** [23].

The polymer bound metalloporphyrins of Fe(III) and other metals for epoxidation of olefins using hydrogen peroxide as an oxidant have a higher catalytic activity as compared to homogeneous system [24]. Polymer supported transition metal complexes for catalytic epoxidation of olefin using iodosylbenzene (PhIO) as the terminal oxidant have been used [25], where in the rate of epoxidation is shown to be relatively low, but proceeding steadily.

Asymmetric epoxidation of allylic alcohols is catalyzed by polymer anchored amino alcohol-molybdenum complexes. The polymer yielded a low **ee** in the epoxidation of allylic alcohol compared to the non-supported complex [26].

In the present study an attempt has been made to investigate the catalytic epoxidation of norbornene and *cis*-cyclooctene to the corresponding epoxides i.e. norbornene oxide and *cis*-cyclooctene oxide respectively, using polymer bound metal complexes as catalysts The synthesized polymer bound metal complexes of ruthenium (III) and manganese (II) were used to study the above mentioned reactions in the presence of *tert*-butylhydroperoxide under mild operating conditions The influence of various parameters such as concentration of the catalyst and the substrate, temperature of the system and usage of various solvents were investigated. Furthermore, stability of the catalysts was also studied by the life cycle efficiency of the respective catalysts.

Table 1
Reaction of epoixides

Reaction number	Reagent*	Product name
1	H_2O	vicinal diol
2	ROH	β-hydroxyether
3	RCOOH	β-hydroxyester
4	HX	halohydrin
5	H_2S	β-hydroxythiol
6	HCN	β-hydroxynitrile
7	$R\text{-}CH_2\text{-}CO_2Et$	lactone
8	NH_3	monoalkanolamine
9	PR_3	olefin
10	CO_2	carbonate

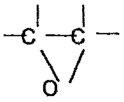
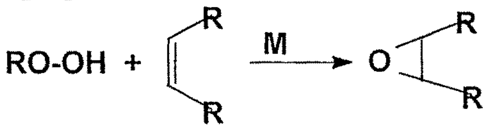
*Reagent reacts with epoxide 

Table 2
Alkene epoxidation by transition metal catalyzed reaction with alkyl hydroperoxides[23]



R	Alkene	Catalyst	% Epoxide
t-Bu	Cyclohexene	MoO_3	99
t-Bu	Cyclohexene	$MoO_3(acac)_2$	86
Cumyl	Cyclohexene	V-naphtha	97
sec-Bu	Cyclopentene	V-octoate	98
t-Bu	1-Octene	Na_2MoO_4	89
t-Bu	1-Octene	$Na_4(PMo_{12}O_4)$	89
Cumyl	1-Octene	MoO_3	84
t-Amyl	1-Propene	Mo-naphth	78
Cumyl	2-Methyl-2-Pentene	Na_2MoO_4	97

4.1 POLY(STYRENE-DIVINYLBENZENE) SUPPORTED RUTHENIUM(III) COMPLEXES

The Ru(III) complexes supported on modified polystyrene-Schiff bases (Scheme given in Chapter-2) were evaluated for their catalytic activity in epoxidation of norbornene and *cis*-cyclooctene The different catalysts employed in this study are designated as under

Ru-A	5% Poly(S-DVB)Ru(III)(1,3-dap-SB)
Ru-B	8% Poly(S-DVB)Ru(III)(1,3-dap-SB)
Ru-C	5% Poly(S-DVB)Ru(III)(4,4'-dabp-SB)
Ru-D	8% Poly(S-DVB)Ru(III)(4,4'-dabp-SB)

4.1.1 CATALYTIC ACTIVITY

Tertiary butyl hydroperoxide (TBHP, t-BuOOH) was used as the terminal oxidant in the epoxidation of *cis*-cyclooctene and norbornene in presence of catalysts, **Ru-A** to **Ru-D** at room temperature to 40°C and/or 50°C Control experiments showed that the alkenes did not undergo epoxidation in the absence of either the catalyst or oxidant. When the molecular oxygen was used as the source of oxidant in place of t-butyl hydroperoxide practically no reaction occurred The results of epoxidation of *cis*-cyclooctene and norbornene in methylene chloride and acetonitrile using supported Ru-catalysts are given in **Table 4.1** and **4.2.**

Analysis of epoxidation products showed that both in the case of *cis*-cyclooctene and norbornene, the corresponding epoxides were selectively formed in presence of t-butyl hydroperoxide. All the catalysts facilitate the epoxidation at room temperature with generally low yield of products (5.8 - 9.9 % of norbornene oxide and 15.0 - 20.0 % of *cis*-cyclooctene oxide) However, at slightly elevated temperature (40-50^{0}C) there is significant increase in the corresponding yields of epoxides (13.9 - 18.5 % of norbornene oxide and 20 2 - 29.0% of *cis*-cyclooctene oxide). The observation is evident for both norbornene and *cis*-cyclooctene

Catalytic activity was much more pronounced in methylene chloride medium than in acetonitrile. Interestingly, in both the olefins, G.C. analysis showed the selective formation of epoxides. From the data obtained, it appears that the observed selectivities and yields are comparable to other mononuclear and binuclear Ru(III)-Schiff base complexes [27-31]. In general, the polymeric Ru-bound catalysts **Ru-B** and **Ru-D** showed marginally better catalytic activity than **Ru-A** and **Ru-C**. A few experiments were also carried out to find the extent of epoxidation at different time intervals for oxidation of *cis*-cyclooctene at 40^{0}C. A plot of time Vs % conversion is shown in **Fig. 4.1.** With all the catalysts i.e Ru-A to Ru-D even after 24 h the reaction is found to proceed slowly, though there is no marked increase in yields. The slower rate of the reaction (24h) exhibited by polymer bound catalysts described above is attributed mainly to the slower diffusion of substrate olefins into the polymer matrix where the active sites are located [32]

To evaluate the effect of various reaction parameters on catalytic performance a systematic study was carried out on the epoxidation of *cis*-cyclooctene as the substrate using the **Ru-A** to **Ru-D**. The extent of epoxidation was measured at different temperatures, catalyst concentration and amount of substrate used (**Table 4.3-4.5**). It is clear from the results obtained that all three parameters influence the epoxidation of olefins. Schiff base complexes of other metal ions such as Fe(II), Ni(II) and Cu(II) anchored on to a solid support such as zeolites, clay and macroporous polymers are reported to catalyze olefin epoxidation using iodosylbenzene as the oxygen source [33-34].

Direct comparison of activity of homogeneous Ru(III) complexes with Schiff base ligands used in present study would reflect the actual catalytic efficiency of supported vis-à-vis unsupported catalysts under optimized reaction condition. The results of homogeneous catalysis are summarized in **Table 4.6**. Comparison of catalytic activity based on ruthenium content shows that supported catalyst shows more efficiency than its nonsupported counterpart

Table 4.1
Epoxidation of norbornene with polymer anchored Ru catalysts[a]

Run	Catalyst	Solvent	Temperature (°C)	Yield of epoxide[b] (%)
1	Ru-A	CH_2Cl_2	25	09 8
2	Ru-B	CH_2Cl_2	25	09 6
3	Ru-C	CH_2Cl_2	25	08 4
4	Ru-D	CH_2Cl_2	25	05.8
5	Ru-A	CH_2Cl_2	40	17 4
6	Ru-B	CH_2Cl_2	40	18 5
7	Ru-C	CH_2Cl_2	40	14.3
8	Ru-D	CH_2Cl_2	40	17.6
9	Ru-A	CH_3CN	25	09 0
10	Ru-B	CH_3CN	25	09.9
11	Ru-C	CH_3CN	25	07 9
12	Ru-D	CH_3CN	25	06 0
13	Ru-A	CH_3CN	50	15.0
14	Ru-B	CH_3CN	50	18.0
15	Ru-C	CH_3CN	50	13.9
16	Ru-D	CH_3CN	50	16 5

[a] *Conditions : Catalyst A-D=0 25 g, Norbornene (5 mmol); TBHP (2mmol), Time 24h,*

[b] *yield based on substrate taken*

Table 4.2
Epoxidation of *cis*-cyclooctene with polymer anchored Ru catalysts[a]

Run	Catalyst	Solvent	Temperature (°C)	Yield of epoxide[b] (%)
1	Ru-A	CH_2Cl_2	25	17.2
2	Ru-B	CH_2Cl_2	25	20.0
3	Ru-C	CH_2Cl_2	25	15.9
4	Ru-D	CH_2Cl_2	25	17.5
5	Ru-A	CH_2Cl_2	40	21.8
6	Ru-B	CH_2Cl_2	40	29.0
7	Ru-C	CH_2Cl_2	40	21.6
8	Ru-D	CH_2Cl_2	40	23.0
9	Ru-A	CH_3CN	25	15.6
10	Ru-B	CH_3CN	25	18.9
11	Ru-C	CH_3CN	25	15.0
12	Ru-D	CH_3CN	25	16.0
13	Ru-A	CH_3CN	50	20.2
14	Ru-B	CH_3CN	50	27.7
15	Ru-C	CH_3CN	50	21.0
16	Ru-D	CH_3CN	50	23.2

[a] *Conditions Catalyst A-D 0.25 g, cis-Cyclooctene (5 mmol); TBHP (2mmol), Time 24h*

[b] *yield based on substrate taken*

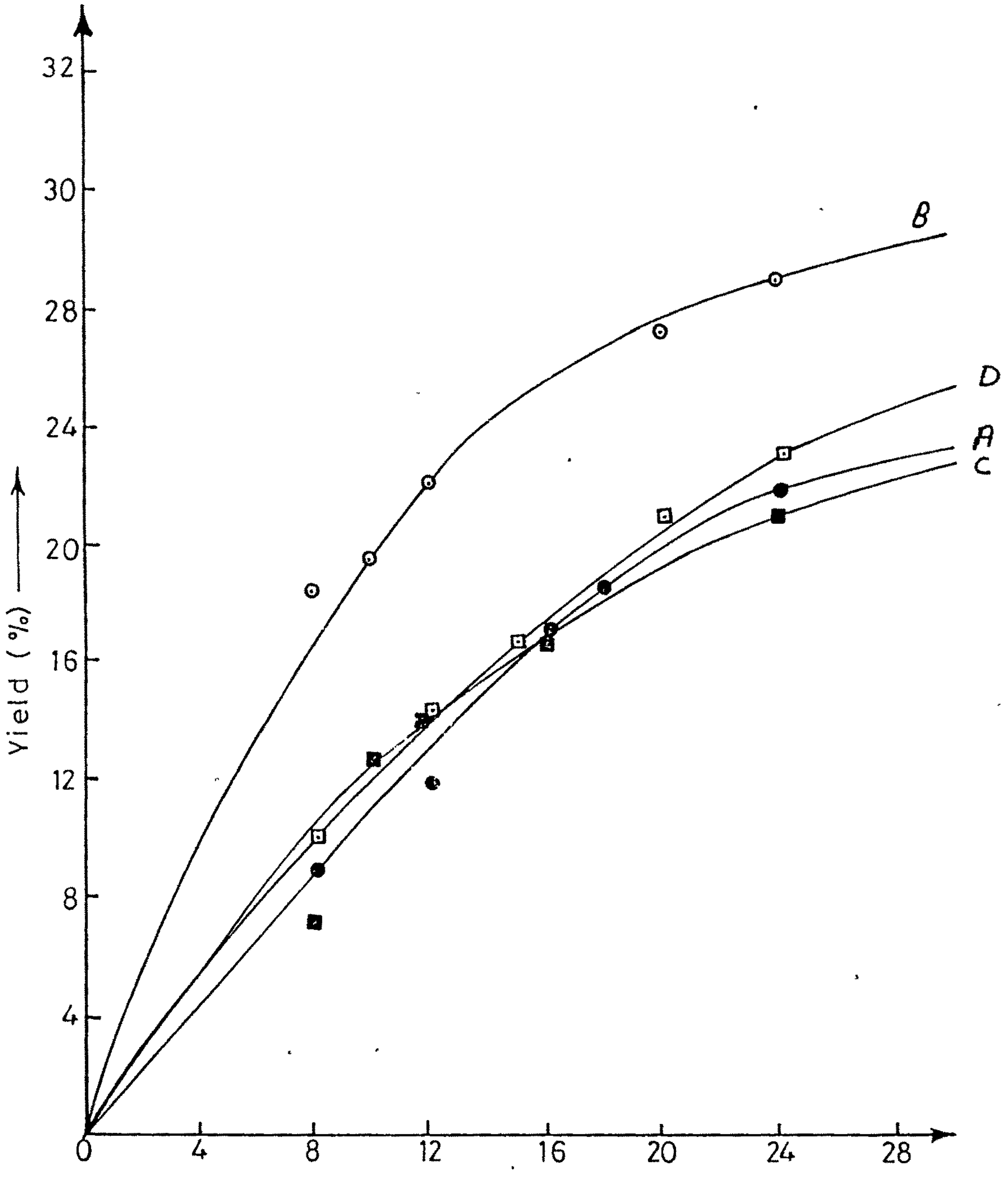


Fig. 4.1 Profile of conversion *VS* time of catalysts (A) Ru-A (B) Ru-B (C) Ru-C (D) Ru-D

Table 4.3
Epoxidation under the different amount of substrate[a]

Catalyst	Amount of substrate (mmol)	Yield of epoxide[b] (%)
Ru-A	2	08 8
	3	12 7
	4	18 4
	5	21 8
Ru-B	2	08 5
	3	15 9
	4	24 8
	5	29.0
Ru-C	2	07 6
	3	11 9
	4	18 6
	5	21 6
Ru-D	2	08 1
	3	13 3
	4	20 8
	5	23 0

[a] *Reaction conditions · cis-Cyclooctene, Solvent(CH_2Cl_2),20ml,*
Temp ,40^0C, Catalyst,0 25 g; Time, 24h;TBHP ; 2mmol

[b] *yield based on substrate*

Table 4.4
Epoxidation under the different amount of catalyst[a]

Catalyst	Amount of catalyst (gm)	Yield of epoxide[b] (%)
Ru-A	0 15	13 4
	0 25	21.8
	0 35	23 5
	0 45	25 9
Ru-B	0 15	20 8
	0 25	29 0
	0 35	29 9
	0 45	31 2
Ru-C	0 15	12 7
	0 25	21 6
	0 35	22 8
	0 45	24 5
Ru-D	0 15	18 5
	0 25	23 0
	0 35	24 7
	0 45	27 4

[a] *Reaction conditions cis-Cyclooctene,5 mmol; Solvent(CH_2Cl_2),20ml, Temp ,40^0C , Time, 24h;TBHP, 2mmol*

[b] *yield based on substrate*

Table 4.5
Epoxidation under the different temperature[a]

Catalyst	Temperature (°C)	Yield of epoxide[b] (%)
Ru-A	25	17 5
	30	18 5
	35	21 3
	40	23 0
Ru-B	25	20 0
	30	21 8
	35	25 0
	40	29 0
Ru-C	25	15 9
	30	17 0
	35	18 2
	40	21 6
Ru-D	25	17 2
	30	18 0
	35	19 9
	40	21 9

[a] *Reaction conditions · cis-Cyclooctene,5 mmol; Solvent(CH_2Cl_2),20ml, Catalyst,0 25g;Time, 24h, TBHP, 2 mmol*

[b] *yield based on substrate*

Table 4.6
***cis*-Cyclooctene epoxidation with homogeneous Ru-catalysts**[a]

Catalyst	Temperature (°C)	Yield of epoxide[b] (%)
[Ru(1,3-dap-SB)Cl_3]	25	20.8
	40	28.9
[Ru(4,4'-dabp-SB)Cl_3]	25	18 8
	40	24.0

[a] *Reaction conditions : cis-Cyclooctene,5 mmol; Solvent(CH_2Cl_2),20ml, Catalyst,0.5g, TBHP,2 mmol; Time, 24h*

[b] *yield based on substrate*

4.2 POLY(STYRENE-DIVINYLBENZENE) SUPPORTED Mn(II)-SCHIFF BASE COMPLEXES

The Mn(II) complexes supported on modified polystyrene-Schiff bases were evaluated for their catalytic activity in epoxidation of norbornene and *cis*-cyclooctene The different catalysts employed in this study are designated as under

Mn-A	5%Poly(S-DVB)Mn(II)(1,3-dap-SB)
Mn-B	8%Poly(S-DVB)Mn(II)(1,3-dap-SB)
Mn-C	5%Poly(S-DVB)Mn(II)(4,4'-dabp-SB)
Mn-D	8%Poly(S-DVB)Mn(II)(4,4'-dabp-SB)

4.2.1 CATALYTIC EPOXIDATION

Catalysts **Mn-A** to **Mn-D** were employed in the epoxidation of electron rich olefins such as norbornene and *cis*-cyclooctene as substrate. The results showed that, the epoxidation at room temperature gave lower yield of products However, at slightly elevated temperature (40-50^{0}C) there is an increase in the corresponding yields of epoxides **(Table 4.7- 4.8)** in the case of both norbornene and *cis*-cyclooctene Catalytic activity is more pronounced in methylene chloride medium than in acetonitrile medium In both the olefins there was selective formation of corresponding epoxides. Maximum activity was exhibited by **Mn-A** and **Mn-B** catalysts derived from 1,3-diaminopropane Schiff base The degree of cross linking in the polymer support as well as the mode of binding of the Schiff base to the Mn(II) centre probably determines the relative activity of the catalyst during the epoxidation Initially an induction period of about 30-40 min was observed for all the four **Mn-A** to **Mn-D** catalysts Moreover, comparable olefin conversions could be reached only after 24 h reaction time Few experiments were carried out to find the extent of epoxidation at different time intervals as shown in **Fig. 4.2.** Such a low rate of catalysis has often been encountered by other workers using transitional metal complexes bound to surface of functionalised polymer [19,20] This behaviour is primarily due to the slow diffusion of substrate olefins from the solution phase to the active metal centres in the polymer matrix leading to the rate limiting process In the present case despite the relatively poor swellability of the microporous polymer bound metal complexes (<6%) in common organic solvents the overall conversions of upto 45% epoxides indicates that catalytic sites are essentially localized in the accessible regions of the polymer matrices

In order to understand the effect of various reaction parameters on catalytic performance a systematic study was carried out on the epoxidation of norbornene and *cis*-cyclooctene as substrate using **Mn-A** to **Mn-D** catalysts The extent of epoxidation observed at different amount of substrate, catalyst concentration and temperature are summarized in **Table 4.9- 4.11**. From the results obtained it is clear that different amount of substrate, catalyst and temperature influence the epoxidation reaction.

The activity determination of homogeneous Mn-Schiff base catalysts was carried out for epoxidation of norbornene as substrate and TBHP as oxidant The results of the epoxidation reaction are summarized in **Table 4.12** Comparison of catalytic activity calculated on the basis of active metal species indicates that supported catalysts are significantly more efficient than their homogeneous counterparts In other words, to obtain comparable activity, a higher concentration of homogeneous complex than supported complex is required

Table 4.7
Epoxidation of norbornene with polymer anchored Mn-catalysts[a]

Run	Catalyst	Solvent	Temperature (°C)	Yield of epoxide[b] (%)
1	Mn-A	CH_2Cl_2	25	30 1
2	Mn-B	CH_2Cl_2	25	32 5
3	Mn-C	CH_2Cl_2	25	21 9
4	Mn-D	CH_2Cl_2	25	29.4
5	Mn-A	CH_2Cl_2	40	40 1
6	Mn-B	CH_2Cl_2	40	45.1
7	Mn-C	CH_2Cl_2	40	30 6
8	Mn-D	CH_2Cl_2	40	37.7
9	Mn-A	CH_3CN	25	06 5
10	Mn-B	CH_3CN	25	08 8
11	Mn-C	CH_3CN	25	04.1
12	Mn-D	CH_3CN	25	05.8
13	Mn-A	CH_3CN	50	18 6
14	Mn-B	CH_3CN	50	23.4
15	Mn-C	CH_3CN	50	11 2
16	Mn-D	CH_3CN	50	13.4

[a] *Conditions Catalyst A-D=0 25 g, Norbornene (5 mmol), TBHP (2mmol), Time 24h*

[b] *yield based on substrate taken*

Table 4.8
Epoxidation of *cis*-cyclooctene with polymer anchored Mn-catalysts[a]

Run	Catalyst	Solvent	Temperature (°C)	Yield of epoxide[b] (%)
1	Mn-A	CH_2Cl_2	25	08 9
2	Mn-B	CH_2Cl_2	25	10 1
3	Mn-C	CH_2Cl_2	25	06 6
4	Mn-D	CH_2Cl_2	25	09 4
5	Mn-A	CH_2Cl_2	40	12 9
6	Mn-B	CH_2Cl_2	40	13.9
7	Mn-C	CH_2Cl_2	40	11.0
8	Mn-D	CH_2Cl_2	40	12.2
9	Mn-A	CH_3CN	25	02.1
10	Mn-B	CH_3CN	25	02 3
11	Mn-C	CH_3CN	25	01 8
12	Mn-D	CH_3CN	25	02.3
13	Mn-A	CH_3CN	50	03.9
14	Mn-B	CH_3CN	50	04.6
15	Mn-C	CH_3CN	50	03.4
16	Mn-D	CH_3CN	50	03.8

[a] *Conditions Catalyst A-D 0.25 g; cis-Cyclooctene (5 mmol); TBHP (2mmol); Time 24h*

[b] *yield based on substrate taken*

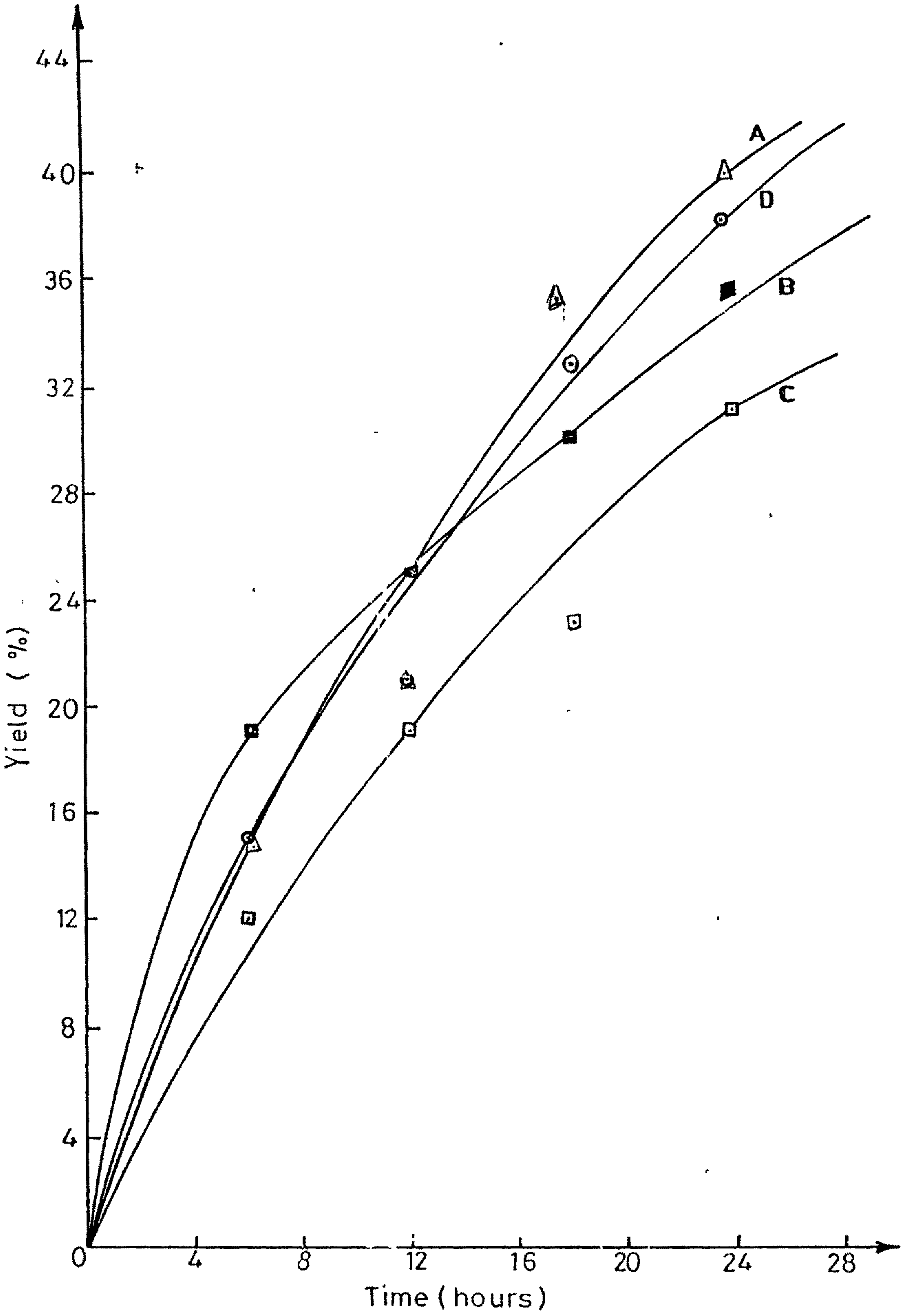


Fig. 4.2 Profile of conversion *VS* time of catalysts (A) Mn-A (B) Mn-B (C) Mn-C (D) Mn-D

Table 4.9
Epoxidation under the different amount of substrate[a]

Catalyst	Amount of substrate (mmol)	Yield of epoxide[b] (%)
Mn-A	05	40 1
	10	43 0
	15	46 8
Mn-B	05	45 1
	10	48 2
	15	53 8
Mn-C	05	30 6
	10	36 8
	15	40 9
Mn-D	05	37 7
	10	42 0
	15	45 2

[a] *Reaction conditions . Norbornene, Solvent(CH_2Cl_2),20ml, Temp ,40^0C; Catalyst,0.25 g, Time, 24h; TBHP, 2mmol.*

[b] *yield based on substrate*

Table 4.10
Epoxidation under the different amount of catalyst[a]

Catalyst	Amount of catalyst (gm)	Yield of epoxide[b] (%)
Mn-A	0.15	30 2
	0 25	40.1
	0 35	45 0
Mn-B	0.15	38 0
	0 25	45 1
	0 35	51 9
Mn-C	0 15	23 6
	0 25	30 6
	0 35	36 6
Mn-D	0 15	24 2
	0 25	37 7
	0 35	42 8

[a] *Reaction conditions : Norbornene,5 mmol , Solvent(CH_2Cl_2),20ml, Temp ,40^{0}C , Time, 24h, TBHP,2mmol*

[b] *yield based on substrate*

Table 4.11
Epoxidation under the different temperature[a]

Catalyst	Temperature (°C)	Yield of epoxide[b] (%)
Mn-A	25	30 1
	35	37.2
	40	40 1
Mn-B	25	32.5
	35	41 9
	40	45 1
Mn-C	25	21 5
	35	26.7
	40	30 6
Mn-D	25	29 4
	35	32 2
	40	37 7

[a] *Reaction conditions Norbornene,5 mmol, Solvent(CH_2Cl_2),20ml, Catalyst,0 25g,Time, 24h, TBHP, 2mmol.*

[b] *yield based on substrate*

Table 4.12
Norbornene epoxidation with homogeneous Mn-catalysts[a]

Catalyst	Temperature (°C)	Yield of epoxide[b] (%)
[Mn(1,3-dap-SB)Cl_3]	25	35.8
	40	40.9
[Mn(4,4'-dabp-SB)Cl_3]	25	29.9
	40	36.6

[a] *Reaction conditions : Norbornene,5 mmol; Solvent(CH_2Cl_2),20ml, Catalyst,0.5g; TBHP, 2 mmol; Time, 24h*

[b] *yield based on substrate*

4.3 MECHANISTIC ASPECTS

Both homogeneous and heterogeneous catalysts capable of selectively epoxidising a wide range of olefins have been developed. Much progress has been made in understanding the nature of the active catalyst and mechanism involved in their formation [35-41].

For epoxidation of alkenes using *tert*-butylhydroperoxide, the mechanistic model of Sheldom [42], Gould [43], Imanura et.al [44] and Sherrington et al [45] has been extended to the present system. The reaction of alkyl hydroperoxides in the presence of metal catalysts follow two major pathways[41-48]

(1) Homolytic and
(2) Heterolytic

Homolytic decomposition of alkyl hydroperoxides is catalyzed by transition metal complexes and involves *tert*-alkoxy and *tert*-alkylperoxy radicals as reactive intermediates formed *via* the one electron redox processes whereas in heterolytic reactions of alkyl hydroperoxides the principal function of the metal catalyst is to withdraw electrons from the O--O bond *via* coordination, thus making it more susceptible to heterolysis by attacking nucleophiles The extent of charge transfer is related to the lewis acidity of the catalysts, which generally increase with increasing oxidation state of the central metal atom [49] Moreover, it has been found that the peroxometal species are generally favoured with early transition metals viz Mo(VI), W(VI), V(V) etc.[50] On the other hand many from transition metals including ruthenium, iron and manganese follow the metal oxo catalyzed route [46].

Experiments were carried out to ascertain the nature of oxidation using 2,6 di-*tert*-butyl 4-methylphenol (BHT) as a free radical trap which is known to scavenge the peroxy radicals produced by homolytic scission of peroxide bond [51]. The experimental procedure adopted to study the probable mechanistic pathway is as follows

250 mg of polymer supported metal complex was placed in a 2-necked round bottomed flask containing 20ml methylene chloride. The catalyst beads were allowed to swell in the solvent for about 30 min. To this, BHT (0.2 mmol) was added, followed by slow addition of olefins (5 mmol). After a brief agitation, TBHP (70% in H_2O, 2 mmol) was quickly added using a graduating pipette. The solution was stirred for 24h at 40°C, the extent of product formation was estimated by GC analysis using chlorobenzene as internal standard. The results of these studies on representative catalysts are given in **Table 4.13-4.14.**

It is known that BHT scavenges peroxy free radicals suppressing the yield of epoxide by radical autooxidation (homolytic cleavage of peroxide bond) process Results indicate that BHT did not completely suppress the reaction but peroxide yields were reduced. The overall reduction in yields was 24-25 % for ruthenium catalysts and about 28-32 % for manganese catalysts. In experiment the reaction is only partially suppressed and no other free radical induced side products were detected By-products result from sebsequent reactions of alkoxy and alkylperoxy radicals with substrate[52]. For the present Ru(III) and Mn(II) catalysts preliminary results suggest that the major route for epoxide formation is by a heterolytic mechanism. However, simultaneous existence of a homolytic reaction cannot be overruled. A simplified dual mechanistic pathway for the catalytic epoxidation of *cis*-cyclooctene by Ru(III) catalysts in the presence of TBHP is shown in **Scheme 4.1** which can be extended to Mn(II) systems (**Scheme 4.2**). It may be pointed out that the involvement of active oxo-Ru(V) and oxo-Mn(IV) complex during the epoxidation can be postulated for our system but direct experimental evidence for the formation of these species is lacking.

Table 4.13
Epoxidation of *cis*-cyclooctene with polymer supported Ru-catalysts using additives[a]

Catalyst	Additive	Temp.(°C)	Epoxide(%)[b]
Ru-A	BHT	25	13 1(17 2)*
		40	17.9(21 8)
Ru-B	BHT	25	15 1(20.0)
		40	21.9(29 0)
Ru-C	BHT	25	11.9(15.9)
		40	16.1(21.6)
Ru-D	BHT	25	13 1(17.5)
		40	17.3(23.0)

[a] *Reaction conditions : Solvent = CH_2Cl_2(20 ml); cis-Cyclooctene = 5mmol; TBHP = 2mmol, Additive = 0.2mmol*

[b] *yield based on substrate taken*

**value in the parenthesis indicate the % yield the absence of additive*

Table 4.14
Epoxidation of norbornene with polymer supported Mn-catalysts using additives[a]

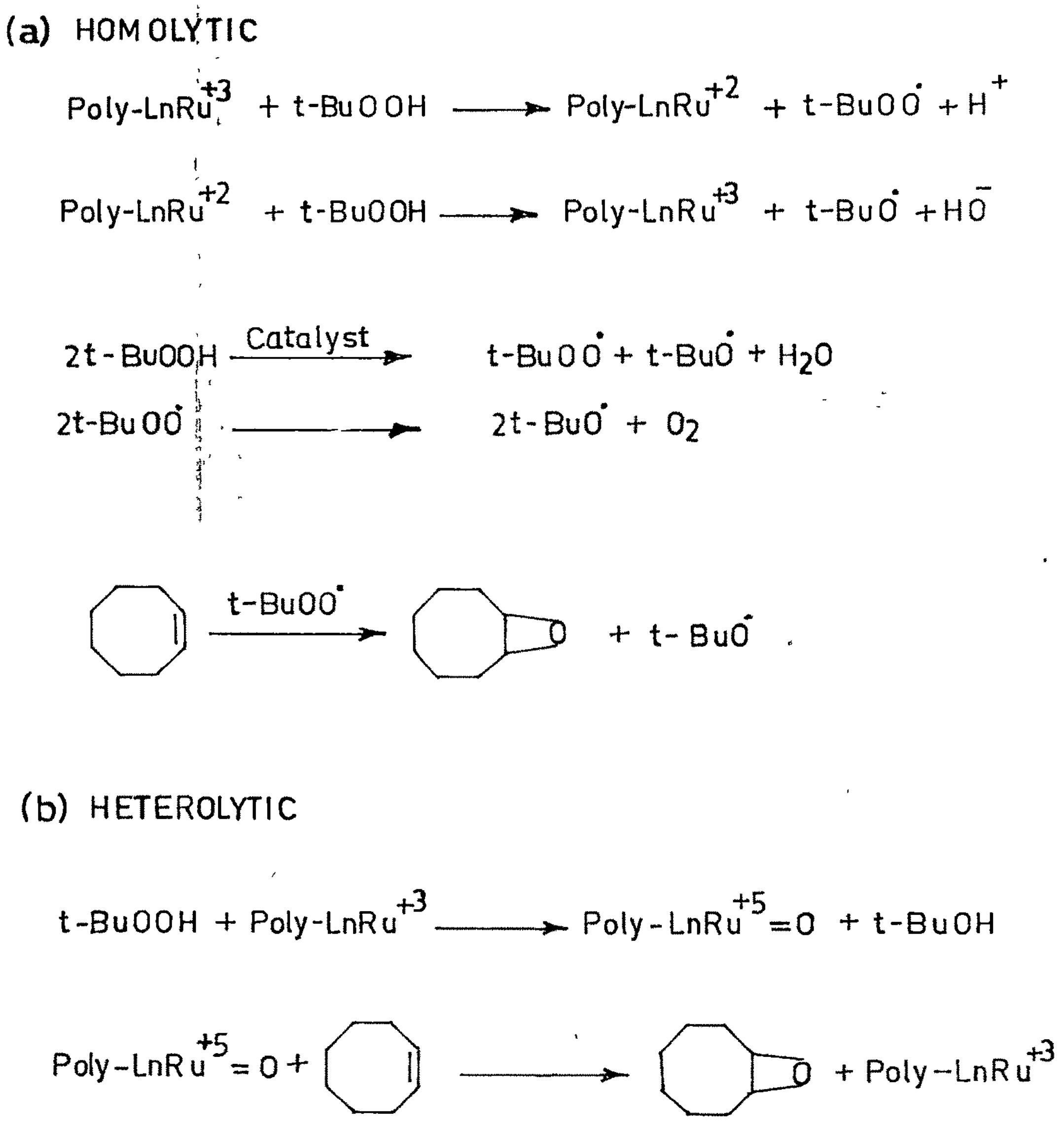
Catalyst	Additive	Temp.(^{o}C)	Epoxide(%)[b]
Mn-A	BHT	25	21.8(30.1)*
		40	29.1(40.1)
Mn-B	BHT	25	22.0(32.5)
		40	33.3(45.1)
Mn-C	BHT	25	15.1(21.9)
		40	22.0(30.6)
Mn-D	BHT	25	21.4(29.4)
		40	27.4(37.7)

[a] *Reaction conditions . Solvent = CH_2Cl_2(20 ml), Norbornene = 5mmol; TBHP = 2mmol, Additive = 0.2mmol*

[b] *yield based on substrate taken*

**value in the parenthesis indicate the % yield the absence of additive*

Mechanism



(a) HOMOLYTIC

$$\text{Poly-LnRu}^{+3} + t\text{-BuOOH} \longrightarrow \text{Poly-LnRu}^{+2} + t\text{-BuO}\dot{\text{O}} + \text{H}^{+}$$

$$\text{Poly-LnRu}^{+2} + t\text{-BuOOH} \longrightarrow \text{Poly-LnRu}^{+3} + t\text{-Bu}\dot{\text{O}} + \text{H}\bar{\text{O}}$$

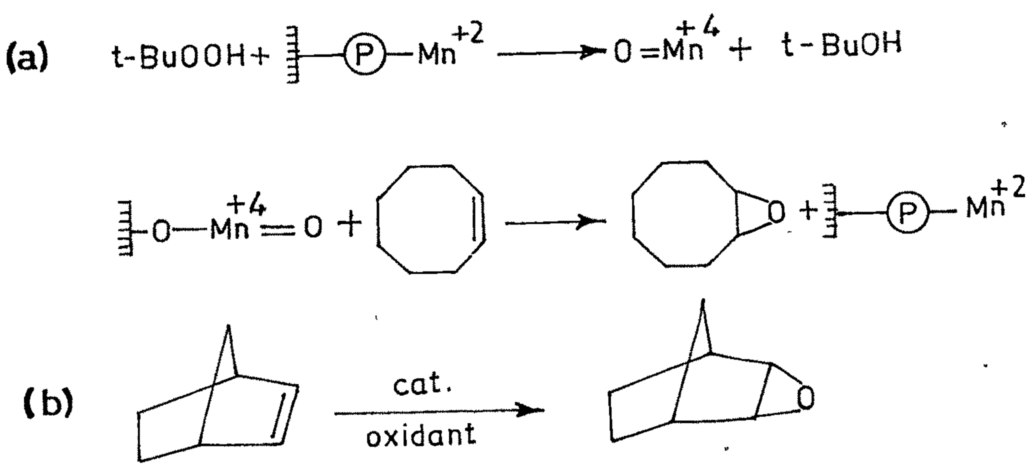
$$2t\text{-BuOOH} \xrightarrow{\text{Catalyst}} t\text{-BuO}\dot{\text{O}} + t\text{-Bu}\dot{\text{O}} + H_2O$$

$$2t\text{-BuO}\dot{\text{O}} \longrightarrow 2t\text{-Bu}\dot{\text{O}} + O_2$$

(b) HETEROLYTIC

$$t\text{-BuOOH} + \text{Poly-LnRu}^{+3} \longrightarrow \text{Poly-LnRu}^{+5}{=}\text{O} + t\text{-BuOH}$$

Scheme 4.1 Proposed mechanism of alkene epoxidation by Ru-supported complex



Scheme 4.2 Proposed mechanism of alkene epoxidation by Mn-supported complex

4.4 LIFE CYCLE STUDIES

One of the main objective of supporting a homogeneous metal complex on to a polymer is to enhance the life of the resulting catalyst To be truly effective polymer supported catalyst, it is critical that recovery be simple, efficient and that the recovered catalyst retain their activity through multiple cycles [32,35] A few polymer supported Ru(III) and Mn(II) catalysts were selected to study the extent of recyclability The results of the experiments carried out are presented in **Table 4.15.**

From **Table 4.15** it can be inferred that the catalysts can be recycled about 5-6 times However, there is a progressive loss in activity with lowering of epoxide yields The trend is depicted in **Fig 4.3**. Estimation of ruthenium and manganese present in the catalysts after 5-6 cycles revealed a lowering of ruthenium and manganese content by 25-30% The slow deactivation of the catalyst is accompanied by a gradual colour change of the catalyst surface with every recycle

Table 4.15
Recycling studies of catalysts in epoxidation of cis-cyclooctene[a]

No. of cycle	Epoxide(%)[b]			
	Ru-B	**Ru-D**	**Mn-B**	**Mn-D**
1	29 0	23 0	13 9	12 2
2	27 9	22 3	13 2	11 4
3	27 0	21 0	12 2	10 1
4	26 2	20 0	11.7	09 6
5	21 0	17.7	10 8	08 5
6	17.1	13 2	06.0	05 3

Reaction condition : Catalyst=0 25 g , Substrate=cis-Cyclooctene (5 mmol);
Solvent= CH_2Cl_2 *(20 ml), Temp.= 40 °C*
Oxidant= TBHP(2 mmol)

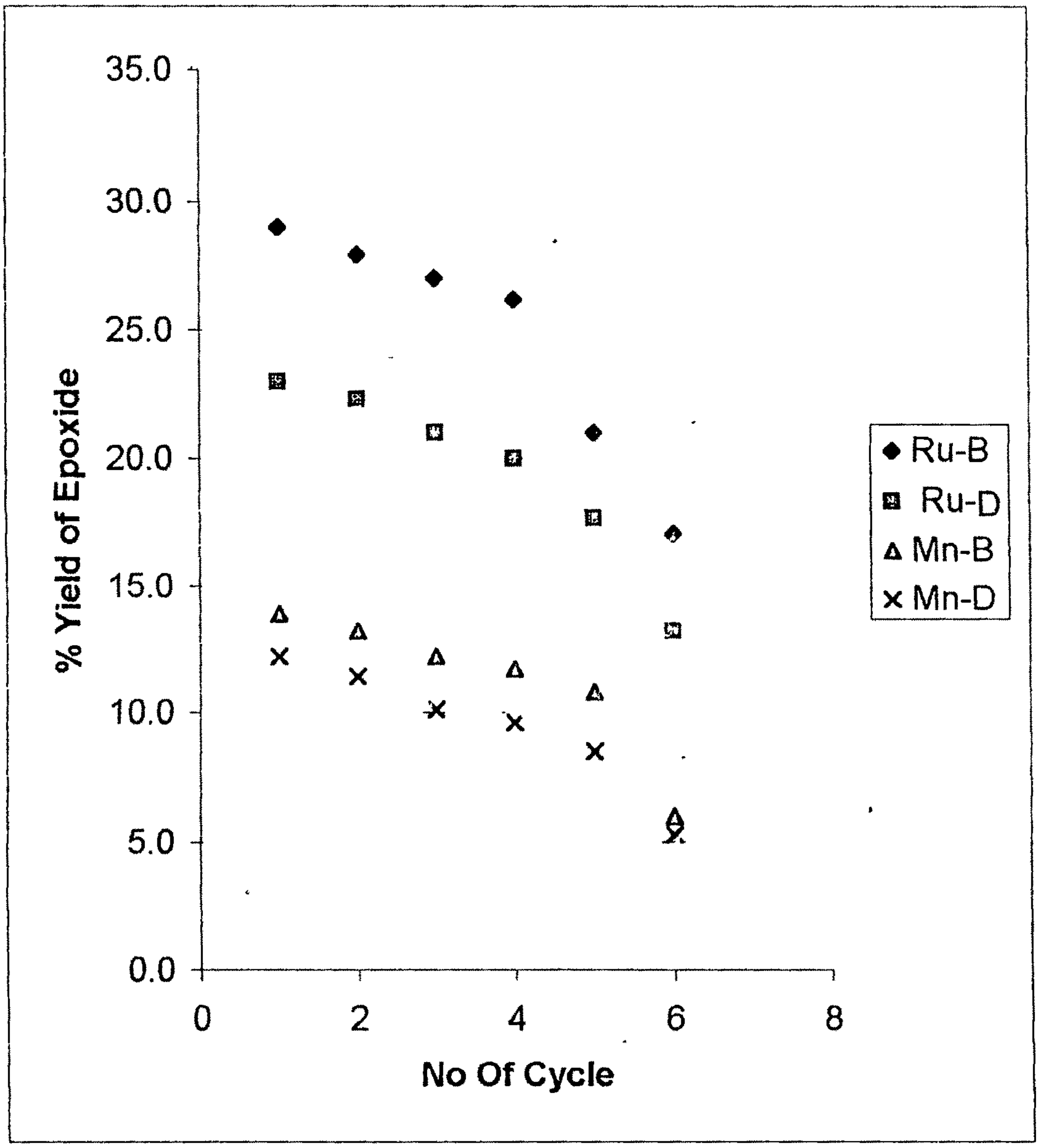


Fig :4.3 Profile of catalyst Recycling Study

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