

Synthesis and catalytic activity of Fe(III) anchored to a polystyrene–Schiff base support

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Abstract

Cross-linked styrene-divinylbenzene copolymer was functionalized into bidentate Schiff base bearing ligands. Immobilization of iron(III) on to the polymer matrix resulted in the synthesis of catalytically active metal complexes. These supported catalysts were found to be effective in the epoxidation of *cis*-cyclooctene and styrene in presence of *tert*-butylhydroperoxide under mild conditions. The influence of various reaction parameters on conversion and selectivity to products of epoxidation has been discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Poly(styrene-divinylbenzene)–Schiff base support; Epoxidation; Iron catalysts

1. Introduction

The immobilization of metal complex catalysts on polymer supports, in an attempt to combine the advantages of homogeneous and heterogeneous catalysis has remained an area of considerable interest [1–3]. A major objective lies in the design and synthesis of polymeric supports with appropriate functional groups for attachment to the active metal centers. Styrene-divinylbenzene polymer, the most commonly employed support, has been chemically modified into a ligand having a variety of coordination sites, such as β -diketones ($\text{O} \text{---} \text{O}$) [4], dipyridylamine ($\text{N} \text{---} \text{N}$) [5], diphosphine ($\text{P} \text{---} \text{P}$) [6], glycine ($\text{N} \text{---} \text{O}$) [7],

ethylenediamine ($\text{N} \text{---} \text{N}$) [8], etc. Salen type homogeneous complexes of transition metals, such as Ni(II), Mn(II) are known to be effective catalysts for epoxidation of olefins [9–11]. Homogeneous transition metal complexes anchored to polymeric supports have been investigated for their catalytic performance in specific organic reactions, such as hydrogenation, oxidation, isomerization and asymmetric epoxidation, etc. The preparation and characterization of Schiff base bearing polymers and their reaction with metal complexes have been studied by us and other workers [12–15]. These Schiff bases having multidentate coordination sites form complexes with transition metal ions readily. In the present paper, we report on the synthesis and characterization of iron(III) supported on functionalized polystyrene–Schiff base ligands and examined them as possible catalysts in the epoxidation of *cis*-cyclooctene and styrene in presence of *tert*-butylhydroperoxide as terminal oxidant at ambient temperature.

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2. Experimental

2.1. Materials

Chloromethylated poly(styrene-divinylbenzene) copolymer spherical beads (18–44 mesh size) with 8% and 14% cross-link were supplied by Ion-Exchange India Ltd. (Mumbai, India). Anhydrous FeCl_3 (Ranbaxy), *tert*-butyl hydroperoxide (TBHP) (Lancaster, 70% in H_2O) and 2-aminopyridine (Merck) were used without further purification. *cis*-Cyclooctene (Lancaster) and polymer grade styrene were freshly distilled before use. All other chemicals were of analytical grade (>99%) and the solvents used were purified by standard methods [16].

2.2. Analysis

Elemental analysis was carried out using the micro-analyzer of Carlo-Erba strumentazione. The loading of Fe on to the polymer support was estimated using GBC 902 AAS instrument (Australia) after digesting a known amount of catalyst with conc. HNO_3 (10 ml) and subsequent dilution in a volumetric flask with distilled water. Surface area of the polymer before and after complexation with the metal was determined using the BET relationship on a Carlo-Erba surface analyzer. Infrared spectra in the 50–4000 cm^{-1} range were recorded on a Nicolet Magna 550 spectrophotometer. Thermogravimetric analysis of the catalysts was carried out on a TA instruments 2950 thermal analyzer upto 600°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere. A vacuum generators ESCALAB MKII equipment with Mg $\text{K}\alpha$ and Al $\text{K}\alpha$ source was used for surface characterization of catalysts

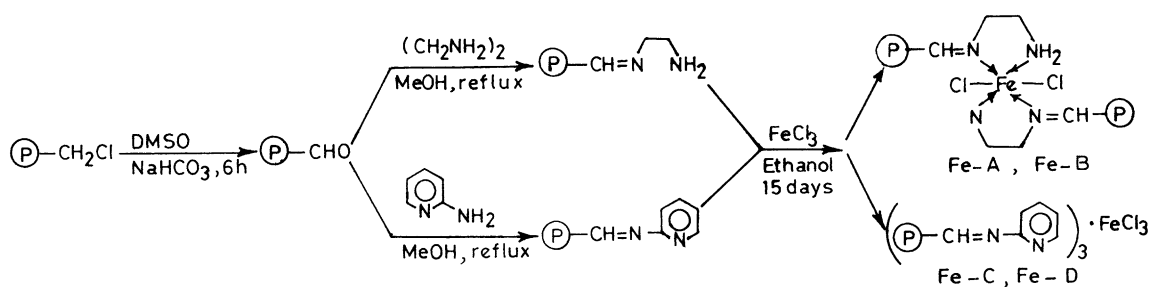
by XPS. Diffuse reflectance spectra (200–600 nm) were recorded on a Shimadzu UV-240 instrument using optical grade BaSO_4 as the reference. The samples of the reaction mixtures withdrawn during the epoxidation were analyzed using Shimadzu 15A gas chromatograph with a flame ionization detector (FID) and a carbowax column (2 m). The temperature program was 80–150°C, 4°C min^{-1} heating rate with N_2 flowrate of 30 ml min^{-1} . The bulk density and swelling behavior of the freshly prepared catalysts in polar as well as non polar solvents were determined as previously described [17] at $27 \pm 1^\circ\text{C}$.

2.3. Preparation of polymer bound Schiff base ligand

The synthesis involves oxidation of the Merrifield resin (20 g) using DMSO and NaHCO_3 at 155°C to an aldehydic functionality [15]. The polymer beads bearing –CHO group were allowed to swell in methanol (25 ml) for 1 h followed by dropwise addition of ethylenediamine (0.5 mol in 25 ml methanol). The contents were refluxed for 8 h to ensure complete condensation and formation of the base. It was separated by filtration and drying. Similar procedure was adopted for synthesizing Schiff base of 2-aminopyridine.

2.4. Loading of Fe(III) on to the support

The Schiff base bearing polymer beads (10 g) was allowed to swell in ethanol (50 ml) for 45 min. To this was added 1% FeCl_3 solution in ethanol (50 ml) dropwise. The contents were initially heated to 50°C for 6 h, cooled and stirred on a shaker for 12 days at 30°C. The bright yellow colored beads, impregnated with the



Scheme 1. Synthesis of poly(styrene-divinylbenzene) supported iron-Schiff base complexes.

metal complex were filtered, washed thoroughly with ethanol and finally dried in vacuum at 70°C for 24 h (see Scheme 1).

2.5. Procedure for catalytic epoxidation

In a typical experiment, 250 mg of polymer supported Schiff base Fe complex was placed in a two-necked round bottom flask containing 20 ml methanol. The catalyst beads were allowed to swell in the solvent for about 30 min. To this was added *cis*-cyclooctene (10 mmol) slowly. After brief agitation, TBHP (70%, 4.25 mmol) was quickly added using a graduated pipette. The solution was stirred for 24 h at 50°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 estimation of the extent of product formation by GC analysis.

3. Results and discussion

The Fe(III) complexes supported on modified polystyrene–Schiff bases were characterized by various physicochemical methods and evaluated for their activity in epoxidation of *cis*-cyclooctene and styrene. The different catalysts employed in this study are designated as under:

- Fe-A: 8% poly(S-DVB)Fe(III)(en-SB);
- Fe-B: 14% poly(S-DVB)Fe(III)(en-SB);
- Fe-C: 8% poly(S-DVB)Fe(III)(ap-SB);
- Fe-D: 14% poly(S-DVB)Fe(III)(ap-SB).

Table 2
Physical properties of catalysts

Property	Fe-A	Fe-B	Fe-C	Fe-D
Surface area (m ² g ⁻¹)	45.7	57.1	49.5	59.1
Moisture content (wt.%)	2.2	1.9	1.9	1.7
Bulk density (g cm ⁻³)	0.44	0.43	0.44	0.44
Pore volume (cm ⁻³ g ⁻¹)	0.14	0.12	0.23	0.26

3.1. Catalyst characterization

The analytical data of the polymer bound complexes at different stages of preparation is presented in Table 1. The maximum Fe loading in the freshly prepared catalysts was found to be in the range of 5.3×10^{-5} to 8.0×10^{-5} mmol g⁻¹ resin. Some of the important physical properties of the newly synthesized catalysts are provided in Table 2. The slightly higher surface area observed in both Fe-C and Fe-D than in Fe-A or Fe-B may possibly be due to the relative differences in the size of Schiff base ligand of 2-aminopyridine and ethylenediamine [18]. The choice of a suitable solvent is an important factor for studying the catalytic behavior of polymer supported homogeneous catalysts. Polar solvents were generally found to be better swelling agents than aliphatic or aromatic non-polar solvents (Table 3). With an increase in cross-link density of the polymer the swellability decreases which is ascribed to the differences in the rigid network of the matrix. Water exhibited higher percentage swelling, however, for practical purposes, methanol and acetonitrile were used as the solvent of choice for carrying out catalytic reactions to overcome miscibility problem with the reactants.

Table 1
Elemental analysis at different stages of catalyst synthesis

Compound	C (%)	H (%)	N (%)	Fe (mmol g ⁻¹)
8% P(S-DVB)-CHO	76.56	5.90		
14% P(S-DVB)-CHO	86.20	7.29		
8% P(S-DVB)-en-Schiff base	72.35	7.07	6.20	
14% P(S-DVB)-en-Schiff base	84.64	7.56	1.86	
8% P(S-DVB)-2ap-Schiff base	75.80	6.74	2.58	
14% P(S-DVB)-2ap-Schiff base	83.88	7.31	2.07	
Fe-A	69.70	6.86	5.86	7.68×10^{-5}
Fe-B	82.88	7.33	1.68	6.23×10^{-5}
Fe-C	75.86	6.81	1.22	5.34×10^{-5}
Fe-D	82.69	7.50	1.78	8.01×10^{-5}

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

Solvent	Fe-A	Fe-B	Fe-C	Fe-D
Water	5.4	5.3	5.4	5.3
Methanol	3.0	2.9	3.1	2.9
Ethanol	2.1	2.0	2.1	2.0
Acetonitrile	2.5	2.3	2.4	2.3
Benzene	1.3	1.2	1.2	1.2
Tetrahydrofuran	1.3	1.2	1.3	1.2
1,4-Dioxan	1.1	1.1	1.1	1.0
<i>n</i> -Heptane	0.9	1.0	1.0	0.9

The mode of attachment of metal ion onto the support was confirmed by comparison of the IR spectral bands of the polymers before and after loading with Fe³⁺ ion, both in the mid (4000–400 cm⁻¹) and far (600–50 cm⁻¹) IR regions. The formation of the Schiff base on the polymer support is indicated by a strong band appearing at 1640 cm⁻¹ assigned to the C=N stretching frequency. This band shows a decrease in intensity and shift to lower wave numbers after complexation suggesting the coordination of the Schiff base to the central Fe(III) ion through the azomethine nitrogen. A medium intensity band at ~3400 cm⁻¹ due to ν NH of ethylenediamine containing ligand showed a marginal low frequency shift in the corresponding metal supported catalysts (Fe-A and Fe-B). In case of Fe-C and Fe-D, the pyridyl ring nitrogen stretching vibration of the Schiff base (780 cm⁻¹) shows a positive shift in the spectra of catalysts indicating coordination through the 'N' of pyridine. Low intensity bands were observed at 316 and 385 cm⁻¹ in the far IR spectra of all the catalysts. These bands which were not detected in the parent Schiff bases were assigned to ν Fe–N and ν Fe–Cl vibrations, respectively (Table 4) [19,20].

However, due to the relatively low intensity bands in this region an unambiguous distinction between ν Fe–N(azomethine) and ν Fe–N(pyridyl) could not be made. Thus, the structure of the complexes depicted in Scheme 1 needs further confirmation.

The UV–VIS electronic spectra of supported Fe–Schiff base catalysts are shown in Fig. 1. Since Fe(III) (d⁵) is a moderately oxidizing ion, many of its complexes exhibit ligand to metal charge transfer transitions (LMCT). In general, transitions to both L → e_g, L → t_{2g} levels may be expected [21]. Due to low metal loadings the intensities of the bands in the spectrum are affected. A low intensity band at ~26,315 cm⁻¹ (380 nm) and a very low intensity band at ~20,410 cm⁻¹ (490 nm) are observed in all our catalysts which are attributed to the spin forbidden absorption bands. Above 33,300 cm⁻¹ only CT bands are observed. These assignments are well within the range reported for other Fe(III) complexes of pyridyl and other nitrogen containing ligands [21,22].

Scanning electron micrograph (SEM) at various stages of preparation of the catalysts were recorded to understand morphological changes occurring on the surface of the polymeric matrix. Initial examination of the SEMs reveal that the Fe(III) atoms are finely distributed across the smooth spherical surface of the beads observable at 10⁴ × magnification. However, accurate information regarding the change in the surface morphology before and after the catalytic cycle cannot be provided due to the very low loading (~10⁻⁵ mol g⁻¹) of the metal on the support. A representative micrograph is shown in Fig. 2. Similarly in the photoelectron spectra, the Fe peaks in the region (712–714 eV) were obscured by intense background spectrum (probably arising due to high carbon

Table 4
Important IR bands (cm⁻¹) of P(S-DVB)–Schiff base and the supported catalysts^a

Catalysts	ν N–H	ν C=N	Py-ring	Py-ring 'N' + ν C=N stretch	ν Fe–Cl	ν Fe–N
8% P(S-DVB)-en–Schiff base	3410(ms)	1672(s)				
14% P(S-DVB)-en–Schiff base	3430(ms)	1676(s)				
8% P(S-DVB)-2ap–Schiff base	3415(ms)	1679(s)	1454(ms), 1507(ms)	777(ms)		
14% P(S-DVB)-2ap–Schiff base	3420(ms)	1679(s)	1454(ms), 1493(ms)	764(ms)		
Fe-A	3403(ms)	1659(s)			383(w)	310(w)
Fe-B	3423(ms)	1660(s)			385(w)	316(w)
Fe-C	3403(ms)	1666(s)	1454(ms), 1513(ms)	764(ms)	386(w)	316(w)
Fe-D	3423(ms)	1669(s)	1493(ms), 1413(ms)	758(ms)	385(w)	316(w)

^a s: Sharp; ms: medium sharp; w: weak.

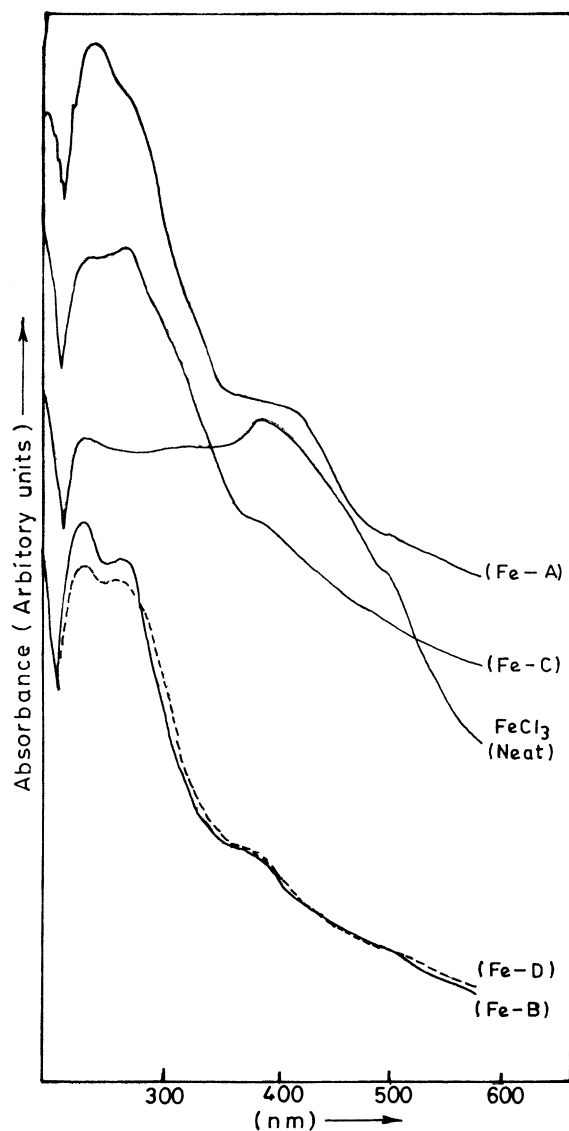


Fig. 1. UV-VIS reflectance spectra of the catalysts.

content in the polymer), thus, definite conclusions on the oxidation state of Fe in the fresh and spent catalysts could not be made. Again low concentration of Fe was found to limit surface characterization [23].

Thermogravimetric analysis of the Fe supported catalysts reveal that they are not stable above 300°C. The TG profile indicated that the unsupported polymers degrade at higher temperatures which is also accompanied by higher weight loss (Table 5). The weight loss observed above 400°C in all the catalysts may be

Table 5
Thermal data of polymer supported Fe(III)-Schiff base complexes

Ligand/catalyst	Degradation temperature (°C)	Weight loss (%)
8% P(S-DVB)-(en-SB)	412.9	47.2
Fe-A	363	27.0
	425	55.0
14% P(S-DVB)-(en-SB)	394.4	61.1
Fe-B	356.5	15.0
	444.5	40.0
8% P(S-DVB)-(2ap-SB)	378.9	32.7
Fe-C	368	30.0
	436	65.0
14% P(S-DVB)-(2ap-SB)	408.9	73.8
Fe-D	379.3	25.0
	500.5	79.0

due to the dissociation of attached ligand moieties as well as scission of polymeric chain. However, in the present study which involves use of hydroperoxide for oxidation reactions the preferred working temperature for the above catalysts is below 80°C.

3.2. Catalytic epoxidation

Catalysts Fe-A to Fe-D were employed in the epoxidation of electron rich olefins, such as *cis*-cyclooctene and styrene. These results are compiled in Tables 6 and 7. In presence of TBHP, all the catalysts effect the epoxidation at room temperature with generally low yield of products (1.4–2.8% of cyclooctene oxide and 6.9–17.3% combined yield of styrene oxide + benzaldehyde). However, at slightly elevated temperature (50°C) there is a marked increase in the corresponding yields of epoxides (7.4–23.2% of cyclooctene oxide and 38.1–79.6% combined yields of styrene oxide + benzaldehyde). This observation is evident for both cyclooctene and styrene. Catalytic activity is much more pronounced in acetonitrile medium than in methanol. Interestingly, with *cis*-cyclooctene GC analysis showed the selective formation of cyclooctene oxide. On the other hand in the reaction with styrene surprisingly, the major product obtained was the secondary oxidation product benzaldehyde (8–68.3%) whereas the epoxide yield

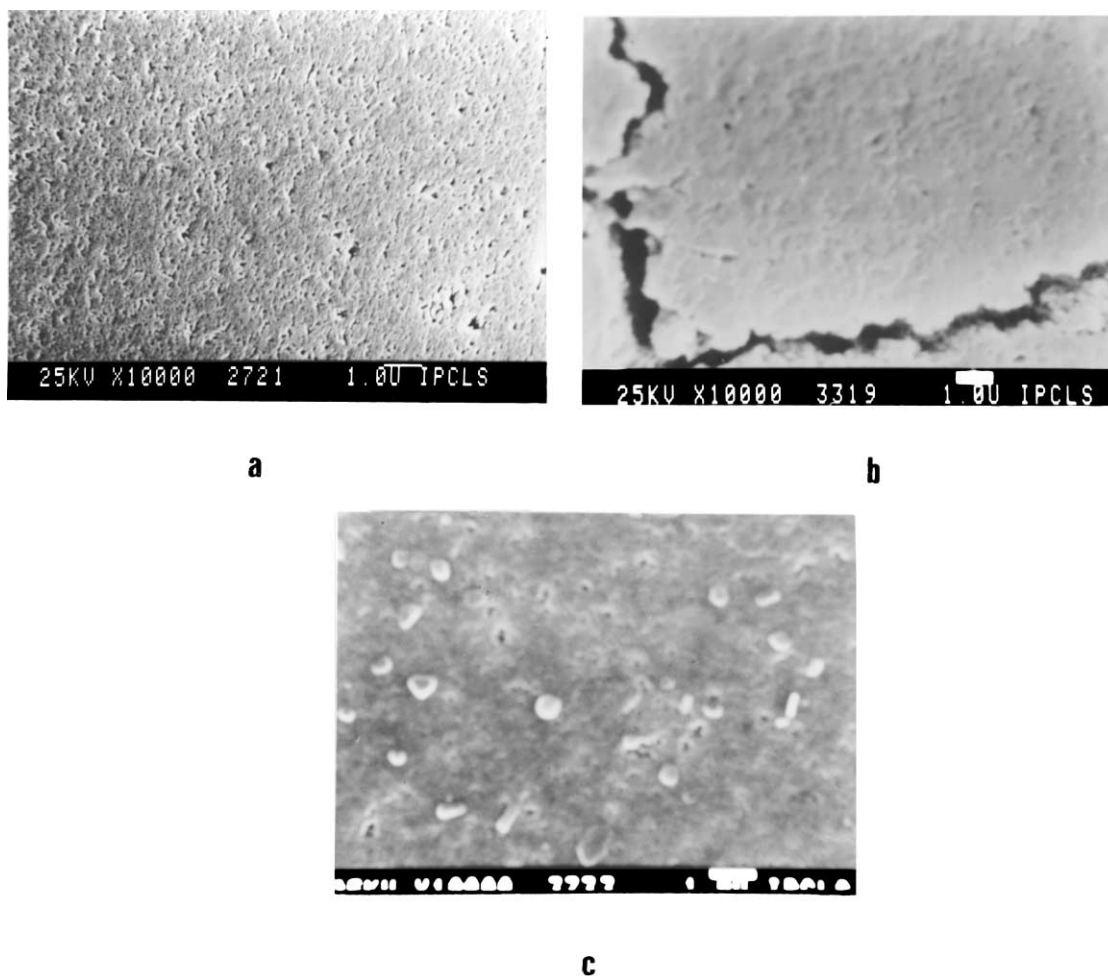


Fig. 2. Scanning electron micrographs of (a) chloromethylated poly(styrene-divinylbenzene); (b) polymer-Schiff base ligand; (c) Fe-B.

was much less (0.9–11.3%). The predominant formation of aldehyde indicates that the reaction with the peroxide proceeds beyond the epoxide stage resulting in the oxidative cleavage of styrene [24,25]. Furthermore, in order to overrule the possibility whether Fe(III) plays any role in the rearrangement of intermediate epoxide to benzaldehyde, a blank reaction was conducted using styrene oxide as the substrate. No benzaldehyde formation was observed. Thus, we conclude that the primary product of styrene oxidation is benzaldehyde. Both Fe-B and Fe-D showed higher activity than Fe-A or Fe-C catalysts.

Schiff base complexes of other metal ions, such as Mn(II), Ni(II) and Cu(II) anchored onto solid supports

such as zeolites, clay and macroporous polymer are reported to catalyze olefin epoxidation using iodosylbenzene as the oxygen source [26–28]. The catalytic behavior and the selectivity of the end products obtained with the present Fe complexes are comparable and in some cases better than those reported. For proper understanding of the catalytic efficiency of supported vis-a-vis unsupported homogeneous Fe-Schiff base complexes, direct comparison of activities under optimized conditions is desirable. Presently, to our knowledge, systematic data on the activity of homogeneous Fe-Schiff base catalysts is not available. The slower rate of reaction (~24 h) exhibited by the polymer bound catalysts described above is

Table 6
Catalytic epoxidation of *cis*-cyclooctene with supported Fe-catalysts^a

Catalyst	Solvent	Temperature (°C)	Cyclooctene oxide (%) ^b
Fe-A	Acetonitrile	25	2.8
	Methanol	25	1.9
	Acetonitrile	50	10.4
	Methanol	50	7.4
Fe-B	Acetonitrile	25	2.5
	Methanol	25	2.6
	Acetonitrile	50	20.8
	Methanol	50	12.6
Fe-C	Acetonitrile	25	2.5
	Methanol	25	1.4
	Acetonitrile	50	17.3
	Methanol	50	13.3
Fe-D	Acetonitrile	25	2.8
	Methanol	25	2.2
	Acetonitrile	50	23.3
	Methanol	50	14.2

^a Reaction conditions: 250 mg of catalyst; 10 mmol substrate; 4.25 mmol TBHP; 20 ml solvent; 24 h.

^b Yield based on oxidant taken.

Table 7
Styrene epoxidation with polymer supported Fe catalysts^a

Catalyst	Solvent	Temperature (°C)	Styrene oxide (%) ^b	Benzaldehyde (%) ^b
Fe-A	Acetonitrile	25	1.7	8.0
	Methanol	25	1.0	7.2
	Acetonitrile	50	6.6	57.2
	Methanol	50	2.1	36.0
Fe-B	Acetonitrile	25	1.2	9.9
	Methanol	25	0.9	7.3
	Acetonitrile	50	7.2	64.3
	Methanol	50	3.4	48.8
Fe-C	Acetonitrile	25	0.9	10.0
	Methanol	25	0.6	6.2
	Acetonitrile	50	10.7	59.0
	Methanol	50	5.1	37.0
Fe-D	Acetonitrile	25	0.8	16.4
	Methanol	25	1.3	13.3
	Acetonitrile	50	11.3	68.3
	Methanol	50	5.9	52.6

^a Reaction conditions: 250 mg of catalyst; 10 mmol substrate; 4.25 mmol TBHP 24 h; 20 ml solvent.

^b Yield based on oxidant taken.

Table 8
Recycling study of catalysts Fe-A and Fe-C in epoxidation of *cis*-cyclooctene using TBHP^a

Cycle no.	Epoxide (%) ^b	
	Fe-A	Fe-C
1	7.4	13.3
2	6.9	13.1
3	5.3	12.1
4	4.9	11.7
5	4.8	10.8
6	2.8	6.0

^a Reaction conditions: 250 mg of catalyst; 10 mmol *cis*-cyclooctene; 20 ml methanol; 4.25 mmol TBHP; 50°C; 24 h.

^b Yield based on oxidant taken.

attributed mainly to the slower diffusion of substrate olefins into the polymer matrix where the active sites are located [29,30].

3.3. Catalyst recycle

One of the main objectives of supporting a homogeneous metal complex on to the polymer is to enhance the life of the resulting catalyst. We have made a

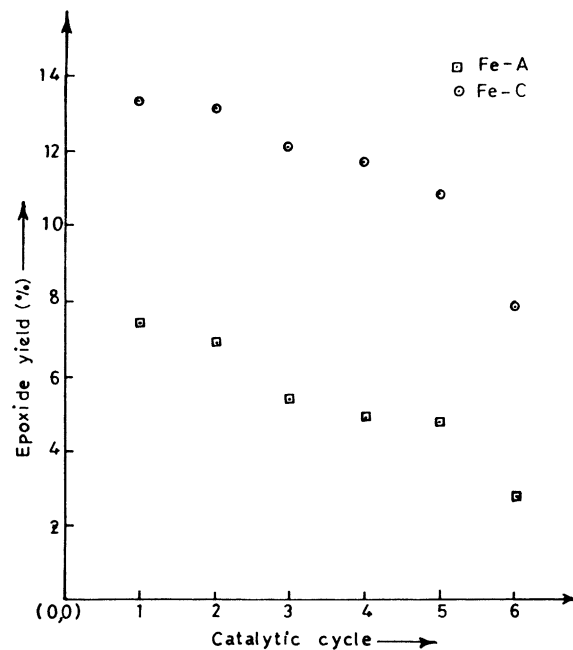
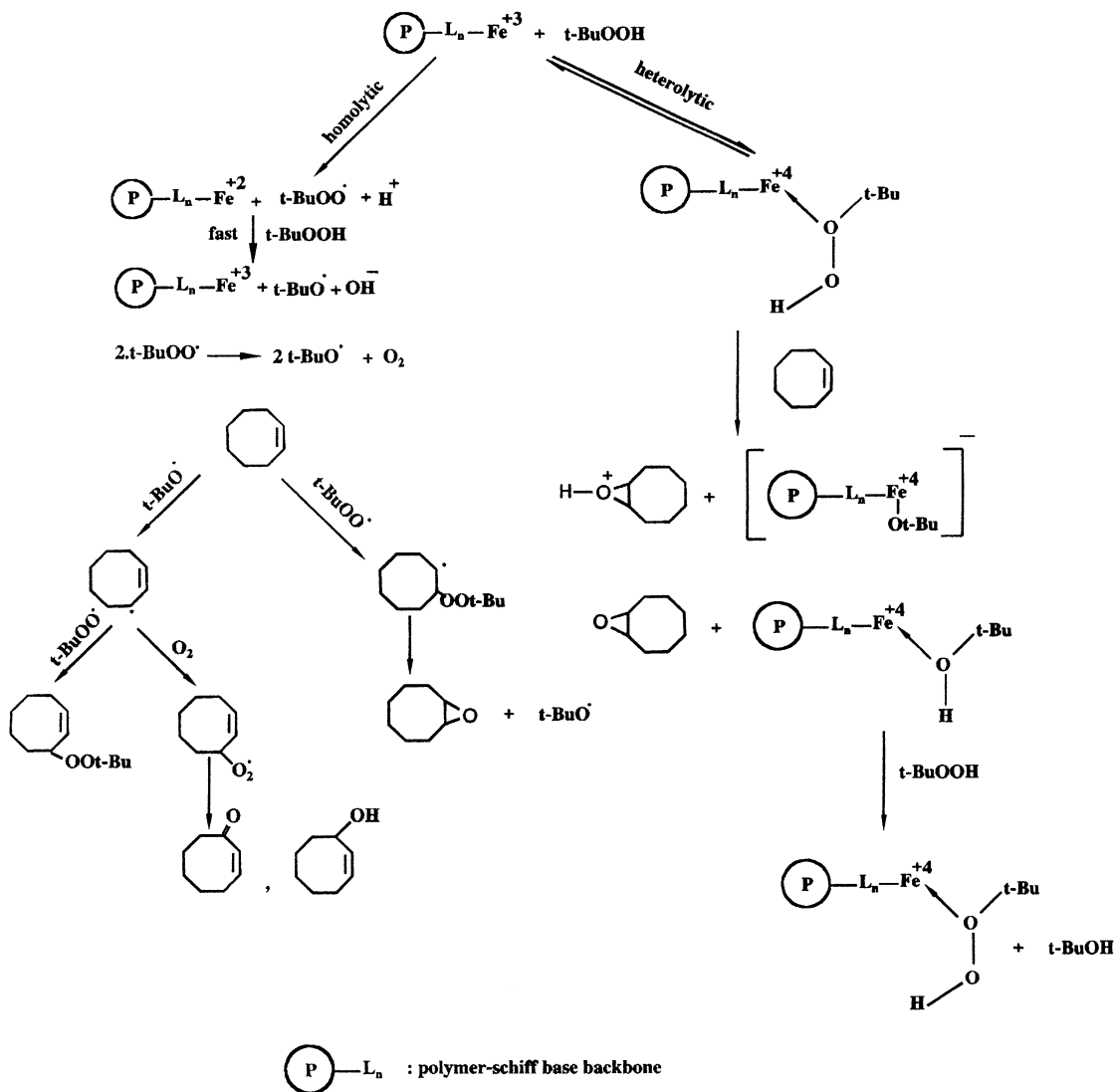


Fig. 3. Profile of catalyst recycle.

preliminary study of the recycling efficiency of catalysts Fe-A and Fe-C using *cis*-cyclooctene as the model substrate. The catalysts were separated from the reaction mixture after each experiment by filtration, washed with the solvent and dried carefully before using it in the subsequent run. These results are shown in Table 8. From the table, it can be inferred that the catalysts can be recycled about five to six times. However,

there is a progressive loss of activity with lowering in epoxide yields. Estimation of Fe present in the recycled catalysts after six cycles revealed a lowering in Fe content by about 30–35% than that present at the end of first cycle. The slow deactivation of catalyst is accompanied by a gradual change in color of the catalyst surface with every recycle. This trend is depicted in Fig. 3.



Scheme 2. Proposed mechanistic pathways.

3.4. Mechanism of olefin epoxidation

Two major pathways involving either a high valent metal peroxo/oxo species or free radical intermediates have been proposed for the oxidation alkenes by hydroperoxides [30–32]. In order to ascertain the nature of oxidation, a free radical trap, 2,6-di-*tert*-butyl-4-methylphenol (BHT, 30 equivalents) was added to the reaction mixture prior to addition of TBHP in the epoxidation of *cis*-cyclooctene with Fe-B and Fe-C at 50°C in methanol. Results indicated that BHT did not completely suppress the reaction but the epoxide yields were reduced (7.5% in case of Fe-B and 9.0% in case of Fe-C). The overall drop in yields was 32–40%. In another test for possible involvement of free radicals in this reaction, experiments were conducted in presence of CCl₄ using catalysts Fe-B and Fe-C. Analysis showed considerable lowering in epoxide yields (2.9% with Fe-B and 5.0% with Fe-C). Significantly in both these experiments the reaction is only partially suppressed and no other free radical induced side products were detected. By-products result from subsequent reactions of alkoxy and alkylperoxy radicals with the substrate [33]. For the present Fe(III) 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. The mechanistic model of Sheldon and coworkers [34,35] and Gould [36] can be extended for our system. A simplified dual mechanistic pathway for the catalytic epoxidation of cyclooctene by Fe(III) in presence of TBHP is shown in Scheme 2. It may be pointed out that direct experimental evidence for the formation of the high valent active complex as shown ($\text{P}=\text{L}_n-\text{Fe}^{5+}=\text{O}$) is lacking. Attempts are underway to examine the role of coordination geometry of Fe(III) ion linked to the polymer bound Schiff base and the nature of active species generated during the catalytic cycle.

4. Conclusions

Iron(III) anchored on Schiff base bound poly(styrene-divinylbenzene) copolymer has been shown to catalyze the epoxidation of styrene and *cis*-cyclooctene in presence of alkylhydroperoxide under

mild conditions. The catalysts can be recycled several times without any loss in selectivity. Slow deactivation of the catalysts observed over extended reuse, which can limit their application needs further investigation.

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