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Polymer supported Ru(III) complexes, synthesis and catalytic activity

R. Antony[a], **G. L. Tembe**[a], **M. Ravindranathan**[a] and **R. N. Ram**[b,*]
[a]*Research Centre, Indian Petrochemicals Corporation Limited, Vadodara, 391 346, India*
[b]*Chemistry Department, Faculty of Science, M.S. University of Baroda, Baroda, 390 002, India*
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Crosslinked chloromethylated polystyrene–divinylbenzene polymers were chemically modified into Schiff base bearing ligands. Catalytically active metal supported polymers containing Ru(III) moieties were synthesized from these ligands for use in the selective epoxidation of olefins in presence of *tert*-butyl hydroperoxide as oxidant. These ruthenium anchored polymers were characterized by spectral and thermoanalytical methods. Catalyst morphology and physicochemical properties such as surface area, bulk density and swelling behaviour in different solvents were studied. The effects of reaction parameters such as catalyst concentration, temperature, time and solvent on conversion and selectively in the epoxidation of *cis*-cyclooctene and styrene are discussed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(styrene–divinyl benzene); epoxidation; ruthenium supported polymer)

INTRODUCTION

In recent years the design and synthesis of highly functionalized polymers carrying catalytically active metal species has generated considerable interest, as these materials offer several practical advantages over their homogeneous soluble counterparts[1–4]. Chemical transformation of polystyrene into a coordinating ligand has been reported using glycine[5], dipyridylamine[6], acetylacetone[7], ethylenediamine[8], trimethylene–diamine[9] etc. Though Schiff bases are one of the most versatile and thoroughly studied ligands, very few reports are available on the polymer anchored Schiff bases and their application in catalysis[10–12]. In an earlier work we investigated the catalytic activity of polymer supported ruthenium–amine complexes, mainly in the hydrogenation of olefins and nitroaromatic compounds[5,9,13]. A different strategy was adopted in the present study, to bind powerful chelating agents like Schiff bases to the polymer resin and subsequently complex them with Ru(III). Catalytic epoxidation of olefins is both an important industrial reaction and a useful synthetic method for fine chemicals. Simple ruthenium salts like RuO_4, $RuCl_3$, in conjunction with oxygen donors, e.g. $NaIO_4$[14], NaOCl[15] and certain coordination complexes like $RuCl_2(Ph_3P)_2$[16], binuclear ruthenium Schiff bases[17] in the presence of PhIO, have been shown to selectively epoxidize olefins under homogeneous conditions.

In this paper we present our results on the synthesis of new poly(styrene–divinylbenzene) bound Schiff base ligands and their ruthenium complexes. The polymer linked Ru(III) complexes were evaluated for their catalytic behaviour towards epoxidation of styrene and *cis*-cyclooctene in the presence of *tert*-butyl hydroperoxide (TBHP) as the oxidant.

EXPERIMENTAL

Materials

Hydrated ruthenium trichloride (Loba Chemie), 2-aminopyridine (Merck), *cis*-cyclooctene (Aldrich) were used as received. Chloromethylated poly(styrene–divinylbenzene) with 8% and 14% crosslinking (18–44 μm) were supplied by Ion-Exchange Ltd. (Bombay, India). All other chemicals and solvents were of analytical grade and were purified by standard methods[18].

Synthesis of polymer bound Schiff base ligand

In a typical experiment chloromethylated poly(styrene–divinylbenzene) beads (20 g) were oxidized to the aldehyde by reaction with DMSO and $NaHCO_3$ at 155°C for 6 h, as previously described[19]. The dried aldehyde bearing polymer was allowed to swell for 1 h in methanol (50 ml). To this a solution of ethylene diamine (0.5 M in 25 ml methanol) was added dropwise over a period of 45 min with constant stirring. The contents were refluxed for 6–8 h. After cooling to room temperature the pale yellow coloured polymer beads were filtered, washed thoroughly with methanol, petroleum ether (40–60°C) and dried *in vacuo* at 70°C for 24 h. The formation of Schiff base of the resin was confirmed by analytical and infra-red (i.r.) spectral data. The Schiff bases from 2-aminopyridine were similarly prepared by using 0.24 mol of the amine in place of ethylene diamine.

Incorporation of Ru(III) on to Schiff bases bearing resin. Polymeric ligand (10 g) was kept in contact with 50 ml ethanol in a round-bottom flask for 1 h. To this was added an ethanolic solution (50 ml) of hydrated $RuCl_3$ (1% w/v) over a period of 45 min with occasional shaking. The mixture was then agitated on a shaker at room temperature. After 15 days the grey coloured ruthenum loaded beads were filtered and carefully washed with ethanol.

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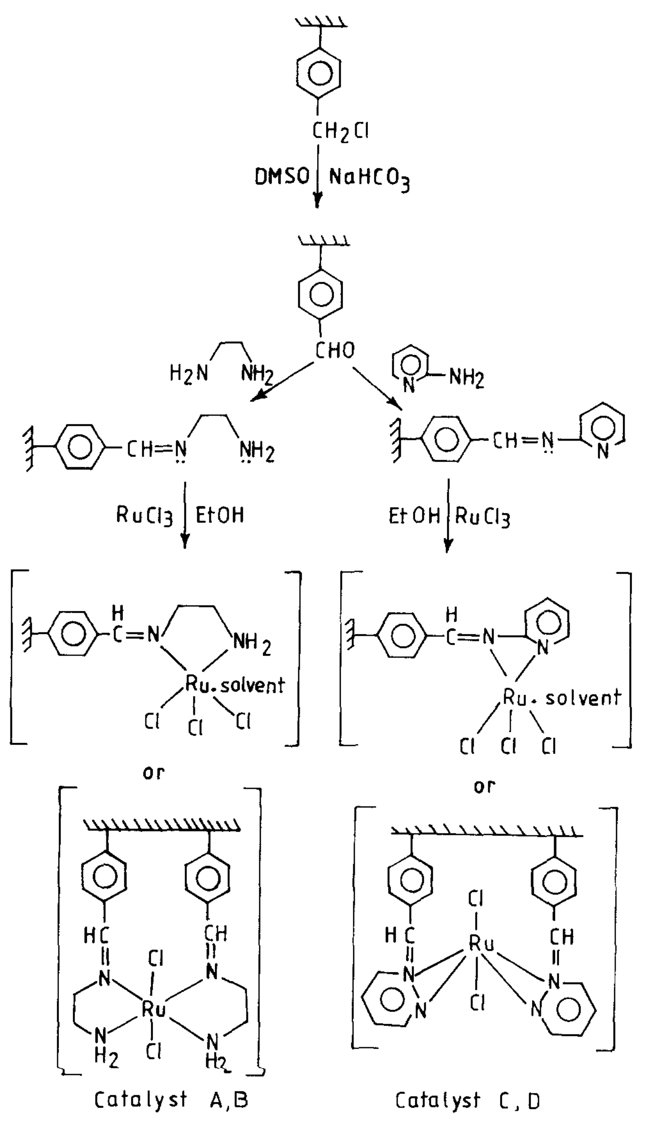
[*] To whom correspondence should be addressed



Scheme 1 Synthesis of Ru(III) supported poly(styrene–divinylbenzene) Schiff base complexes

Table 1 Physical properties of the polymer-supported Ru(III) catalysts[a]

Property	Catalysts A	B	C	D
Surface area ($m^2 g^{-1}$)	62.69	61.29	46.17	48.31
Moisture content (wt%)	2.79	1.04	2.86	0.72
Bulk density ($g cm^{-3}$)	0.44	0.43	0.45	0.43
Pore volume ($cm^3 g^{-1}$)	0.33	0.33	0.21	0.32

[a] Surface area of the supports: 8%P(S-DVB) CH_2Cl = 39.1 $m^2 g^{-1}$; 14%P(S-DVB)CH_2Cl = 46.3 $m^2 g^{-1}$

The polymer supported metal complex thus obtained was dried *in vacuo* for 24 h at 70°C.

Epoxidation of olefins

The general procedure for olefin epoxidation using the supported Ru(III) catalyst was as follows. The resin bound Ru(III) catalyst (0.25 g) was kept in contact with ethanol (20 ml) for 30 min. Then, *cis*-cyclooctene (10 mmol) was added followed by TBHP (5 mmol, 70% in water). A known amount of chlorobenzene was taken in the reaction mixture as an internal standard. The contents were stirred at room temperature (27 ± 1°C) for a specified time. Aliquots of reaction mixture were carefully withdrawn at regular intervals and analysed by gas chromatography (GC). The same method was adopted for all the catalysts and at specified temperatures.

Measurements

The elemental analysis of polymer metal complexes was carried out using a Carlo-Erba Strumentazone microanalyzer. For the estimation of ruthenium content bound to the polymer, a known quantity of catalyst was decomposed with conc. HCl (10 ml) and filtered. To the filtrate was added 12.5 ml of a standard solution of Nitroso-R salt. The absorbance of the colour developed was measured spectrophotometrically at 510 nm[20] using an ultra-violet–visible (u.v.–vis) spectrophotometer. Thermal analysis of the catalysts was made on a TA Instruments 2950 thermal analyser at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. Scanning electron micrographs (SEMs) were taken on a Jeol JSM T-300 instrument. I.r. and far i.r. spectra was recorded on a 50–4000 cm^{-1} range on a Nicolet Magna 550 spectrophotometer. Diffuse reflectance spectra (300–500 nm) were measured on a Shimadzu UV-240 instrument using $BaSO_4$ as the standard. GC analyses of the epoxidation products were carried out on a Shimadzu 15A gas chromatograph on a 15% carbowax column (1/8" × 2 m) using a flame ionisation detector (FID). Nitrogen was used as the carrier gas with a flow rate of 30 ml min^{-1}. The surface areas of the support and the catalysts were determined on a Carlo-Erba surface analyser using the Brunauer–Emmett–Teller (BET) relationship. Swelling studies were made in polar and nonpolar solvents at 27 ± 1°C.

RESULTS AND DISCUSSION

The chemical modification of crosslinked chloromethylated poly(styrene–divinyl benzene) poly(S-DVB); and the loading of ruthenium onto this support was carried out as per the sequence shown in *Scheme 1*. Two types of possible structures for these polymer supported Ru(III) metal complexes are also shown in this Scheme. The four catalysts used in this study are designated as follows.

Catalyst A : 8% Poly(S-DVB)Ru(en-SB)
Catalyst B: 14% Poly(S-DVB)Ru(en-SB)
Catalyst C: 8% Poly(S-DVB)Ru(2AP-SB)
Catalyst D : 14% Poly(S-DVB)Ru(2AP-SB)

The physical properties of the newly synthesized catalysts are presented in *Tables 1* and *2*. The surface area of catalysts **C** and **D** bearing 2-amino pyridine Schiff bases are found to be lower than those derived from ethylene diamine (**A** and **B**). This difference of 13–16.5 m^2g^{-1} may be due to the relative size difference in the two types of Schiff bases formed on the polymer matrix.

The attachment of Schiff bases derived from ethylene diamine and 2-aminopyridine on the functionalized polymer was confirmed by their elemental analysis. The higher percentage of nitrogen found in catalysts **A** and **C** compared to that in catalysts **B** and **D** is attributed to the lower degree of crosslinking in the former (8% as against 14% in **B** and **D**). This can be explained as follows. In the case of polymer supports with a higher degree of crosslinking, the network has a dense and relatively larger number of inaccessible domains, with the result that less functionalization is achieved[21].

Polar solvents were generally found to be better swelling agents for all the catalysts than the non-polar solvents like

Table 2 Elemental Analysis of chloromethylated polymers, their Schiff bases and supported Ru(III) catalysts

Compound	C%	H%	Cl%	N%	Ru(mmol g^{-1}resin)
8% P(S-DVB)CH$_2$Cl	67.62	5.67	22.32	–	–
14% P(S-DVB)CH$_2$Cl	81.79	7.03	14.21	–	–
8% P(S-DVB)(en-SB)	76.55	7.08	–	3.03	–
14% P(S-DVB)(en-SB)	84.72	7.46	–	1.84	–
8% P(S-DVB) (2AP-SB)	72.41	6.29	–	1.12	–
14% P(S-DVB) (2AP-SB)	82.84	7.13	–	1.05	–
Catalyst **A**	73.79	6.65	–	2.61	8.1×10^{-3}
Catalyst **B**	84.28	7.48	–	1.58	9.2×10^{-3}
Catalyst **C**	74.66	6.32	–	0.71	3.6×10^{-3}
Catalyst **D**	81.26	7.48	–	0.44	7.8×10^{-3}

Table 3 Swelling data of supported catalysts (mol%)

	Catalyst			
Solvent	**A**	**B**	**C**	**D**
Water	5.27	5.50	5.36	5.82
Ethanol	2.05	2.12	2.30	2.21
Methanol	2.92	3.05	3.20	3.62
Acetonitrile	2.30	2.40	3.06	2.43
Benzene	1.19	1.25	1.06	1.07
Tetrahydrofuran (THF)	1.38	1.40	1.03	1.22
Heptane	0.95	0.99	0.92	1.00

Table 4 T.g.a. data of polymeric Schiff bases and its ruthenium complexes

Sample	Degr. temp (°C)	Weight loss (%)
8% P(S-DVB) (en-SB)	412.9	47.2
14% P(S-DVB) (en-SB)	394.4	61.1
8% P(S-DVB) (2AP-SB)	378.9	32.7
14% P(S-DVB) (2AP-SB)	408.9	73.8
Ru(III) Catalyst-**A**	415.4	60.5
Ru(III) Catalyst-**B**	409.5	78.4
Ru(III) Catalyst-**C**	386.3	51.5
Ru(III) Catalyst-**D**	412.4	85.3

heptane, benzene etc. (*Table 3*). This is logical, because with an increase in the degree of crosslinking of the polymer support, the percentage swelling decreases, indicating the rigid nature of the support. Thus, the solvent of choice should combine good swelling ability and high polarity for catalytic use. Methanol was found to be a good solvent among those studied and exhibited properties better for dissolution of the substrate.

The mid i.r. (4000–400 cm^{-1}) and far i.r. spectra (500–50 cm^{-1}) of polymer supported ruthenium complexes at different stages of synthesis (*Scheme 1*) was used to understand the nature of coordination of the metal to the polymer. A medium intensity band in the region 3400^{-1} corresponding to NH-stretching vibration of ethylenediamine containing polymer ligand showed a marginal low frequency shift in the corresponding metal supported catalysts (**A** and **B**). A strong band at 1660 cm^{-1} ascribed to the C = N stretching (azomethine) in case of the Schiff base bearing polymer undergoes a downward shift with slight reduction in intensity in the supported metal catalysts. This indicates coordination of the ligand nitrogen (through the azomethine 'N') to the Ru(III) metal ion. Complexation through the pyridine ring nitrogen to the ruthenium metal was indicated by a positive shift of the ring stretching vibration (1170–1120 cm^{-1}) in the case of the supported

Table 5 Epoxidation of *cis*-cyclooctene with polymer anchored Ru catalysts[a]

Run	Catalyst	Solvent	Temp. (°C)	Cyclooctene oxide (mmol)	Cyclooctene oxide[b] (%)
1	**A**	CH$_3$CN	26	0.43	4.3
2	**B**	CH$_3$CN	26	0.56	6.6
3	**C**	CH$_3$CN	26	0.62	7.4
4	**D**	CH$_3$CN	26	0.89	10.1
5	**A**	CH$_3$CN	50	1.03	12.1
6	**B**	CH$_3$CN	50	1.19	14.2
7	**C**	CH$_3$CN	50	2.52	29.5
8	**D**	CH$_3$CN	50	3.65	42.9
9	**A**	CH$_3$OH	26	0.20	4.9
10	**B**	CH$_3$OH	26	0.26	6.3
11	**C**	CH$_3$OH	26	0.52	12.6
12	**D**	CH$_3$OH	26	0.70	16.9
13	**A**	CH$_3$OH	50	0.98	23.2
14	**B**	CH$_3$OH	50	0.89	20.9
15	**C**	CH$_3$OH	50	1.15	27.6
16	**D**	CH$_3$OH	50	1.27	30.4

[a] Conditions: Catalyst **A**–**D** = 0.25 g; *cis*-cyclooctene (10 mmol); TBHP (4 mmol); 24 h
[b] Yield based on oxidant consumed

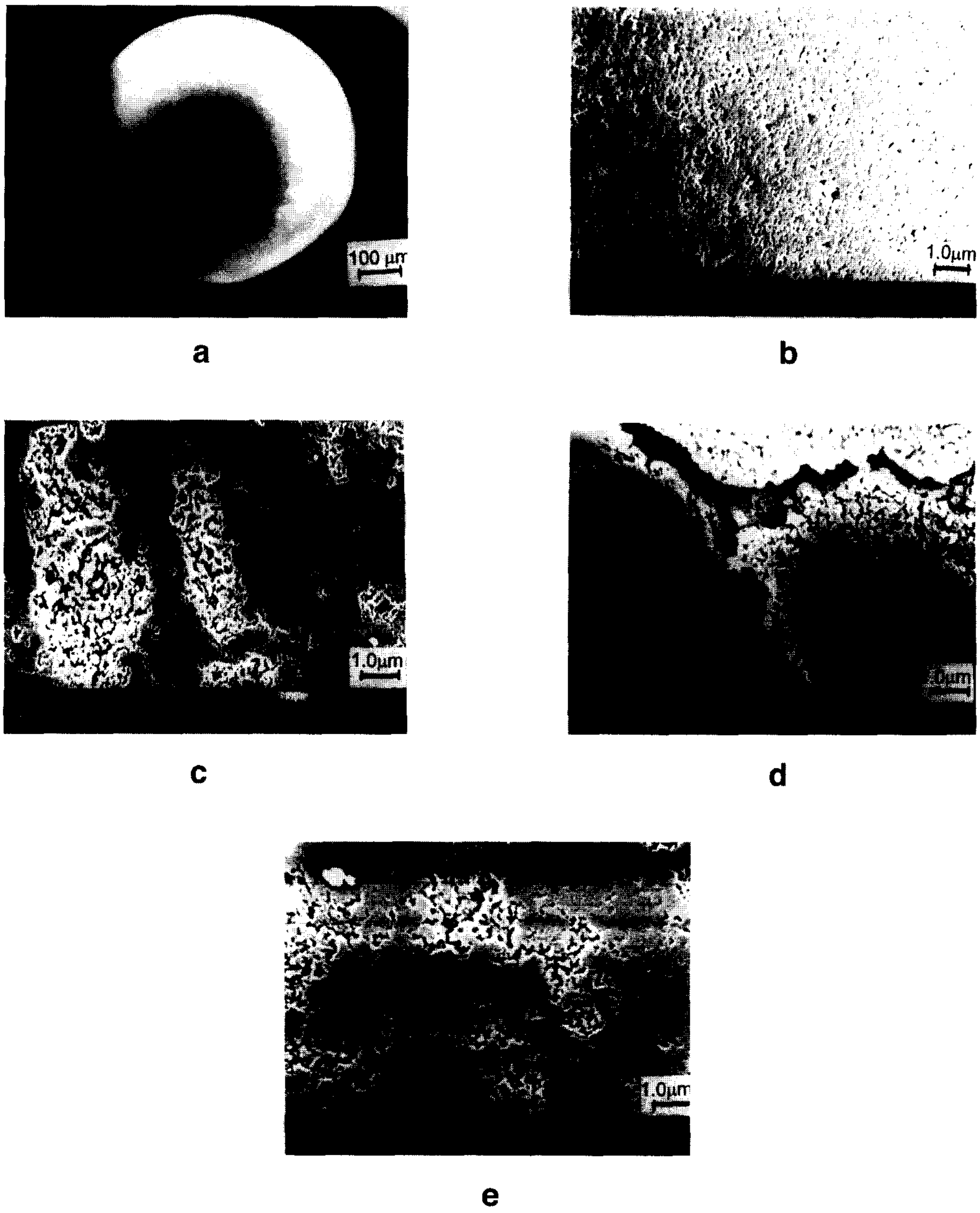


Figure 1 SEMs: (a,b) chloromethylated poly(styrene–divinyl) benzene and the corresponding Ru(III) supported catalysts; (c) 14% P(S-DVB) (en-SB) (catalyst **B**); (d) 8% P(S-DVB) (2AP-SB) (catalyst **C**); (e) 14% P(S-DVB) (2AP-SB) (catalyst **D**)

catalysts **C** and **D**. In the far i.r. spectra, two new low intensity bands in the region 374–385 cm^{-1} were assigned to the Ru–N and Ru–Cl vibrations. These bands which were observed in all the catalysts were missing in the spectra of the polymer ligands[22,23].

The u.v.–vis reflectance spectra of the newly synthesized catalysts in the $BaSO_4$ matrix exhibit two weak intensity absorption bands in the regions 350 nm and 420 nm respectively. The absence of characteristic strong ligand metal charge transfer bands indicates that the latter absorption may be due to d–d transition of Ru(III)[24].

SEMs of polymeric Schiff base ligands and their ruthenium complexes show that unsupported catalysts have a smooth spherical structure. The loading of ruthenium metal onto the surface appears to be fine, which could be observed at high resolutions. Energy dispersive X-ray studies (EDXA) also indicated changes in the morphology of the supported catalysts. Representative SEM micrographs are shown in *Figure 1*. However, it is difficult to draw a definite conclusion regarding the distribution of Ru and chlorine atoms (concentration changes) across the cross-section of the fresh catalysts, and the spent catalyst recovered after the catalytic reactions, probably due to a low level of metal loading on the polymer beads, which was generally in the range of 0.5×10^{-4} mmol Ru g^{-1} resin for our system.

Thermogravimetric analysis (t.g.a.) of the unsupported polymers indicate degradation at lower temperatures compared to the ruthenium loaded matrix (*Table 4*). The lower stability of the metal supported polymers is also revealed by higher weight loss which may be due to dissociation of the Schiff base ligand moieties from the catalyst.

Catalytic epoxidation with poly(styrene–divinyl benzene)–Schiff base supported Ru complexes

TBHP was used as the terminal oxidant in the epoxidation of *cis*-cyclooctene and styrene in the presence of catalyst

Table 6 Oxidation of styrene in presence of Ru-supported catalysts and TBHP[a]

Run	Catalyst	Solvent	Temp. (°C)	Styrene oxide (mmol)	Styrene oxide[b] (%)	Benzaldehyde (mmol)	Benzaldehyde[b] (%)
1	**A**	CH_3CN	26	0.20	4.8	0.21	4.9
2	**B**	CH_3CN	26	0.06	1.3	0.28	6.6
3	**C**	CH_3CN	26	0.08	1.7	0.32	7.5
4	**D**	CH_3CN	26	0.03	0.74	0.24	5.7
5	**A**	CH_3CN	50	0.73	17.2	3.46	81.6
6	**B**	CH_3CN	50	0.50	11.8	3.59	84.5
7	**C**	CH_3CN	50	1.10	26.0	3.12	73.5
8	**D**	CH_3CN	50	1.13	26.7	3.13	73.8
9	**A**	CH_3OH	26	0.07	1.8	0.95	22.4
10	**B**	CH_3OH	26	0.05	1.4	0.53	12.5
11	**C**	CH_3OH	26	0.27	6.4	0.86	20.4
12	**D**	CH_3OH	26	0.19	4.7	0.81	19.1
13	**A**	CH_3OH	50	0.33	7.8	1.19	28.1
14	**B**	CH_3OH	50	0.19	4.7	1.03	24.3
15	**C**	CH_3OH	50	0.20	28.4	1.55	36.5
16	**D**	CH_3OH	50	0.66	15.6	1.58	37.2

[a] Conditions: catalyst, 0.25 g; styrene, 10 mmol; TBHP, 4 mmol; time, 24 h
[b] Yield based on oxidant consumed

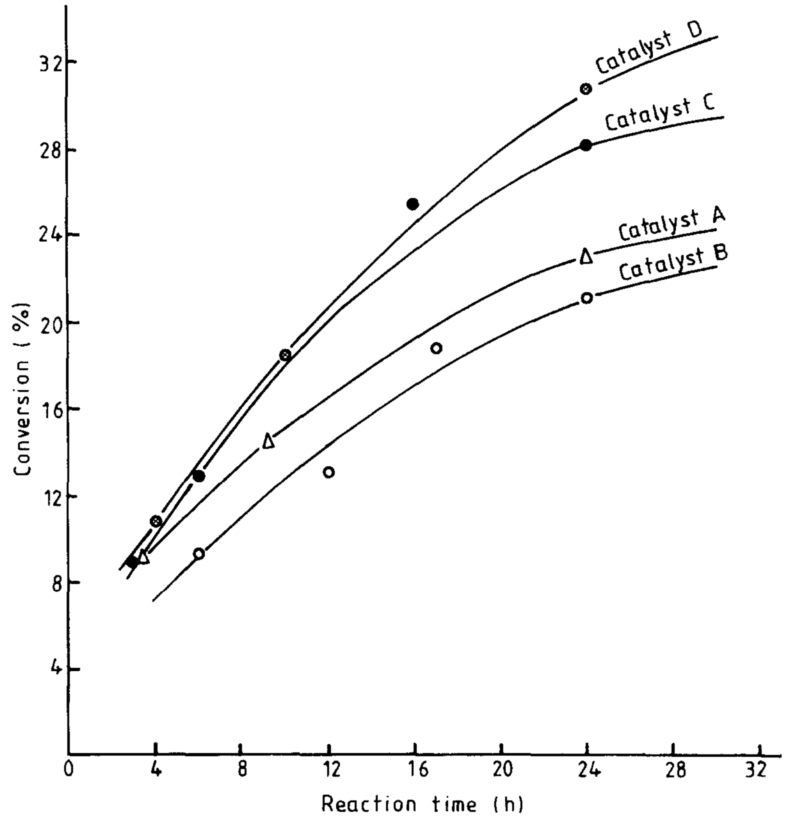
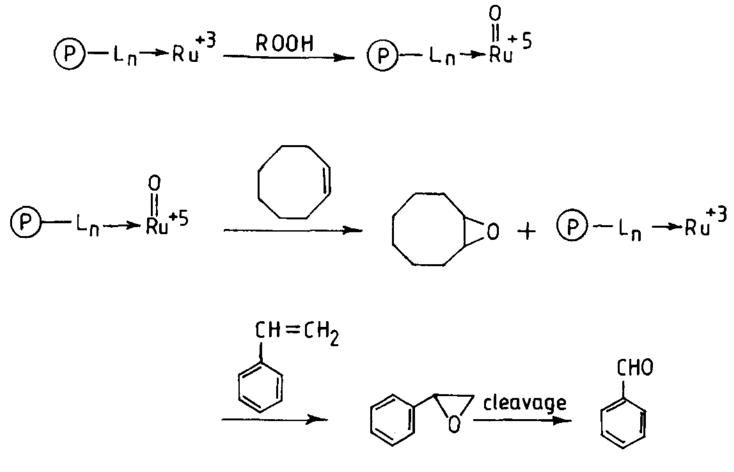


Figure 2 Effect of reaction time on conversion of cyclooctene to epoxide in presence of t-BuOOH and Ru(III) supported catalysts; solvent CH_3OH; 50°C reaction temp.; catalysts **A**(△), **B**(○), **C**(●), **D**(⊗)

A–D at ambient temperature and at 50°C. It was found that the alkenes employed did not undergo epoxidation in the absence of either the catalyst or an oxidant. When molecular oxygen was used as the source of oxidant in place of TBHP, practically no reaction occured. The results of epoxidation of cyclooctene and styrene in acetonitrile and methanol using supported Ru catalysts are compiled in *Tables 5* and *6*. Analysis of oxidation products showed that in case of *cis*-cyclooctene, the corresponding epoxide, cyclooctene oxide, was selectively formed. The yields increased more substantially at 50°C than at 26°C (*Table 5*). From the data presented it appears that the observed selectivities and yields are comparable with those of other mononuclear and binuclear Ru(III) chloride complexes with Schiff base complexes[17,25]. Direct comparison of activity of homogeneous Ru(III) chloride complexes with Schiff base ligands used in the present study would reflect the actual catalytic efficiency of supported *vis-à-vis* unsupported



Scheme 2 Proposed mechanism of alkene epoxidation

catalyst under optimized reaction conditions. However, data on the activity of the homogeneous ruthenium catalysts are presently not available. Maximum activity was exhibited by catalysts **C** and **D** derived from 2-amino pyridine Schiff base (runs 7, 8, 15, 16, *Table 4*). The degree of crosslinking in the polymer support as well as the mode of binding of the Schiff bases (bidentate in the case of 2-aminopyridine and monodentate or chelating in case of ethylene diamine) to the Ru(III) center probably determines the relative activity of the catalysts during the epoxidation. Methanol was a better solvent compared to acetonitrile for oxidation under similar reaction conditions.

In the case of styrene, interestingly, secondary oxidation product benzaldehyde was formed in substantial quantities in addition to the expected styrene oxide (*Table 6*). This indicates that under the experimental conditions the reaction with TBHP proceeds beyond the epoxide stage resulting in oxidative cleavage of styrene. The other oxidation product phenyl acetaldehyde was not observed but a small amount of acetophenone formation ($< 0.3\%$) was detected. An increase in epoxide yield with temperature was noted for styrene also. From *Table 6* it can be inferred that the ability of the catalysts for oxidation of styrene is much higher than for that of cyclooctene.

A few experiments were carried out to find the extent of epoxidation at different time intervals as shown in *Figure 2* for epoxidation of cyclooctene at 50°C. In the case of catalysts **B** and **C** the activity is nearly complete in about 20 h and reaches a plateau thereafter. With catalysts **A** and **D** the reaction proceeds slowly even after 24 h, though there is no marked increase in yields (refer to runs 13–16, *Table 5*). Though direct comparison of activity of present catalyst systems could not be made with analogous homogeneous Schiff base Ru(III) complexes, nevertheless the trends in reactivity are comparable, and in a few cases better performance was exhibited by supported catalysts (refer to *Table 4*)[26].

Mechanism of epoxidation

The two major mechanistic pathways for metal catalysed oxygen transfer are known to involve either peroxometal or oxometal species as the active intermediate[26]. 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 ruthenium follow the metal oxocatalysed route[27]. These mechanistic processes observed in homogeneous complex catalysis may be applicable in the polyer supported metal complexes. For Ru(III) supported polymeric catalysts, the possible structures of which are shown in *Scheme 1*, the following metal oxo based mechanism (*Scheme 2*) may be proposed.

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

CONCLUSION

Ruthenium (III) immobilized on functionalized poly-(styrene–divinyl benzene) was shown to affect oxidation of cyclooctene and styrene in a catalytic manner in the presence of alkyl hydroperoxide. The degree of crosslinking in the polymer support and the nature of Schiff bases bound to the metal have a bearing on the epoxide formation. Kinetic experiments reveal that at elevated temperature the activity of the catalysts towards epoxidation is significantly enhanced.

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