

Catalytic oxidation of alkanes and alkenes by polymer-anchored amino acid–ruthenium complexes

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Abstract

A synthetic strategy was developed to anchor an amino acid, L-valine, on to chloromethylated styrene–divinyl benzene co-polymer beads with 6% and 8% cross-linking. The polymeric ligands containing bidentate N,O donor sites were treated with a solution of ruthenium(III)chloride to form the metal complex on the support. These immobilized Ru(III) complexes were characterized by elemental analyses, FT-IR, ESR, SEM and thermal analysis. Physico-chemical properties of the supported catalysts were also studied. The catalytic oxidation of cyclohexane and toluene were investigated using the catalysts in presence of *tert*-butyl hydroperoxide as the terminal oxidant at ambient and at 45 °C. In the case of cyclohexane the formation of cyclohexanol and cyclohexanone were observed. Benzaldehyde was selectively obtained with toluene as substrate. The catalysts are also active in the epoxidation of olefins such as styrene and norbornylene. Recycling studies indicate that the catalyst can be recycled three to four times without significant degradation of polymer matrix. The probable mechanistic pathway has been described.

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1. Introduction

Heterogenization or immobilization of active metal complexes on polymeric supports has evolved as a promising strategy for combining the advantages of homogeneous and heterogeneous catalysts due to their easy isolation from the products by filtration and the possibility of recycling them by continuous operation in a reactor [1,2].

Transition metal complexes of Ti(IV), Mo(VI), Mn(III), Cr(VI) and Fe(III) with polymer-supported Schiff bases (N₂O₂ donor set) have been shown to be active catalysts for oxidation of alkane/alkene in presences of hydrogen peroxide, PhIO, *tert*-butyl hydroperoxide, NaOCl, etc., as the oxidants [3–6]. Apart from Schiff bases polymeric supports with

coordinating ligands such as β-diketones (O,O) [7], dipyriddy amine (N,N) [8], diphosphine (P,P) [9], etc., have frequently been employed to form metal complexes for catalytic applications. The chemical modification of a polymer incorporating bifunctional ligand such as an amino acid (N,O donor) has however received less attention. A major problem associated with anchoring of optically active amino acids to polymeric supports is the presence of reactive amino and carboxylic functionalities. Additionally racemization, product separation/purification, which are strongly influenced by pH and other reaction conditions, can create further complications. Literature search revealed the first instance of an amino acid complex of copper(II) bound to cross-linked poly(styrene–divinyl benzene) resin [10].

Homogeneous Ru(III) complexes of nitrogen- and oxygen- containing ligands are capable of catalyzing the oxidation of olefins in presence of PhIO, O₂ or *t*-BuOOH

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as the oxygen source [11–13]. However, systematic studies on polymer-supported analogues, in general, are lacking. In the present work, a simple synthetic method has been devised to anchor an amino acid L-valine on chloromethylated poly(styrene–divinyl benzene) resin followed by complexation with Ru(III) metal ion. These polymer-supported catalysts were evaluated for their performance in the oxidation of alkanes and olefins using *tert*-butyl hydroperoxide as the oxidant under mild reaction conditions.

2. Experimental

2.1. Materials

Chloromethylated poly(styrene-co-divinyl benzene) as spherical beads with 6% and 8% cross-link (18–44 mesh, chlorine content 16% and 17.5%, respectively) were received from Ion-Exchange India Ltd. The commercial resin was pre-treated with aqueous dioxane (50:50 v/v) and finally washed with methanol and dried under vacuum at 90 °C for 8 h before chemical functionalization. Hydrated RuCl₃ (Loba Chemie), L-valine (Merck), styrene (Merck), norbornylene (Aldrich), cyclohexane (Merck) and toluene (Merck) were used as received. AR-grade 1,4-dioxane, methanol, acetonitrile and ethanol were freshly distilled using standard methods prior to use [14]. *tert*-Butyl hydroperoxide (TBHP, 70% aqueous solution, Merck) was used as received. The active oxygen content in commercial TBHP was determined iodometrically following a literature method [15].

2.2. Measurements

Elemental analyses of polymer metal complexes were carried out using a Carlo-Erba Strumentazione microanalyser. The total Ru content on the polymeric support after loading was estimated using an Optima 4300DV Inductively Coupled Plasma Emission Spectrometer (Perkin-Elmer). Chlorine content was estimated gravimetrically by precipitation of chloride as AgCl. Surface area of supports and the Ru-anchored polymer was determined on a Carlo-Erba surface analyzer employing BET relationship. UV–vis reflectance spectra of catalysts were recorded on a Shimadzu UV 240 and Perkin-Elmer UV–vis–NIR Lambda 19 instrument using spectroscopic-grade BaSO₄ as a standard. UV–vis spectra in solution (200–900 nm) were recorded on Shimadzu UV 2201 spectrophotometer. IR and far-IR spectra of polymer-supported Ru-complexes at various stages of synthesis were recorded on a Nicolet Magna 550 spectrophotometer. Thermo gravimetric analyses of compounds were carried out on Shimadzu DT-30 instrument at a heating rate of 10 °C min⁻¹ under an atmosphere of nitrogen. Scanning electron micrographs of catalysts and supports were taken on a CAMICA SU30 instrument with SE electrode at 20 kV. X-band (9.5 MHz) electron spin resonance spectra of polymer-anchored Ru(III) complexes were recorded at room tempera-

ture on a Varian E112 spectrometer. TCNE was used as the ‘g’ marker. The analyses of various liquid products obtained in the catalytic oxidation/epoxidation reactions were carried out on Shimadzu 15A gas chromatograph using a 15% Carbowax column (1/8" × 2 m) and Data lab GC 9000 using capillary column AT-1 (0.32 mm × 15 M × 0.25 μ thickness) attached to a flame ionization detector and N₂ as carrier gas. Product identification was also carried on a Finnigan MAT 9001 GCQ-GC/MS system operated in the full scan mode and a quadrupole ion trap mass analyzer. The swelling behavior of supported catalysts in representative polar and non-polar solvents was carried out at 27 ± 1 °C by a previously described procedure [16].

2.3. Synthesis of polymer-anchored amino acid

Pre-washed chloromethylated styrene–divinyl benzene copolymer beads (12 g) were allowed to swell in 35 ml methanol for 1 h. An aqueous solution of L-valine (9 g) in 250 ml distilled water was separately prepared. The swollen polymer in methanol and the amino acid solution were refluxed for 16 h in presence of pyridine. The overall molar ratio of different reagents based on percent replaceable chlorine on resin approximately corresponds to 1:1.25:1.25 for Cl:amino acid:base. The contents were cooled and kept aside for one week with occasional shaking. At the end of this period, pH of the reaction mixture came down from the initial value of 7.1 to 5.1. The colour of the beads changed from off-white to pale yellow indicating the attachment of the amino acid. The L-valine linked polymer beads were filtered, washed with hot water followed by ethanol and finally dried under vacuum at 90 °C for 8 h to yield 13.8 g of product. The liganded polymers 8% or 6% poly(S-DVB)-L-val were used in subsequent complexation step.

2.4. Ruthenium loading

The loading of ruthenium on the polymer was carried out as follows: Poly(S-DVB)-L-val (12.5 g) was kept in contact with ethanol (50 ml) for 45 min. To this was added an ethanolic solution (100 ml) of hydrated ruthenium(III) chloride (1.25 g, 0.0048 mol); the contents gently agitated on a shaker at constant speed for 8 days at 25 °C (pH = 2.5). The colour of the beads changed from pale yellow to gray during this period indicating the formation of metal complex on the polymer matrix (pH of the solution remained around 2.7 after 8 days.) At the end of this period the gray-coloured polymer was filtered, washed thoroughly with ethanol, dioxane and methanol to ensure the removal of any unreacted metal chloride and dried in vacuum for 6 h at 90 °C.

2.5. Catalytic oxidation

A typical experimental procedure for the oxidation of alkanes and olefins using polymer-anchored Ru(III) catalysts is described below:

Table 1
Analytical data of polymer support, ligand and Ru-anchored catalysts

Compound	C%	H%	Cl%	N%	Ru%
8% Poly(S-DVB)CH ₂ Cl	70.38	5.77	17.56		
6% Poly(S-DVB)CH ₂ Cl	76.26	6.36	16.14		
8% Poly(S-DVB)-L-val	60.15	5.00	9.47	2.56	
6% Poly(S-DVB)-L-val	63.28	5.44	9.48	2.47	
Ru A	57.23	4.79	ND	2.61	1.71
Ru B	59.90	5.23	ND	2.70	1.30

ND: not determined.

The catalyst (0.2 g) was initially allowed to swell in acetonitrile (10 ml) for 30 min in a two neck round bottom flask equipped with a nitrogen inlet and a condenser. To this was added 2 mmol of the substrate followed by *tert*-butyl hydroperoxide (5 mmol). A known amount of an internal standard (chlorobenzene) was added to the above solution prior to the run. The flask was stoppered and the mixture stirred magnetically at different temperatures under nitrogen atmosphere taking care to avoid any loss of solvent vapours during agitation. At the end of specified time, the contents were analyzed by GC. Control experiments in the absence of catalyst showed practically no or only traces (~0.1%) of oxidation product formation. Peak positions of various reaction products were compared and matched with the retention times of authentic samples. Identity of the products was also confirmed by GC-MS.

3. Results and discussion

3.1. Complex formation

The reaction of hydrated ruthenium(III) chloride with polymer-anchored L-valine was conducted in the pH range of 2.4–2.5 at a metal:ligand molar ratio of 1:2 (based on mmole L-valine anchored). A maximum Ru loading up to 1.7% was obtained (Table 1). Depending on the solution pH, L-valine can coordinate to metal ion through either or both of amino (NH₂) or carboxyl (CO₂⁻) groups. For the trivalent Ru⁺³ ion, it is expected that the formation of [Ru(L-val)₂Cl₂]Cl type of chelate may be favoured [17]. Based on *p**K*_a values, Gillard et al. reported similar (N,O) chelation for different amino acid complexes at lower pH range [18]. The two polymer-anchored Ru complexes used in the present work for catalytic oxidation of olefins and alkanes are designated as under:

Ru A: 8% poly(S-DVB)-L-val Ru(III) complex

Ru B: 6% poly(S-DVB)-L-val Ru(III) complex

3.2. Catalyst characterization

Some of the important physical properties of these catalysts have been measured and the data compiled in Table 2. Ru B has a slightly higher surface area and larger pore volume than Ru A. The metal loading on Ru A with 8% cross-link (Ru 1.7%) was higher than Ru B with 6% cross-link (Ru

Table 2
Physical properties of poly(S-DVB)-supported Ru catalysts

Sample	Surface area (m ² g ⁻¹)	Bulk density (g cm ⁻³)	Pore volume (cm ³ g ⁻¹)
8% Poly(S-DVB)CH ₂ Cl	32.7	0.44	0.20
6% Poly(S-DVB)CH ₂ Cl	38.3	0.38	0.29
Ru A	23.5	0.51	0.14
Ru B	36.9	0.46	0.18

1.3%) (Table 1). Though nearly similar swelling behaviour was observed for the two catalysts in acetonitrile (1.6 mol%; Table 3), there is an increase in Ru uptake by at least about 24% for a cross-link difference of 2%. The results of swelling behavior indicate that it increased in polar solvents than in non-polar aliphatic and aromatic hydrocarbon solvents.

In order to ascertain the attachment of amino acid and the metal on the polymer support-IR spectra were recorded separately in mid (4000–400 cm⁻¹) and far IR (600–30 cm⁻¹) regions at different stages of synthesis. The sharp C–Cl peak (due to –CH₂Cl group) at 1261 cm⁻¹ in the starting polymer was practically absent or seen as a weak band after introduction of valine on the support. A strong band at 3423 cm⁻¹ in poly(S-DVB)-L-valine is assigned to –NH (*sec* amine) vibration. Medium-intensity band due to C–N stretching appears at 1082 cm⁻¹ both in the supported ligand and in the catalysts. A slight shift in the –NH str. band (~12 cm⁻¹) in Ru A and Ru B indicates the coordination of ‘N’ of amino acid to the metal [19]. The characteristic absorptions due to ν_{asym} COO⁻ str. and ν_{sym} COO⁻ str. of carboxylic group are seen at 1639 cm⁻¹ and 1487 cm⁻¹, respectively, in the ligand as well as in Ru A and Ru B. Weak bands in the far IR region at ~300–310 cm⁻¹ and 440–460 cm⁻¹ have been assigned to ν Ru–Cl and ν Ru–N/O vibrations [20,21].

The diffuse reflectance spectra (200–700 nm) of Ru A and Ru B display nearly identical features with two strong absorption bands at 350 nm and 400 nm, respectively, with reference to the BaSO₄ standard. These are assigned to $\pi \rightarrow t_{2g}$ charge transfer bands as has been observed for many mono nuclear Ru(III) compounds [20–23]. No other spin-allowed d–d transitions were observed in the visible region. Based on the structural features of six coordinate complexes derived from RuCl₃ and bidentate ligands, for e.g. [Ru(en)₂Cl₂]Cl (en = NH₂(CH₂)₂NH₂) or [Ru(bipy)₂Cl₂]Cl (bipy = 2,2'-bipyridyl), it is possible to envisage similar octahedral

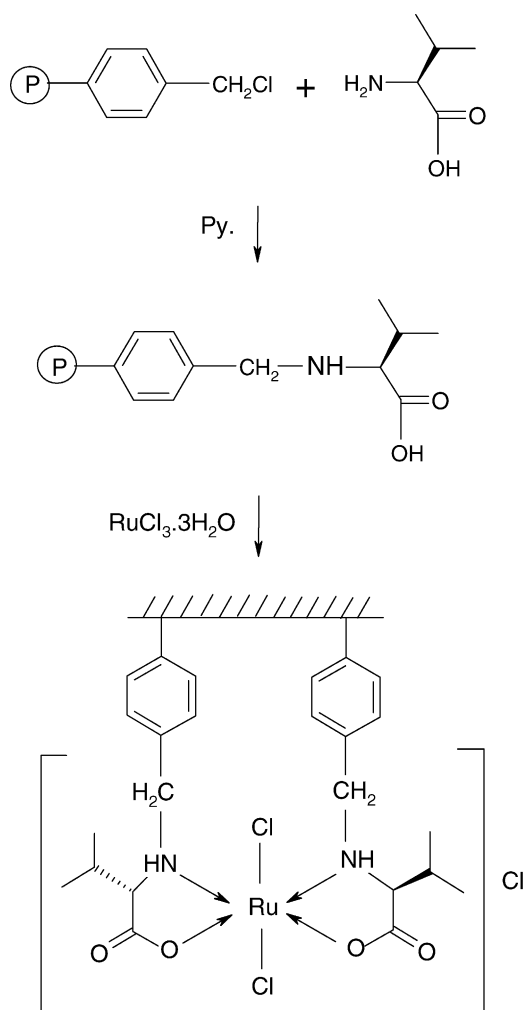
Table 3
Swelling data of Ru A and Ru B in different solvents (mol%)

Solvent	8% Poly(S-DVB)CH ₂ Cl	6% Poly(S-DVB)CH ₂ Cl	Ru A	Ru B
Acetonitrile	1.99	2.02	1.61	1.62
Benzene	1.07	1.11	0.84	0.95
Dichloromethane	1.48	1.77	1.27	1.35
Ethanol	1.70	1.90	1.62	1.64
<i>n</i> -Heptane	0.58	0.59	0.47	0.58
Methanol	2.73	2.82	2.19	2.34
Tetrahydrofuran	1.44	1.53	0.98	0.91
Toluene	1.08	1.13	0.81	0.80

stereochemistry for the present L-valine complexes represented as $[\text{Poly}(\text{L-val})_2\text{RuCl}_2]\text{Cl}$ (Scheme 1).

Scanning electron micrographs (SEM) at various stages of preparation of the polymer-supported L-valine and the ruthenium complexes were recorded to understand morphological changes occurring on the surface of the polymer. Scanning was done at 50–100 μ range across the length of the polymer beads. Comparison of images taken at a magnification of $\sim 3 \times 10^3$ showed that the smooth and flat surface of the starting poly(S-DVB) (Fig. 1a) is distinctly altered, exhibiting considerable roughening of the top layer upon anchoring of the amino acid (Fig. 1b). After metal incorporation, randomly oriented dark depositions on the external surface of the resin were seen (Fig. 1c).

A single-step degradation peak in the TG was observed for the unsupported polymer in the 410–440 $^\circ\text{C}$ temperature range. On the other hand, both ruthenium-supported catalysts degrade at considerably lower temperatures (Table 4). The variation in cross-linking in Ru A and Ru B does not, however, show much deviation in their thermal stabilities as seen from



Scheme 1. Synthesis of poly(S-DVB)-supported amino acid-Ru(III) complex.

Table 4
TG data of polymeric supports and anchored Ru(III) catalysts

Compound	Degree temperature ($^\circ\text{C}$)	Weight loss (%)
8%Poly(S-DVB)CH ₂ Cl	440	21.0
6%Poly(S-DVB)CH ₂ Cl	410	21.0
Ru A	111	2.4
	370	21.2
Ru B	110	2.0
	350	21.0

the weight loss which was around 21% at 350–370 $^\circ\text{C}$. It appears that either the dissociation of covalently bound amino acid ligand moieties or a partial scission of polymeric chain might be occurring at this temperature. Some weight loss ($\sim 2\%$) was also observed at ~ 110 $^\circ\text{C}$ due to loosely bound surface moisture or volatiles on the surface of catalysts.

The X-band EPR spectrum of Ru A recorded in the solid state at room temperature displays broad signals as shown in Fig. 2. The spectra can be interpreted assuming an axial symmetry for an isolated $S = 1/2$ low spin (t_{2g})⁵ Ru(III) ion using the Spin-Hamiltonian suggested by Drago et al. [24]. The broadening of signals with increase in temperature is on account of the effects of large spin-orbit coupling constant (λ) for Ru(III). As the temperature is raised the orbital angular momentum on the metal probably couple with electron spin leading to extremely short relaxation times accompanied by broad EPR lines. The spectrum of Ru A (Fig. 2) is characterized by two resonances in the g_{\perp} region ($g_{\perp} = 2.91$) which are split into two components with the g_{\parallel} resonance observed at 2.26. No hyperfine splitting is noticed at this temperature. Interestingly, the spectral features have been ascribed to the presence of mixed valent Ru (III)/(II) species for dimeric ruthenium complexes [21,24–26]. The ESR spectra of high-spin Ru^{+2} ($4d^6$) ion would be difficult to observe and are not consistent with the spectrum in this study. Similarly low-spin Ru^{+2} ($4d^6$) ion would be ESR silent. Therefore, it seems unlikely that the observed spectral feature in our case can be due to the simultaneous existence of Ru in two different oxidation states on a rigid polymeric support.

3.3. Catalytic evaluation

The ability of the newly synthesized polymer bound Ru(III)-L-valine complexes (Ru A and Ru B) to catalyze the oxidation of various alkanes and alkenes were systematically examined in the presence of TBHP as the terminal oxidant. Blank experiments revealed that no reaction occurred in the absence of either the catalyst or the oxidant. The results of oxidation carried out at two different temperatures are compiled in Table 5. All compounds undergo oxidation in presence of the Ru-supported catalysts and in some cases very high selectivities are obtained. Toluene oxidation results in selective formation of benzaldehyde whereas in case of cyclohexane both cyclohexanol and cyclohexanone were obtained (Table 5). Styrene oxidation results in multiple

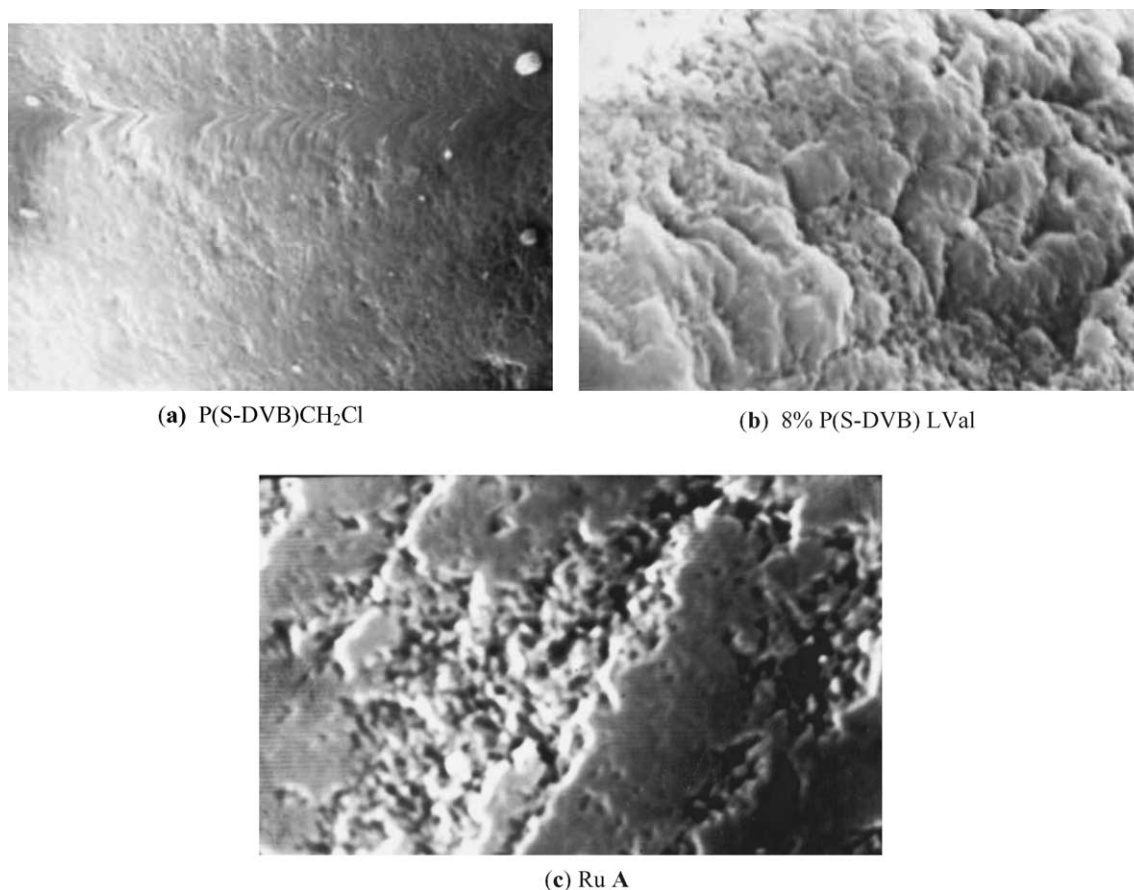


Fig. 1. Scanning electron micrographs of (a) poly(S-DVB)CH₂Cl, (b) 8% poly(S-DVB)-L-val, (c) Ru A (magnification, 3×10^3).

product formation viz. epoxide, benzaldehyde and acetophenone. In this reaction, interestingly aldehyde is the major product. Norbornylene selectively yields corresponding epoxide. In the examples discussed above, both Ru A and Ru B display comparable activity towards both alkanes and olefins.

For a proper understanding of the efficacy of the present polymer-supported Ru catalysts vis-à-vis its homogeneous counterpart, namely Ru(L-valine)₂Cl₂ complex, direct comparison of catalytic activities under optimized reaction conditions is desirable. In the absence of relevant data on oxidations of alkanes using homogeneous amino acid–metal catalysts, an attempt was made to generate in situ (without isolation) a simple L-valine complex of Ru(III) by mixing the ligand and the metal chloride in 1:2 molar ratio in an aqueous solution at a pH of ~ 2.2 . After a reaction period of 24 h (reaction temperature 45 °C) an aliquot of the solution corresponding to 0.026 mmol Ru was taken up for subsequent oxidation reaction with toluene and cyclohexane in presence of TBHP under identical reaction conditions. The overall yields were higher than for the supported catalysts (Table 5) and were found to be 11.2% and 30.1%, respectively. A plausible reason for lower activity exhibited by the polymer bound Ru A and Ru B may be due to the slower rate of diffusion of

substrates into the polymer matrix at the sites where active catalytic species are located [27].

3.4. Catalyst recycling

One of the main objectives of supporting a homogeneous metal complex on to a polymer support is to evaluate the potential of the catalyst for practical applications. A preliminary study of the recycling efficiency of Ru A using toluene and cyclohexane as model substrates was undertaken. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with solvent and dried carefully to constant weight before using it in the subsequent run. These results are shown in Table 6. It can be inferred that the catalyst can be recycled at least about four times. However, there is a progressive loss of activity accompanied by diminished yields. Estimation of Ru present in the recycled catalyst after four cycles gave a value of 0.82% Ru which corresponds to $\sim 50\%$ depletion of active metal center than that present at the start of the first cycle. In order to verify whether the catalysts operate in a truly heterogeneous manner, the 'hot filtration' probe suggested by Sheldon et al. [28] was applied to our system. The result of this test confirmed that the catalysts behave in a truly heterogeneous

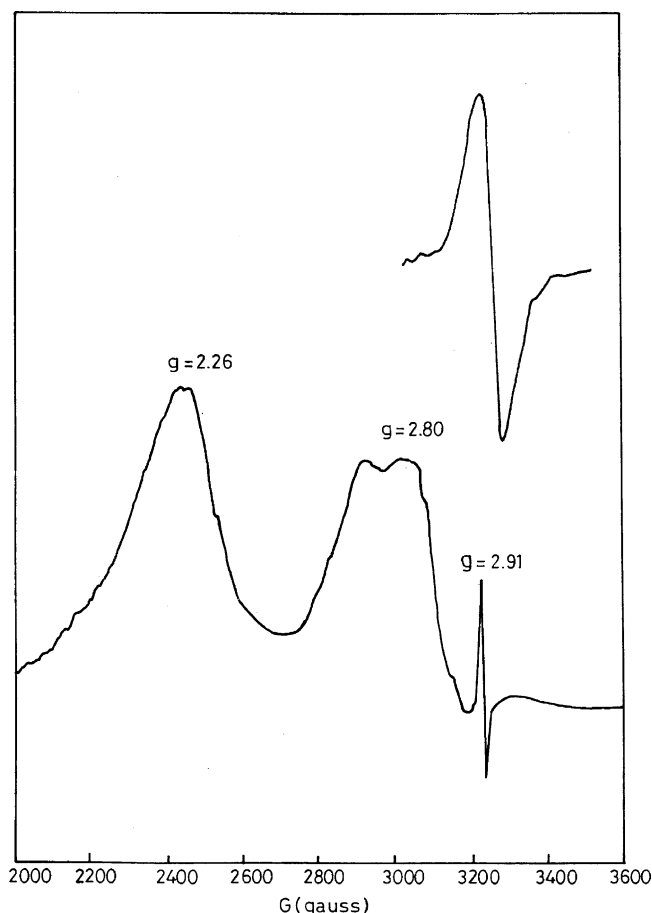


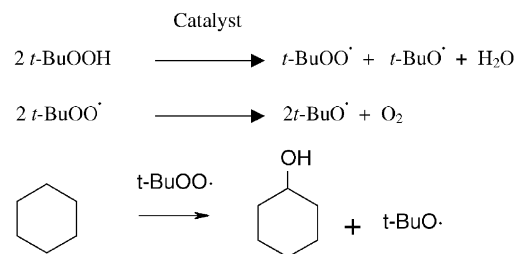
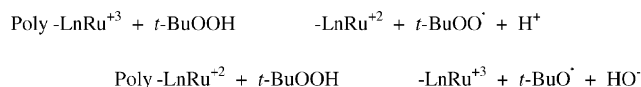
Fig. 2. ESR spectra of Ru A. Inset: resonance signal with field set at 3.2 kG, scan range 400 G, gain 1.25×10^4 .

manner [29]. More importantly, the Ru species leached into the filtrate is not responsible for the observed catalytic activity.

3.5. Mechanism

It has now been well recognized that the metal-catalyzed oxidation of olefins and or alkanes in presence of alkyl hydroperoxides can proceed via two distinctly different mechanisms; one involving a high valent metal oxo/peroxo species or the other which involve free radical intermediates [30]. In order to gain some insight into the nature of this reaction a series of experiments were carried out using a free radical trap, 2,6-di-*tert* butyl-4-methyl phenol (BHT) in the oxidation of cyclohexane using catalyst Ru A. These results are summarized in Table 7. BHT (25 and 50 equivalents) was added to the reaction mixture prior to addition of TBHP. The overall yield was only marginally reduced from 18.2% to 16.6% with 25 equivalent of BHT in the reaction with cyclohexane and at higher concentrations of BHT (50 equivalents) yields were reduced from 18.2% to 14.0%. It is known that BHT scavenges peroxy free radicals and thus suppress the oxidation reaction proceeding via free radical pathway [31].

For the present catalyst system, formation of products can be explained by the following mechanism:



TBHP decomposition leads to the generation of oxygen in addition to the formation of free *t*-butoxyl radicals. No oxidation was observed in presence of pure O₂ gas, indicating its non-involvement in the reaction. In subsequent tests for free radicals, experiments were conducted with CCl₄. Analysis showed partial reduction in yields for cyclohexane, but no other free radical-induced side products, viz. cyclohexyl

Table 5
Catalytic oxidation with Ru A and Ru B

Catalyst ^a	Substrate ^b	Temperature (°C)	Yield (%) ^d	Products/selectivity (wt.%)		
				PhCHO		
Ru A	Toluene	28	7.1	100.0		
Ru A		45	10.3	100.0		
Ru B		28	6.8	100.0		
Ru B		45	10.1	100.0		
				Cy-one ^e	Cy-ol	Cy-ol/Cy-one
Ru A	Cyclohexane	28	18.2	79.6	20.5	0.26
Ru A		45	29.3	70.7	29.3	0.40
Ru B		28	17.8	85.6	14.4	0.20
Ru B		45	29.0	71.7	28.3	0.38
				Epoxide	PhCHO	PhCOME
Ru A	Styrene ^c	28	40.4	21.2	67.2	11.0
Ru A		45	52.8	37.5	49.3	13.2
Ru B		28	41.8	14.7	70.1	14.7
Ru B		45	53.8	23.8	57.5	18.7
Ru A	Norbornylene ^c	28	30.7	100.0		
Ru A		45	42.7	100.0		
Ru B		28	24.4	100.0		
Ru B		45	40.0	100.0		

Cy-one, cyclohexanone; Cy-ol, cyclohexanol; reaction time, 24 h.

^a 0.2 g.

^b 2.0 mmol.

^c 5.0 mmol.

^d Yield based on starting material.

chloride or bicyclohexyl, were detected [32]. The cyclohexanol to cyclohexanone mole ratio remain unaltered (prior to and after BHT addition reaction, refer Table 5) and was found to be between 0.26 and 0.29. In the works of Que, Fish and others [33–35] using cationic Fe⁺³ catalyst such as [Fe(TPA)Cl₂]⁺ (TPA = tetradentate N₄ ligand, tris (2-pyridyl methyl) amine) oxidation of cyclohexane in presence of TBHP in acetonitrile at room temperature gave almost 1:1 ratio of Cy-ol: Cy-one. A high valent Fe^{IV} = O oxo species was proposed as the active species.

From the results of various mechanistic probes it is possible to predict that the major route for the formation of different products is via a homolytic cleavage of peroxide bond. Nevertheless, the partial suppression of reaction by free rad-

Table 6
Recycling of Ru A in oxidation of toluene and cyclohexane using TBHP^a

Cycle no.	Yield (%) ^b	
	Benzaldehyde ^c	ol/one mixture ^d
1	10.3	29.3
2	8.4	24.0
3	6.2	19.4
4	5.1	15.8

^a Reaction conditions: 200 mg catalyst; 5.0 mmol TBHP; 10 ml acetonitrile; 45 °C; 24 h; 2.0 mmol substrate.

^b Yield based on starting alkane.

^c Toluene.

^d Cyclohexane.

Table 7
Effect of free radical trap on oxidation^a using Ru A

Substrate (mmole)	Additive	Catalyst:additive (mole ratio)	Yield (%)	Cy-ol/Cy-one
Cyclohexane (2.0)	BHT	25	16.6	0.29
		50	14.3	0.30
	CCl ₄	Excess	14.0	0.29

^a Temperature, 28 °C; solvent, CH₃CN; oxidant, TBHP; time, 24 h.

ical traps even under high concentration points to the existence of a second, as yet unclear, mechanism which might involve the metal in higher oxidation state. The existence of such dual mechanistic pathways: i.e. one proceeding in a heterolytic manner (via Ru(VI) or Ru(IV) oxo species) and the other by radical auto oxidation process essentially leading to the same products has been indicated by earlier workers [32,36].

4. Conclusions

Ruthenium (III) anchored on L-valine-bound styrene-divinyl benzene copolymer has been shown to catalyze the oxidation of alkanes/alkenes in presence of alkyl hydroperoxide under mild conditions. The catalysts can be recycled without any loss in selectivity. Slow deactivation of the catalysts was observed over extended reuse, which can limit their application. Apart from the reaction

conditions, the nature of amino acid and the stability of its metal complex on the surface of polymer support will determine the formation of active species responsible for product selectivity in oxidation reactions.

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