

Oxidation of benzyl alcohol using polymer anchored Ru(III) complex as catalyst

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Abstract

Polymer-anchored Ru(III) complex was synthesized by sequential attachment of ethylenediamine, salicylaldehyde and ruthenium chloride to chloromethylated styrene–divinylbenzene copolymer with 8% cross-linking. Synthesized catalyst was characterized by different techniques such as FTIR, reflectance UV-VIS spectroscopy, ESR, ESCA, SEM and TGA. Various physico-chemical properties such as moisture content, bulk density, surface area and swelling behaviour in different solvents were also studied. Catalytic activity of this catalyst was tested for oxidation of benzyl alcohol by varying the temperature of the system as well as concentration of substrate and catalyst. Values of energy of activation and entropy of activation have been evaluated from the kinetic data. A probable reaction mechanism has been proposed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polymer anchored Ru(III) complex; Heterogenized catalyst; Ruthenium Schiff base complex; Kinetics of oxidation of benzyl alcohol; Energy of activation in benzyl alcohol oxidation; Reaction mechanism for oxidation

1. Introduction

Catalytic oxidation is an area of particular significance for homogeneous catalysis as most of the largest industrial productions involving catalytic oxidation are practised in the homogeneous phase [1]. However, the problems related to corrosion, plating out on the reactor wall, recovery from the reaction mixture and its reuse are limitations in homogeneous catalytic processes. The present day stringent ecological standards have also required attention to envi-

ronmental friendly methods. Recovery of the catalysts and their reusability can be simplified if the homogeneous complex is heterogenized by supporting on an insoluble support. Polymers used as a support have gained attention as they are inert, non-toxic, non-volatile, insoluble and often recyclable [2]. Thus, research for viable polymer supported catalysts has gained prominence in industries as well as in chemical laboratories [3]. The main drawback of the supported catalysts is the leaching of the metal ion from the surface of the support which can be prevented by the use of chelating ligands. A number of papers has been published describing

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the use of TPP as a ligand [4]. There are few publications where N and O donor groups have been used as ligands. We have also reported catalytic activity of different heterogenized homogeneous chelated metal complex catalysts for hydrogenation of olefins and oxidation of cyclohexane and toluene [5–9]. Covalently bound multidentate amines could be further modified to prepare polymer-bound chelates [10]. Recently, Sueto et al. [11] have reported various studies on partial oxidation of benzyl alcohol to benzaldehyde on supported catalysts. The present study reports synthesis of polymer-bound Ru(III) Schiff base complex and oxidation of benzyl alcohol with molecular oxygen using this catalyst.

2. Experimental

2.1. Materials and equipment

Chloromethylated styrene–divinylbenzene copolymer with 8% cross-linked was provided by Ion Exchange, Bombay (India). THF, dioxane, methanol and benzyl alcohol were purified as reported elsewhere [12]. Ethylenediamine and salicylaldehyde were distilled before use. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Lobachemie, Bombay) was used as received.

Elemental analyses and TGA were carried out in our laboratory using a Coleman analyzer and a Shimadzu Thermal Analyzer DT-30, respectively. UV-VIS reflectance spectra of the solid samples were recorded on a Shimadzu UV-240 spectrophotometer with reference to

Table 1
Physical properties of the supported catalyst

	Catalyst	Support
Surface area (NTP) ($\text{m}^2 \text{g}^{-1}$)	99.62	37.37
Pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.14	0.04
Apparent bulk density (g cm^{-3})	0.4287	0.39
Moisture content (wt.%)	1.04	

Table 2
Elemental analyses at different stages of preparation (wt.%)

P			Q			R			
C	H	Cl	C	H	N	C	H	N	Ru
75.38	5.93	17.50	63.17	6.02	3.67	61.56	6.88	4.51	7.12×10^{-2}

P = Chloromethylated polymer.

Q = After functionalization by Schiff base.

R = After complex formation.

non-absorbing BaSO_4 as a standard. IR spectra were recorded on a Perkin-Elmer R-32 instrument. ESR was scanned on a Bruker ESP-300 K band spectrometer using a 100-kHz field modulation. ESR experiment was conducted on powdered sample at 298 K in N_2 atmosphere. Scanning electron micrographs were recorded on Jeol SJM T-300. ESCA were recorded on a physical electronic PHI-5400, USA with Mg K_α as a radiation source. The surface area of the polymer support as well as the catalyst was measured using a Carlo-Erba Strumentazione 1800. Swelling properties of the polymer support as well as the catalyst were studied using different polar and non-polar solvents at constant temperature. The detailed procedure has been described earlier [8].

2.2. Synthesis of the catalyst

Chloromethylated P(S-DVB) polymer beads were washed in the following sequence: aque-

Table 3
Swelling studied using different solvents

Solvent	Swelling (mol%)	
	Polymer support	Catalyst
Water	3.83	4.65
Methanol	2.52	2.02
Ethanol	1.81	1.45
<i>N,N'</i> -Dimethyl formamide	1.27	1.04
Dioxane	1.42	0.89
Tetrahydrofuran	1.00	0.88
Acetone	1.10	0.83
Benzene	0.83	0.82
Cyclohexane	0.68	0.59

ous dioxane, aqueous dioxane containing 10% HCl, methanol and finally with distilled water until the complete removal of free chloride. In order to functionalize the polymer support with Schiff base Salen, it was first treated with an appropriate quantity of ethylenediamine using THF as a solvent at room temperature for 48 h (25 g polymer, 8.4 ml en, 117 ml THF) [8]. The beads were washed in the following sequence: deionized water, methanol and dry dioxane. It was dried at 60°C. It was then refluxed in a solution of salicylaldehyde prepared in benzene

for 24 h [10]. Water of condensation was removed in a dean-stark trap. Resin was cooled, soxhlet extracted with ethanol and dried at 80°C. The functionalized polymer was kept in contact with 200 ml of ethanol for 30 min. An ethanolic solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.3% w/v, 100 ml) was added to it and kept at room temperature for 7 days. A change in colour of the supernatant liquid from dark orange to light orange and that of the polymer beads from yellow to light green indicates the formation of metal complex on the surface of the polymer. The

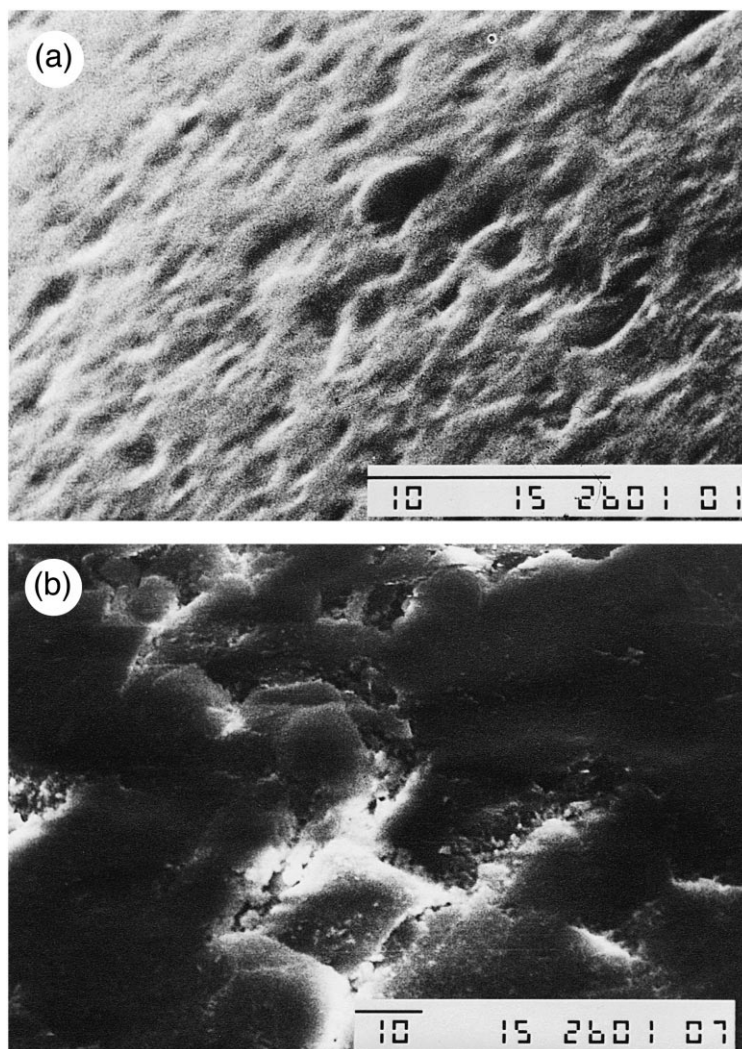


Fig. 1. Scanning electron micrograph of (a) polymer support and (b) catalyst C.

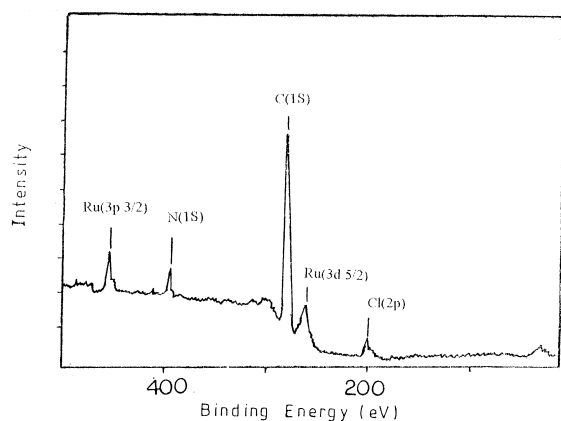


Fig. 2. ESCA spectrum of catalyst C.

quantity of Ru present on the surface of the polymer was determined by refluxing it with concentrated HCl (AR) for 24 h and then estimating the metal concentration in the solution by spectrophotometric method after complexation with nitroso-R salt [13].

Synthesized catalyst was named as catalyst C = 8 P Ru(III) Salen.

2.3. Kinetics of oxidation

The kinetics of oxidation of benzyl alcohol was studied at atmospheric pressure by measuring oxygen uptake using a glass manometric apparatus. The initial rate was calculated from the slope of the plot of oxygen uptake at various intervals of time. The detailed procedure and experimental set-up are described earlier [8]. The products were analyzed by the use of gas chromatograph using a flame ionization detector

Table 4
Various IR frequencies assigned for the polymer supported catalyst (cm^{-1})

Ru-Cl	Ru-O	Ru-N	C=N	N-H
320	513	603	1612	2925

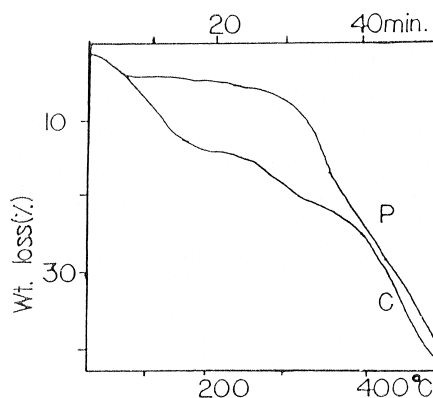


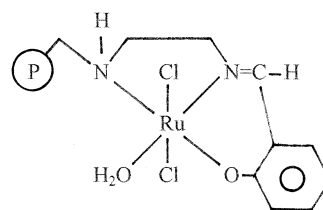
Fig. 3. TGA curves for the polymer support and the catalyst.

and carbowax column. No side product was formed as seen by GC analysis.

3. Results and discussion

3.1. Characterization of catalyst

Physico-chemical properties of the catalyst and the support are given in Tables 1–3. An increase in the surface area was observed after loading the metal ions, which might be due to functionalization of the polymer with bulky ligand. Successful functionalization of the polymer was confirmed by elemental analyses at different stages of preparation of the catalyst. A decrease in swelling was observed as the nature of the solvent was changed from polar to non-polar. Methanol was found to be a suitable solvent for the oxidation reaction because of



Scheme 1.

Table 5
Effect of substrate concentration on oxidation at 35°C, 1 atm pressure using 20 ml methanol as a solvent

[Ru] (mol l ⁻¹) 10 ⁵	[Benzyl alcohol] (mol l ⁻¹)10 ³	Rate of reaction (ml min ⁻¹)	Order of reaction
7.12	4.83	0.35	0.583
	9.66	0.50	
	14.49	0.67	
	19.32	0.80	

better swellability with the catalyst and miscibility with the substrate. A clear change in morphology of the polymer support after ligand and metal ion introduction was observed by SEM (Fig. 1). The UV-VIS reflectance spectra showed d-d transition at 410 nm which might be due to Ru(III). The *g*-value obtained from ESR study was found to be 2.54 which shows Ru is present in low spin +3 oxidation state. This has been further confirmed by ESCA (Fig. 2). ESCA studies of the polymer-bound ruthenium catalyst gave peaks due to Ru(3p 3/2), Ru(3d 5/2), C(1s) Cl(2p) and N(1s) indicating the presence of Ru in low spin +3 oxidation state. The formation of metal complex on the surface of the polymer was confirmed by IR. The various infrared frequencies are assigned as shown in Table 4. TG analysis indicates no change in thermal stability of the polymer after complex formation, however, the thermal stability of the catalyst was found up to 100°C. It is therefore inferred that the catalyst could be used safely up to 100°C (Fig. 3). A probable structure of the

catalyst has been proposed based on the spectroscopic data (Scheme 1).

3.2. Oxidation reactions

The kinetics of oxidation of benzyl alcohol for polymer-bound catalyst C was investigated. The reaction was carried out in a kinetic regime at atmospheric pressure in the temperature range of 30–45°C. The stirring of the reaction mixture was maintained at an optimized rate (600 rpm) throughout the experiment to minimize diffusion [14]. The influence of various parameters on the rate of oxidation was studied (Tables 5–7).

3.2.1. Influence of benzyl alcohol concentration

The effect of substrate concentration on the rate of oxidation was determined in the range of 4.83×10^{-3} to 19.32×10^{-3} mol l⁻¹ at 35°C and 1 atm pressure at constant catalyst concentration of 7.12×10^{-5} mol l⁻¹ of Ru(III) (Table 5). It was observed that the rate of oxidation

Table 6
Effect of catalyst concentration on oxidation of benzyl alcohol^a

[Benzyl alcohol] (mol l ⁻¹)10 ³	[Ru] (mol l ⁻¹)10 ⁵	Rate of reaction (ml min ⁻¹)	Order of reaction
9.66	3.56	0.4	0.483
	7.12	0.5	
	10.68	0.6	
	14.24	0.7	

^aAt 35°C, 1 atm pressure using 20 ml methanol.

Table 7
Effect of temperature on oxidation of benzyl alcohol^a

Temperature (°C)	Rate of reaction (ml min ⁻¹)	Energy of activation (kJ mol ⁻¹)	Entropy of activation (eu)
25	0.31		
30	0.40	32.34	-40.44
35	0.50		
40	0.62		

^aAt 1 atm pressure using 20 ml methanol.

increases linearly with respect to substrate concentration. The order of reaction was calculated from the linear plot of log (initial rate) vs. log [benzyl alcohol] and was found to be 0.58.

3.2.2. Influence of catalyst concentration

The effect of catalyst concentration on the rate of oxidation was studied in the range of 3.56×10^{-5} to 14.24×10^{-5} mol l⁻¹ of Ru(III) at 35°C and 1 atm pressure and constant substrate concentration of 9.66×10^{-3} mol l⁻¹ (Table 6). A linear increase in the rate of reaction was found with increase in catalyst concentration which indicates that there is no dimerization of metal complex in the range studied and mass transfer effect could be neglected [14]. The order of reaction calculated from the plot of log (initial rate) vs. log [catalyst] was found to be fractional with respect to catalyst concentration. This may be due to non-accessibility of catalytic sites, as well as steric hindrance because of complex nature of the catalyst [5].

3.2.3. Influence of temperature

Catalytic oxidation of benzyl alcohol was studied in the range of 30–45°C at a fixed catalyst concentration of 7.12×10^{-5} mol l⁻¹ of Ru(III) at 1 atm pressure and a substrate concentration of 9.66×10^{-3} mol l⁻¹ (Table 7). An increase in the rate with temperature was observed. Energy of activation calculated from the slope of the plot of log (initial rate) vs. 1/T (Fig. 4) was found to be 32.34 kJ mol⁻¹ and

corresponding entropy of activation was found to be -40.44 eu.

3.2.4. Life cycle of catalysts

In order to test stability of the polymer-bound catalyst under repeated catalytic cycles, an experiment was carried out at 35°C by injecting a known amount of substrate (i.e., 20 μl) at 75-min intervals. The rate of oxidation was measured as a function of time for both used and fresh catalysts. The experiment was carried out up to 7 h. The results are summarized in Table 8. It was found that the maximum rate of reaction was maintained for about 3.5 h for fresh catalysts after which it decreased slowly. This might be due to leaching of the metal ions from the surface which was confirmed by estimating the metal content after completion of the experiment. A loss of about 35% of the metal from the support was observed at the end of the reaction.

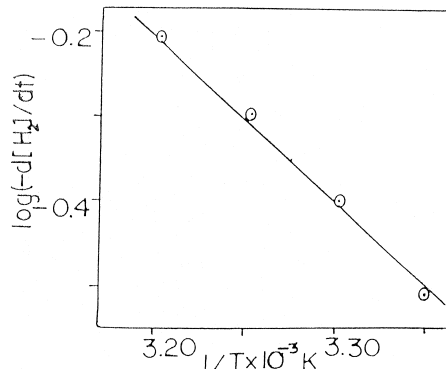


Fig. 4. Arrhenius plot for the polymer anchored catalyst.

Table 8

Life cycle study of polymer anchored catalysts at 35°C, 1 atm pressure using 20 ml methanol

[Ru] (mol l ⁻¹)10 ⁵	[Benzyl alcohol] (mol l ⁻¹)10 ³	Time (min)	Rate of reaction (ml min ⁻¹)	
			Fresh catalyst	Used catalyst
7.12	9.66	60	0.50	0.50
		135	0.50	0.50
		210	0.50	0.45
		285	0.46	0.40
		360	0.39	0.31
		335	0.31	0.25

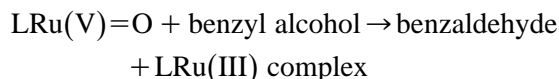
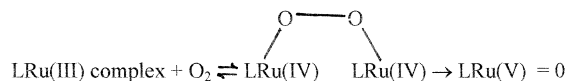
3.2.5. Kinetics of oxidation with homogeneous analogue

Kinetics of oxidation of benzyl alcohol was also carried out using homogeneous [Ru(III) Salen Cl] complex obtained in solution by mixing 1:1 RuCl₃ and Schiff base Salen in methanol. A lower uptake of O₂ was obtained as compared to heterogenized catalyst in spite of the higher concentration of metal ion taken for convenience in measuring the rate of reaction (Table 9). Energy of activation was found to be 103.4 kJ mol⁻¹. This shows a lower catalytic activity in the homogeneous system compared to heterogenized catalyst.

4. Reaction mechanism

The reaction mechanism for oxidation with molecular oxygen by metal ions/complexes in

homogeneous medium is studied widely and the formation of peroxy and oxo complexes was suggested to be responsible for transfer of oxygen to substrate [15,16]. On the basis of experimental results as well as evidence from literature, a probable mechanism can be suggested.



where L is the ligand (Schiff base salicylaldehyde–ethylenediamine). The corresponding rate equation can be expressed as

$$R = k[\text{catalyst}][\text{benzyl alcohol}]$$

where *R* is the initial rate and *k* is the rate constant.

Table 9

Summary of the kinetics of benzyl alcohol oxidation using [Ru(III) Salen Cl] complex in solution at 35°C and 1 atm pressure

Temp°C	[Ru(III)] (mol l ⁻¹)10 ³	[Benzyl alcohol] (mol l ⁻¹)10 ³	Rate of reaction (ml min ⁻¹)
30	1.03	9.66	0.07
35	1.03		0.11
	2.05		0.18
	3.08		0.26
	4.10		0.32
	1.03		0.06
40	1.03	4.83	0.06
		14.49	0.27
		19.32	0.45
		9.66	0.18
45			0.23

Volume of methanol = 20 ml.

5. Conclusion

The Ru(III) Salen complex was successfully heterogenized using the P(S-DVB) copolymer. The attachment and formation of the metal complex on the polymer matrix was confirmed by elemental analysis, IR, UV-VIS, ESR and ESCA. A probable structure is proposed but other possibilities cannot be ruled out. This catalyst was found to be active for oxidation of benzyl alcohol. The energy of activation was found to be $32.34 \text{ kJ mol}^{-1}$ which indicates that the reaction is fast. The recycling efficiency of the catalyst was seen and it was found to be stable for four cycles. After that a decrease in rate was observed which may be due to leaching of the metal ions. Polymer-anchored catalyst was found to be more effective towards oxidation of benzyl alcohol than homogeneous counterpart. The formation of oxo complex and the transfer of oxygen via this route might be responsible for the reaction.

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