CHAPTER 5

KINETICS OF OXIDATION OF BENZYL ALCOHOL

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5.1 Kinetics of oxidation of benzyl alcohol by polymer-bound Ru(III) and Pd(II) complex catalysts

5.1.1 Introduction

Catalytic oxidation is the single most important technology for the conversion of hydrocarbon feedstocks (olefins, alkanes and aromatics) to industrially important oxygenated derivatives (1) The attack of oxygen on the hydrocarbon molecule is the easiest route to functionalize this molecule. Selective oxidation processes in which hydrocarbon molecules are oxygenated to form alcohols, aldehydes or acids are the basis of modern petrochemical industries (2). Catalytic oxidation is the largest area of application in homogeneous catalysis In this field, even for the production of bulk chemicals, homogeneous catalysts appear to compete effectively with heterogeneous ones (3). This observation is obvious from Table 5.1 regarding world capacity of some of the largest industrial productions including catalytic oxidation (4). However, in the era of increased environmental awareness, the main drawback of homogeneous catalysts, i.e difficulty of catalyst separation, recovery and recycle, have prompted researchers to investigate alternatives. Oxidation of organic molecules with heterogeneous catalysts have become an area of renewed interest in recent years because these catalytic reactions are environmentally safe and could replace stoichiometric oxidants (5).

Table 5.1

Homogeneous catalytic oxidation processes for the production of bulk chemicals

Product	Reactant	Year	Capacity 10^6 t/y	Oxidant
terephthalic acid	p-xylene	1987	10.1	O_2
phenol	toluene, cyclohexane, benzene/ propylene	1987	4.2	O_2
acetaldehyde	ethylene	1986	3.0	O_2
acetic acid	acetaldehyde light paraffins	1986	2.3	O_2

Table 5.2

Heterogeneous catalytic oxidation processes for the production of bulk chemicals

Product	Raw material	Catalyst	Ref.
Ethylene oxide	Ethylene	Ag/Al_2O_3	(6)
Propylene oxide	propylene	Ti^{IV}/SiO_2 or Mo^{VI}	(1)
phthalic anhydride	o-xylene	V_2O_5/SiO_2	(1)
Gluconic acid	Glucose	Pd-Bi/C	(8,9)
Acetic acid	ethane	V-P-O-TiO_2	(10)
Methyacrylic acid Methacrolein	isobutane	V-P-Co-O	(11)
phthalic anhydride maleic anhydride	n-pentane	V-P-O	(12)

Table 5.2 describes some of the bulk chemicals manufacturing processes using heterogeneous catalytic oxidation. The gas phase epoxidation of ethylene using molecular oxygen to produce ethylene oxide is one of the most successful examples of heterogeneous catalysis to date (6). In 1995, over 7.62 billion lb of ethylene oxide were produced in the US alone (7).

Catalytic oxidation requires an oxygen source such as iodosylbenzene, t-butylhydroperoxide, sodium hypochlorite, ozone, hydrogen peroxide or molecular oxygen to carry out oxygen transfer to the molecule to be oxidised. Popularity of molecular oxygen as an oxidant in catalytic oxidation is self-evident from Table 5.1 Most of the processes described in Table 5.2 employ molecular oxygen as an oxidant.

Erdohelyi et al (13) have studied oxidation of methane to formaldehyde using K_2MoO_4 deposited on various supports such as SiO_2, Al_2O_3, TiO_2, ZSM-5 and MgO. It was found that the production distribution of the oxidation reaction was influenced by the nature of the support. The highest activity was measured for magnesia-supported catalyst whereas the highest yield of formaldehyde was obtained on silica-supported catalyst. Pereira et al (14) carried out vapour-phase oxidation of toluene to benzaldehyde using V_2O_5-K_2SO_4-SiO_2 catalyst and suggested that the conversion to benzaldehyde depends upon V^{5+}/V^{4+} ratio Supported metal oxidation catalysts are also extensively studied (1). Supported bimetallic (Pd, Bi/C) and trimetallic (Pd, Pt, Bi/C) catalysts were used by Despeyroux et al (15) to oxidise glucose to gluconic acid with high selectivity. 96% selectivity was obtained using a 4% Pd, 1% Pt, 5% Bi-on-charcoal catalyst Pt was found to enhance the activity and Bi enhanced the selectivity of the Pd catalyst Catalytic oxidation of alcohols is a useful method for the preparation of aldehydes and ketones Oxidation of benzylalcohol using metal oxides, zeolites, alumina and acid catalysts has been reported by many researchers (16-19). Benzyl alcohol undergoes disproportionation to benzaldehyde and toluene over alumina and other acid catalysts (18) whereas on metal oxides it undergoes dehydrogenation to yield benzaldehyde and toluene as major products and benzyl benzoate, benzene and methanol in small amounts depending upon reaction conditions (19). Recently, Viswanathan et al. (17) have reported oxidation of benzyl alcohol on ABO_3 (A=Ba, B=Pb, Bi and Cu) type perovskite oxides A higher catalytic activity was found using oxygen as an oxidant. Sueto et al (20) have recently observed high activity of NaZSM-5 supported Cu catalysts in oxidation of benzyl alcohol to benzaldehyde.

Application of heterogenized homogeneous catalyst for oxidation reactions is interesting as in addition to advantages offered by heterogeneous catalyst, it also retains activity and selectivity of homogeneous catalysts. The design and synthesis of cross-linked polymers carrying catalytically active species offer several practical advantages over soluble homogeneous catalysts (21). In addition to retaining the activity and selectivity of well-defined homogeneous catalysts, the polymeric approach to catalyst design offers an efficient means for recovery and recycling of expensive catalysts and is amenable for scaling up for continuous industrial process (21). Therefore, an attempt could be made to reduce the metal leaching problem encountered in inorganic oxide supported catalysts by taking advantages of higher functionalization and modification capacity of polymer as support (22,23). Thus, catalytic oxidation by polymer-bound catalysts has gained prominance in recent years

Historically, the need for more selective metal systems capable of direct activation of dioxygen and transfer to suitable substrate prompted inorganic chemists to explore the reactivity of transition metals (24-27). Development of transition metal complexes as oxidation catalysts also generated a lot of interest (27). Apart from their chemical significance, these catalysts offer a number of advantages as described in chapter 1. A number of metal complexes have been developed for this purpose with the objective of elucidating the mechanism of the oxygenation process as well as for maximizing the catalytic efficiencies. Platinum group metal complexes, in particular, have received much attention in recent years because of the structural variety and their role in catalytic oxidation reactions (28). Of the variety of ligands employed for the purpose, the noteworthy examples include porphyrin derivatives, diamines, aminoacids, carboxylic acids and schiff bases (29-31) Many of these complexes were heterogenized on polymer support and catalytic activity was compared in heterogenized and homogeneous systems. Drago et al (32) synthesized polymer supported chelating amine and schiff base complexes of Fe(II), Cu(II) and Co(II) and tested their catalytic potential for the oxidation of 2,6-dimethylphenol. A high selectivity towards the product 2,6-dimethyl-1,4-benzoquinone was obtained with polymer-bound catalyst compared to homogeneous counterpart. De et al. (21) have reported better selectivity of polymer-bound schiff base complexes of Mn(II) for the epoxidation of olefins compared to homogeneous analogue. Kulkarni et al. (33) recently studied the oxidation of cyclohexane to cyclohexanone with molecular oxygen using a polymer supported schiff base chelated with cobalt palmitate and the observed high yield was probably due to significant role played by the polymer support. No metal leaching was observed for 100 h of experiments which shows strong metal binding. Cobalt(II) pyridine complexes bound to copolymers of styrene and acrylic or methacrylic acid and cross-linked with divinylbenzene were shown to catalyze the auto-oxidation of tetralin dispersed in water at 50°C and 1 bar and the rate of oxidation was found to be higher than the catalyst present in homogeneous system (34). The product of the reaction tetralon is the raw material for the production of the agrochemical intermediate 1-napthol. A colloidal catalyst prepared by attaching cobaltphalocyanine tetrasulfonate (Co PC Ts) via the anionic sulfonate groups to a styrene-divinylbenzene copolymer containing quaternary ammonium ions, was used for the oxidation of 2,6-di-tert-butylphenol and the rate of reaction was found to be 10 times higher than the homogeneous counterpart (35). H_2O_2 is also one of the environmentally benign oxidant. A palladium (II) exchanged polystyrene sulfonic acid resin (Dowex 50 W, H form) was found to catalyze the oxidation of 2-methylnaphthalene with 60% aqueous hydrogen peroxide to give menadione in 55-60% yield at 90-97% conversion (36). Tellurium bound macromolecular styrene-divinylbenzene copolymer was found to be a suitable catalyst for olefin oxidation using H_2O_2 as oxidant (37). Thus the use of H_2O_2 was found to be very interesting for organic laboratory and small-scale procedures due to the simplicity inherent in performing reactions with liquid rather than gaseous reactions (38).

Recently Song et al. (39) have used membrane like heteropolyacid blended polymer film catalyst as fixed bed catalyst for oxidation of ethanol to acetaldehyde in a continuous flow reactor with a high selectivity and yield. Sherrington et al. (40) have reported epoxidation of cyclohezene using polybenzimidazole supported Mo(VI) with high activity and no metal leaching was observed upto nine cycles. Jia et al. (41) have used poly(maleic acid-co-styrene)-triruthenium cluster catalyzed oxidation of styrene with molecular oxygen and a high activity was observed under mild conditions. The catalyst was recycled for more than eight times without a noticeable decrease in its activity. Polymer-supported phase transfer catalysts have also been used for the oxidation of benzyl alcohol to benzaldehyde. Do et al. (42) have reported activity of polymer-bound PTC in anodic oxidation of benzyl alcohol and investigated the effect of pH, concentration of substrate, temperature and amount of polymer on the oxidation reaction.

Thus oxidation of various reactions such as oxidation of olefins by molecular oxygen using polymer-bound transition metal complexes has been studied extensively. Catalytic oxidation of benzyl alcohol to benzaldehyde has also been studied widely because of its expensive use in Fine chemicals and as an intermediate in dyes and drugs. However, not many reports are available in literature on the oxidation of benzyl alcohol over polymer-bound catalysts prepared using ligands containing N and O as donor atoms, and the study of the kinetics of the reaction. In the present investigation, the synthesized polymer-bound schiff base complexes of palladium(II) and ruthenium(III) have been used in order to study the kinetics of oxidation of benzyl alcohol with molecular oxygen under mild operating conditions.

5.2 Experimental

5.2.1 Measurement of catalytic activity for oxidation reactions:

The oxidation reaction was carried out in a magnetically stirred glass reactor using methanol as the solvent for polymer supported palladium and ruthenium catalysts as well as their homogeneous complexes. Methanol was chosen as a solvent for the oxidation reaction because of better swellability of polymer-bound catalyst in it and miscibility with substrate. The progress of the reaction was followed by measuring the uptake of oxygen as a function of time at a constant pressure using a glass manometric apparatus. The experimental set-up and detailed procedure are described in chapter 2.

5.2.2 Analysis of kinetic data:

The kinetic data for the oxidation reaction were obtained in a kinetic regime of a stirring speed of 650 rpm at 35°C. The stoichiometry of the reaction was checked by carrying out a few experiments at constant temperature and oxygen pressure at different concentrations of benzyl alcohol. The initial rate data obtained from oxygen uptake measurements is used to evaluate the kinetic parameters. The products were analysed using a gas chromatograph employing flame ionization detector and carbowax column.

In each kinetic run the uptake of oxygen was measured as a function of time. The initial rate of oxidation was calculated from the slope of the plot of volume of oxygen uptake against time. The influence on the rate of various parameters such as catalyst and substrate concentration, temperature of the system and nature of the solvent has been investigated. From the analysis of the rate data, the order of reaction with respect to the substrate and the catalyst concentration, and the values for energy of activation and entropy of activation have been determined.

5.3 Results and Discussion

5.3.1 Effect of concentration of benzyl alcohol

Fig. 5.3.1 indicates that the variation of oxygen uptake with time increases fast initially followed by a slow reaction and finally it reaches towards equilibrium. The rate of the reaction calculated from the slope of the above plot was found to increase on increasing the concentration of the substrate. The results are summarised in Tables 5.3.1 to 5.3.2. The rate of oxidation of benzylalcohol was found to increase from 0.35 to 0.80 ml min^{-1} as the concentration of benzylalcohol varies from $4.83x10^{-3}$ to $19.32x10^{-3}$ mol l^{-1} at 35°C using 8PRu(III)Salen as a catalyst having Ru content of $7.12x10^{-5}$ mol l^{-1}. The variation of initial rate in the case of 8PPd(II)Salen (Pd content $1.16x10^{-6}$ mol l^{-1}) was found to be from 0.36 to 0.50 ml min^{-1} for oxidation of benzyl alcohol under similar

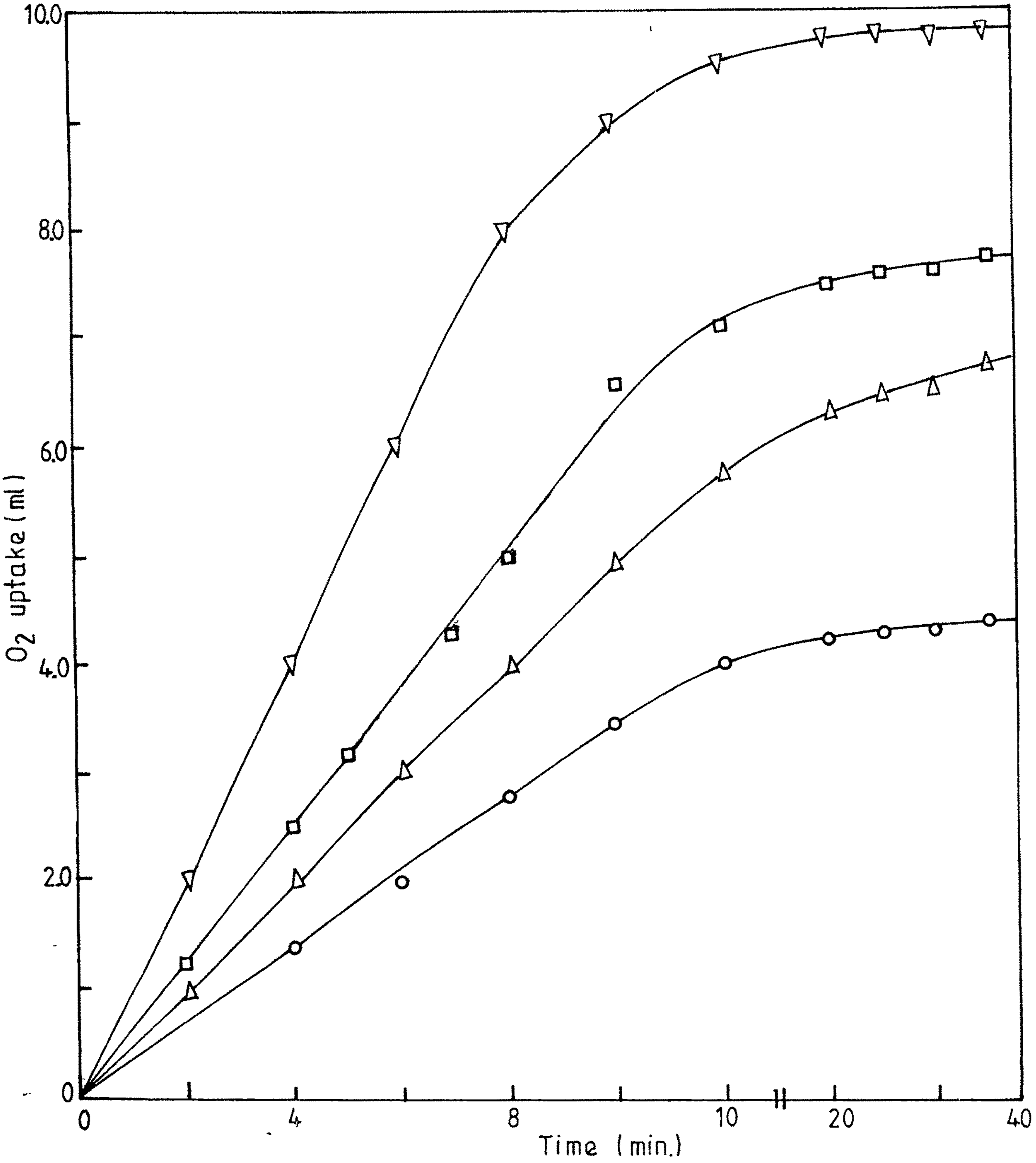


Fig. 5.3.1 Plot of O_2 uptake vs time for the catalyst 8PRu(III)Salen for different concentration of benzyl alcohol.
[Benzyl alcohol] (mol l^{-1}x10^{-3}): ○ 4.93, △ 9 66, □ 14 49, ▽ 19.32

condition.

The plot of log (initial rate) against log [benzyl alcohol] at fixed concentration of the catalyst was found to be linear (fig. 5.3.2 and 5.3.3) and the values for the order of reaction calculated from the slopes of the above plots were found to be fractional with respect to benzyl alcohol concentration.

In the case of homogeneous system inspite of using a larger concentration of Ru(III)/Pd(II) metal ions as catalysts for above reaction, a lower rate was observed as compared to heterogenized homogeneous system Thus at a constant concentration of benzyl alcohol (i.e. 9.66×10^{-3} mol l^{-1}) at 35°C, the initial rate was found to be 0.11 ml min^{-1} with [Ru(III)Salen Cl] (Ru concentration is 1.03×10^{-3} mol l^{-1}) catalyst. With [Pd(II)Salen], (Pd concentration 0.83×10^{-3} mol l^{-1}) the rate was observed to be 0 14 ml min^{-1} (Table 5.3.2). It is evident from the above results that heterogenizing a homogeneous catalyst on a polymeric support has higher activity than their homogeneous counterparts.

Table 5.3.1

Effect of [Benzyl alcohol] on the rate of oxidation using polymer supported catalysts at 35°C and 1 atm pressure

Volume of methanol : 20 ml

Catalyst	[Catalyst] mol l^{-1}	[Benzyl alcohol] mol l^{-1}x10^{3}	Rate of reaction mol min^{-1}	Order of reaction
8PRu(III)Salen	7.12x10^{-5}	4.83	0.35	
		9.66	0.50	0.58
		14.49	0.67	
		19.32	0.80	
14PRu(III)Salen	2.97x10^{-6}	4.83	0.31	
		9.66	0.49	0.66
		14.49	0.65	
		19.32	0.79	
8PPd(II)Salen	1.16x10^{-6}	4.83	0.36	
		9.66	0.42	0.19
		14.49	0.43	
		19.32	0.50	
14PPd(II)Salen	0.45x10^{-6}	4.83	0.15	
		9 66	0.38	0.65
		14.49	0.65	
		19.32	0.92	

Table 5.3.2

Effect of [Benzyl alcohol] on the rate of oxidation using homogeous complexes at 35°C at 1 atm pressure
Volume of methanol : 20 ml

Catalyst	Ru/Pd present (mol l^{-1})10^{3}	[Benzyl alcohol] (mol l^{-1})10^{3}	Rate of reaction ml min^{-1}	Order of reaction
[Ru(III)Salen Cl]	1.03	4.83	0.06	
		9.66	0.11	0.71
		14.49	0.27	
		19.32	0.45	
[Pd(II)Salen]	0.83	4.83	0.04	
		9.66	0 14	0.58
		14.49	0 28	
		19.32	0.45	

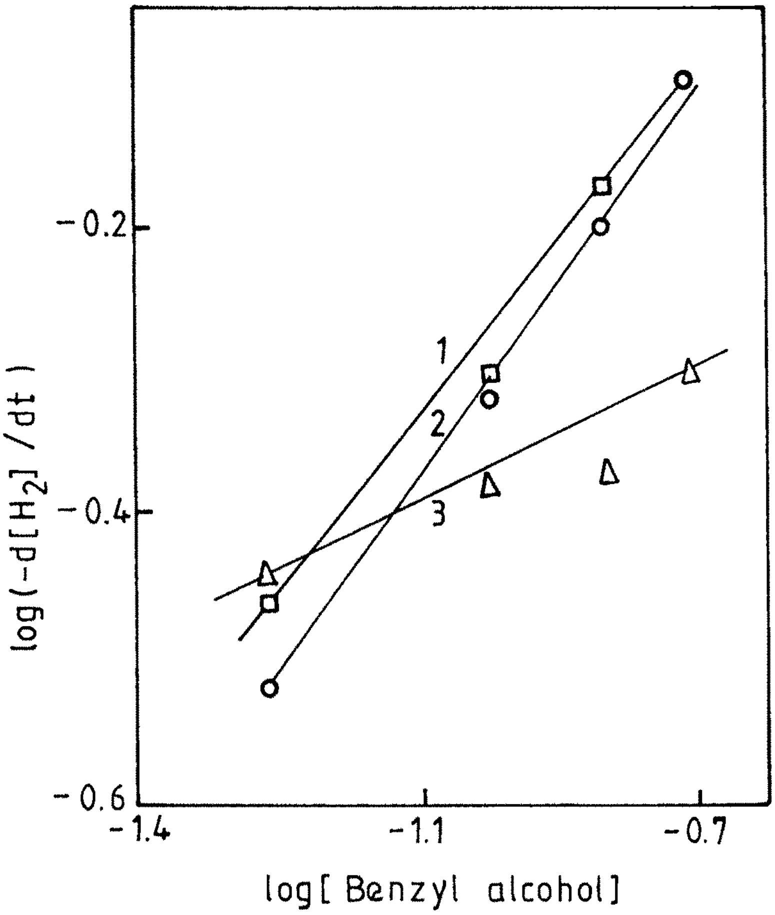


Fig 5.3.2 Plot of log(initial rate) vs [Benzyl alcohol] for catalysts (1) 8PRu(II)Salen (2) 14PRu(III)Salen (3) 8PPd(II)Salen

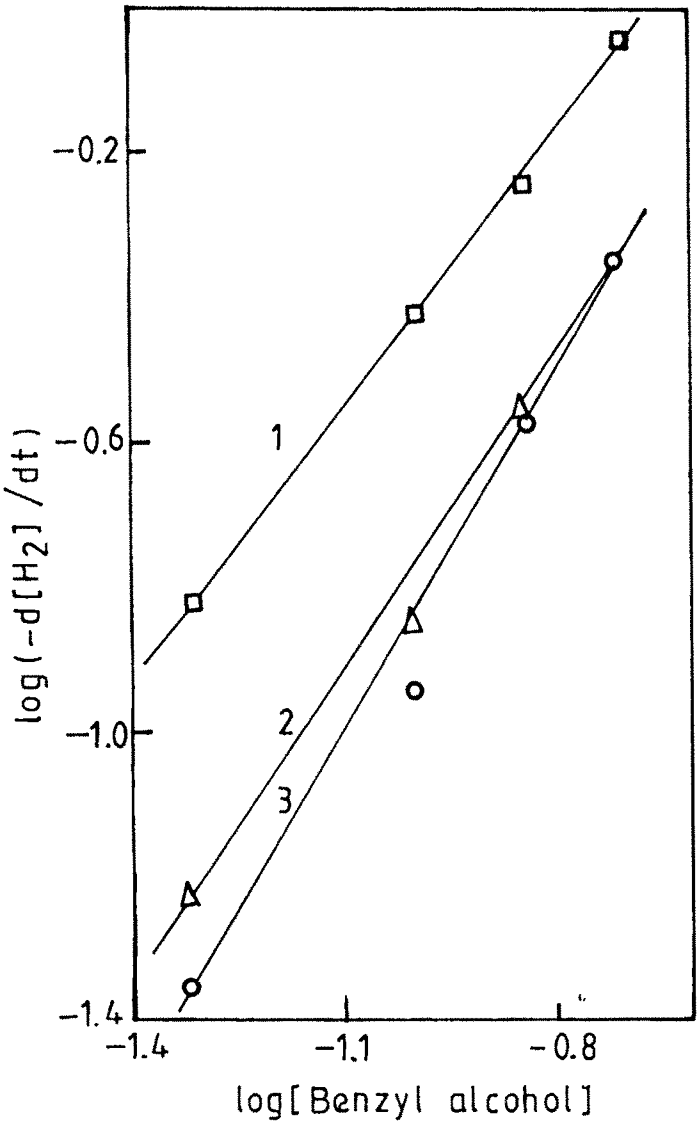


Fig.5.3.3 Plot of log(initial rate) vs log[Benzyl alcohol] for catalysts (1) 14PPd(II)Salen (2) [Pd(II)Salen] and (3) [Ru(III)Salen Cl]

5.3.2 Influence of catalyst concentration

The influence of catalyst concentration on the rate of oxidation of benzyl alcohol for different polymer-bound catalysts has been investigated. An increase in the rate of oxidation was observed as the concentration of Ru(III) and Pd(II) increased on the surface of the polymer. The results are summarized in Tables 5.3.3 to 5.3.4. An enhanced rate of oxidation of benzyl alcohol was observed from 0.40 to 0.70 ml min^{-1} as concentration of Ru(III) was varied from 3.56×10^{-5} to 14.24×10^{-5} mol l^{-1} in case of 8PRu(III)Salen catalyst at 35°C at a fixed concentration of benzyl alcohol (9.66×10^{-3} mol l^{-1}). In the case of 8PPd(II)Salen catalyst the rate was found to increase from 0.29 to 0.54 ml min^{-1} when the concentration of the catalyst was varied from 0.58×10^{-6} to 2.33×10^{-6} mol l^{-1} of Pd(II) keeping a constant concentration of benzyl alcohol as 9.66×10^{-3} mol l^{-1} at 35°C. An increase in the rate with amount of the catalyst is indicative of the fact that there is no dimerization of metal complex in the range studied (43). and mass-transfer effect could be neglected (44).

The study was carried out using the homogeneous complexes under similar condition and an enhanced rate was observed by varying the concentration of the catalysts. The rate of oxidation in case of [Ru(III)Salen Cl] was found to be in the range of 0.11 to 0.32 ml min^{-1} as the concentration of the catalyst was varied from 1.03×10^{-3} to 4.10×10^{-3} mol l^{-1} at 35°C (at a fixed concentration of benzyl alcohol (i.e. 9.66×10^{-3} mol l^{-1}). Other results are given in Table 5.3.6. Thus even on using a higher catalyst concentration, a lower rate of reaction was observed as compared to heterogenized catalysts.

The order of reaction with respect to catalyst concentration was calculated from the plots of log (initial rate) versus log[catalyst] and was found to be fractional in all cases The results are given in Tables 5.3.3 and 5.3.4 and the corresponding plots are given in figures 5.3.4 and 5.3.5). Though the reaction was carried out in a chemically controlled

Table 5.3.3

Effect of [Catalyst] on the rate of oxidation using polymer supported catalysts at 35°C and 1 atm pressure

Volume of methanol . 20 ml
[Benzyl alcohol] = 9.66 x10^{-3} mol l^{-1}

Catalyst	[Catalyst] (mol l^{-1})	Rate of reaction (ml min^{-1})	Order of reaction
8PRu(III)Salen	3.66x10^{-5}	0.40	
	7.12	0.50	0.48
	10.68	0.60	
	14.24	0.70	
14PRu(III)Salen'	1.48x10^{-6}	0.32	
	2.97	0.49	0.32
	4.45	0.61	
	5.94	0.70	
8PPd(II)Salen	0.58x10^{-6}	0.29	
	1.16	0.42	0.41
	1.74	0.49	
	2.33	0.54	
14PPd(II)Salen	0.22x10^{-6}	0.24	
	0.45	0.38	0.55
	0.67	0.47	
	0.89	0.57	

regime, choosing a suitable swelling agent, the observed fractional order might be due to non-accessibility of catalytic sites and steric hinderance because of the complex nature of the catalyst.

5.3.3 Effect of temperature on the rate of reaction

The effect of temperature on the rate of oxidation of benzyl alcohol has been studied in the range of 25-45°C and the results are summarised in Tables 5.3.5 and 5.3.6. The rate of oxidation was found to increase with an increase in temprature for all catalysts. In case of catalyst 8PRu(III)Salen, the rate of oxidation was found to increase from 0.31 to 0.62 ml min^{-1} at a fixed concentration of substrate (i.e. 9.66 x 10^{-3} mol l^{-1}) as the temperature is raised from 25 to 40°C Similarly, in case of catalyst 8PPd(II)Salen, the enhancement in the rate of oxidation was observed from 0.30 to 0.51 ml min^{-1} as the temperature is varied from 30 to 45°C Similar results obtained for 14PRu(III)Salen and 14PPd(II)Salen are given in Table 5.3.5

In case of [Ru(III)Salen Cl] (Ru content 1.03×10^{-3} mol l^{-1}) in homogeneous medium, the rate was found to be in the range of 0.07 to 0.45 ml min^{-1} by varying the temperature from 30 to 45°C at a constant concentration of benzyl alcohol (9.66×10^{-3} mol l^{-1}) while in the case of [Pd(II)Salen] (Pd content = 0.83×10^{-3} mol l^{-1}) an increase in the rate was found from 0.11 to 0.23 mol min^{-1} (Table 5.3.6)

The values of energy of activation calculated from the Arrhenius plots were found to be 32.3 and 47.9 kJ mol^{-1} for catalysts 8PRu(III)Salen and 14PRu(III)Salen respectively; while for 8PPd(II)Salen and 14PPd(II)Salen it was found to be 30.1 and 40.5 kJ mol^{-1} respectively. In case of homogeneous system using Ru(III) and Pd(II)Salen complex as catalysts, the energy of activation was obtained as 103.4 and 38.3 kJ mol^{-1} respectively (figs. 5.3.6a and 5.3.6b). On the basis of the above data, it could be concluded that the synthesised polymer supported complex catalysts have higher catalytic activity then their homogeneous counterparts

The entropy of activation was calculated using the equation

$$k = e.\ KT/h\ \ e^{\Delta S/R}.\ e^{-\Delta E/RT}$$

where K and h are Boltzman and Plank's constant respectively. ΔS is the entropy of activation.

Negative values of entropy of activation obtained for polymer supported catalysts are indicative of the loss of freedom due to fixation of catalysts on polymer matrix (44-45). Similar results were obtained by Taqui Khan et al. in the the study of homogeneous hydrogenation of 1-heptene using Rhodium diphenylphosphine amine complex catalyst. (44)

Table 5.3 4

Effect of [Catalyst] on the rate of oxidation using metal complex catalysts in homogeneous medium at 35°C and 1 atm pressure

Volume of methanol = 20 ml

Catalyst	[Catalyst] (mol l^{-1})10^3	[Benzyl alcohol] (mol l^{-1})10^3	Rate of reaction (ml min^{-1})	Order of reaction
[Ru(III)Salen Cl]	1.03	9.66	0 11	
	2.05		0.18	0.80
	3.08		0.26	
	4 10		0.32	
[Pd(II)Salen]	0.83	9.66	0.14	
	1.67		0.21	0 85
	2 50		0.30	
	3.33		0.40	

Table 5.3.5

Kinetics of oxidation of benzyl alcohol at various temperatures using polymer supported metal complex catalysts at 1 atm pressure

Concentration of Benzyl alcohol = 9.66×10^{-3} mol l^{-1}
Volume of methanol = 20 ml

Catalyst	[Catalyst] (mol l^{-1})	Temperature (°C)	Rate of reaction (ml min^{-1})	Energy of activation (kJ mol^{-1})	Entropy of activation (eu)
8PRu(III)Salen	7.12×10^{-5}	25	0.31		
		30	0.40	32.3	-40.4
		35	0.50		
		40	0.62		
14PRu(III)Salen	2.97×10^{-6}	25	0.30		
		30	0.40	47.9	-28.4
		35	0.49		
		40	0.56		
8PPd(II)Salen	1.16×10^{-6}	30	0.30		
		35	0.42	30.1	-42.5
		40	0 45		
		45	0 51		
14PPd(II)Salen	0.45×10^{-6}	30	0.30		
		35	0.38	40 5	-34.6
		40	0.55		
		45	0.69		

Table 5.3.6

Kinetics of oxidation of benzyl alcohol at various temperatures using metal complex catalysts in homogeneous medium

Volume of methanol = 20 ml
[Benzyl alcohol] = 9.66×10^{-3} mol l^{-1}

Catalyst	[Catalyst] (mol l^{-1})10^3	Temp. (°C)	Rate of reaction (ml min^{-1})	Energy of activation (kJ mol^{-1})	Entropy of activation (eu)
[Ru(III)Salen Cl]	1.03	30	0.07		
		35	0.11	103.4	-2.5
		40	0.28		
		45	0.45		
[Pd(II)Salen]	0 83	30	0.11		
		35	0.14	38.3	-38.3
		40	0.18		
		45	0.23		

[illegible] The formation of peroxo complex with the substrate and subsequent fast insertion and elimination of the product may also be taken into consideration.

5.3.4 Influence of nature of the solvent

The influence of different solvents on the rate of oxidation of benzyl alcohol has been studied at 35°C using concentration of benzyl alcohol as 9.66×10^{-3} mol l^{-1}. The rate of oxidation was found to decrease when the nature of the solvent was varied from a polar to a non-polar character. Thus the rate of reaction for the catalyst 8PRu(III)Salen in methanol was found to be 0.50 ml min^{-1} whereas in benzene it was found to be 0.16 ml min^{-1}. Other results are summarised in Table 5.3.7

A higher catalytic activity in case of polar solvents might be due to the larger swelling which is responsible for more active sites available on the surface. An increase in intraparticle diffusion can not be ruled out (46). Thus selection of a better swelling agent is essential to achieve maximum efficiency of polymer-bound catalysts.

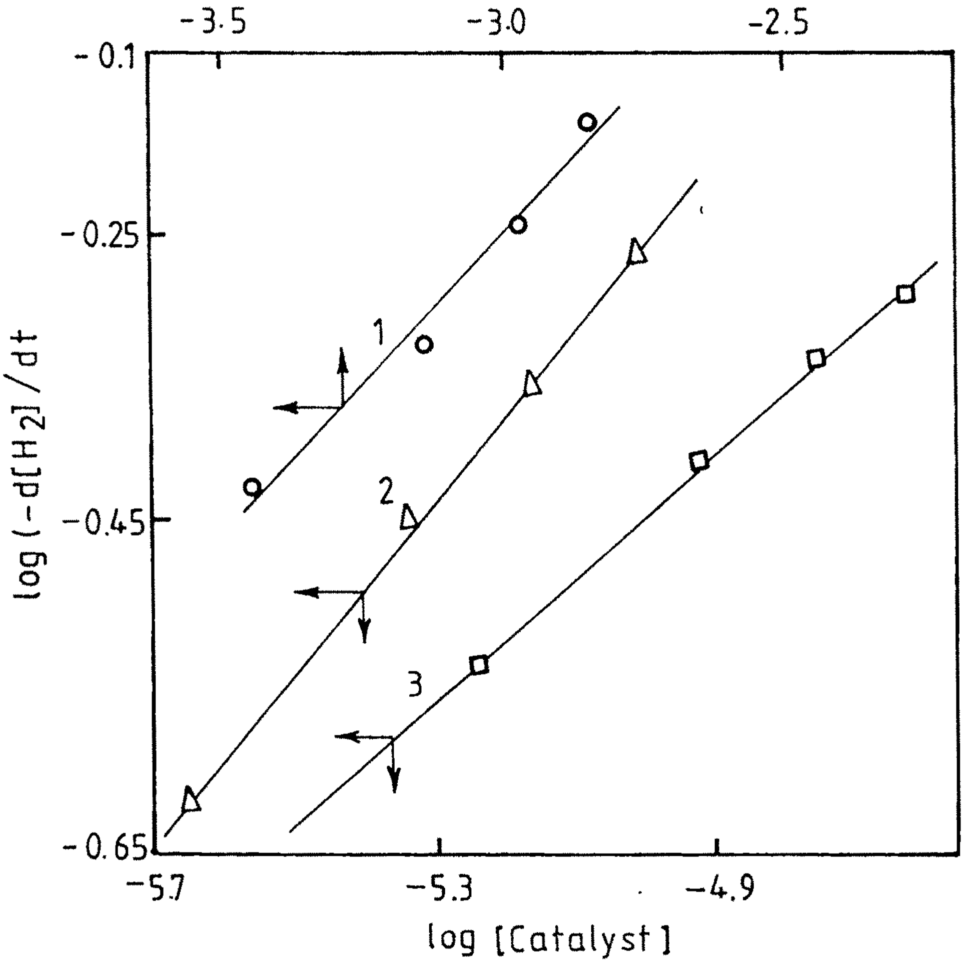


Fig. 5.3.4 Plot of log(initial rate) vs log[catalyst] for (1) 8PRu(III)Salen (2) 14PPd(II)Salen and 8PPd(II)Salen

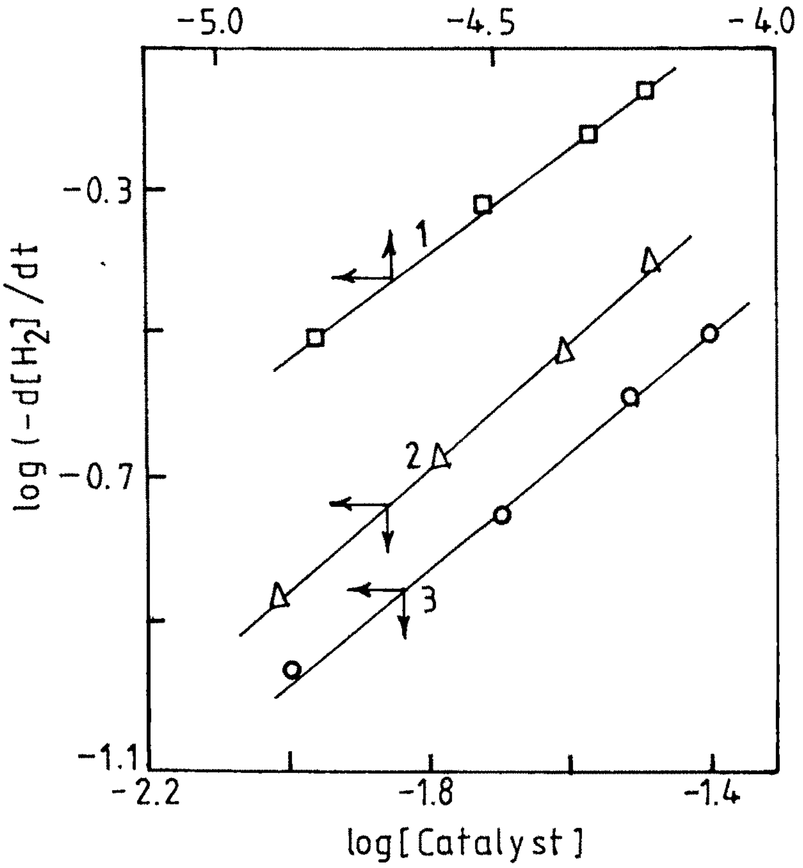


Fig. 5.3.5 Plot of log(initial rate) vs log [catalyst] for catalyst (1) 14PRu(III)Salen (2) [Pd(II)Salen] (3) [Ru(III)Salen Cl]

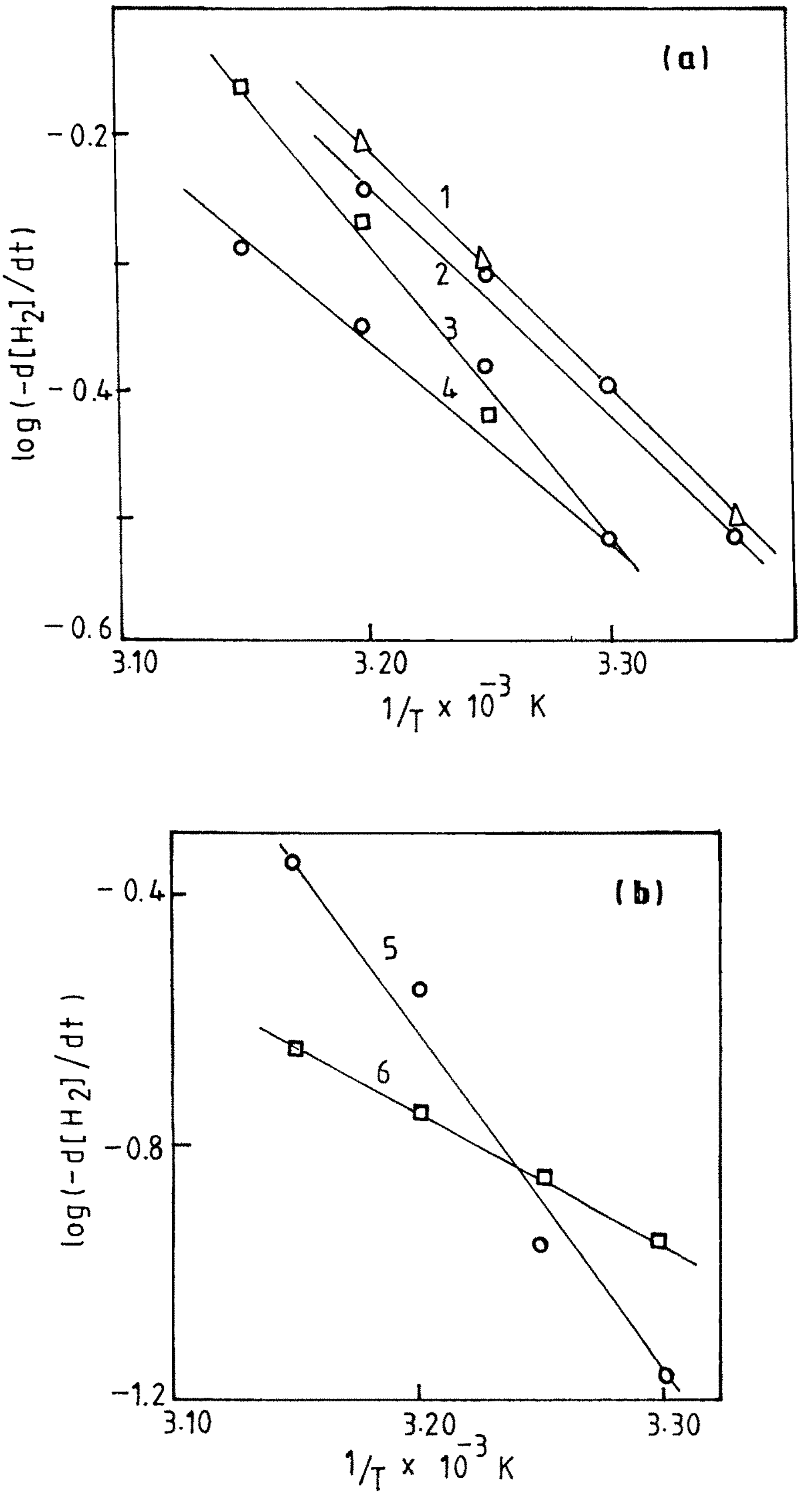


Fig. 5.3.6(a) and (b) Arrhenius plots for polymer supported catalysts (1) 8PRu(III)Salen (2) 14 PRu(III)Salen (3) 14PPd(II)Salen (4) 8PPd(II)Salen and homogeneous complexes (5) [Ru(III)Salen Cl] (6) [Pd(II)Salen]

Table 5 3.7

Solvent dependence in oxidation of benzyl alcohol using polymer-supported catalysts at atmospheric pressure

Reaction temperature = 35°C
Quantity of solvent used = 20 ml
[Benzyl alcohol] = 9.66×10^{-3} mol l^{-1}

Catalyst	[Catalyst] mol l^{-1}	Solvent	Rate of reaction (ml min^{-1})
8PRu(III)Salen	7.12×10^{-5}	Methanol	0.50
		Ethanol	0.46
		THF	0.31
		Benzene	0.16
14PRu(III)Salen	2.97×10^{-6}	Methanol	0.49
		Ethanol	0.45
		THF	0.30
		Benzene	0.13
8PPd(II)Salen	1.16×10^{-6}	Methanol	0.42
		Ethanol	0.37
		THF	0.26
		Benzene	0.14
14PPd(II)Salen	0.45×10^{-6}	Methanol	0.38
		Ethanol	0.32
		THF	0.18
		Benzene	0.11

5.3.5 Study of the life cycle of the catalysts

The main aim of supporting metal catalyst on a polymer support is for the reuse of the catalyst. The polymer-bound catalysts may lose their activity by leaching of the metal ions from the surface to the solution or reduction to free metal (47). In order to investigate the stability of the synthesized catalysts under repeated catalytic cycles, the recycling efficiency was tested for fresh and used catalysts. The experiments were carried out at 35°C for 8 to 10 hrs by injecting a known amount of substrate (i.e 20 μl) at 60 minute interval. The rate of oxidation was measured as a function of time for both fresh and used

Table 5.3.8

Life cycle study of polymer-bound catalysts at 35°C and 1 atm pressure in 20 ml methanol

	Rate of reaction (ml min^{-1})	
Time (min.)	Catalyst 8 PRu(III)Salen	Catalyst 8 PPd(II)Salen
60	0.50 (0.50)	0.42 (0.42)
135	0.50 (0.50)	0.42 (0.42)
210	0.50 (0.45)	0.42 (0.40)
285	0.46 (0.40)	0.41 (0.35)
360	0.39 (0.31)	0.36 (0.31)
435	0.31 (0.25)	0.30 (0.26)

(Value in parenthesis indicate data for used catalyst)

[Ru] for catalyst 8PRu(III)Salen = 7.12×10^{-5} mol l^{-1}

[Pd] for catalyst 8PPd(II)Salen = 1.163×10^{-6} mol l^{-1}

catalysts. The results are summarised in Table 5.3.8. No change in the rate of the reaction was observed upto three cycles and after that a decrease in the rate was observed, The metal content present on the surface was estimated after the completion of the reaction and a loss of 35% of metal was observed from the polymer support. This loss of the metal ions from the surface may be responsible for a decrease in the catalytic activity.

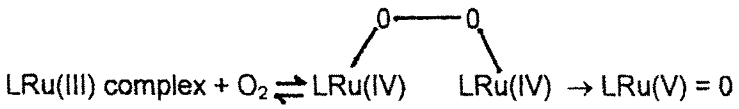
5.4 Reaction mechanism

In the present study the partial pressure of oxygen is kept constant. In all the experiments, the solvent and the catalyst were initially saturated with oxygen followed by injection of benzylalcohol and thereafter actual uptake of oxygen was taken. A slight colour-change of the polymer beads was observed during the reaction which is indicative of the surface complex formation responsible for higher catalytic activity.

To investigate the reaction mechanism of benzyl alcohol oxidation, in a separate experiment, ruthenium chloride was mixed with salen (1:1) in homogeneous medium and oxygen was bubbled through it. A change in intensity of colour was observed from dark brown to light brown. As the substrate (benzyl alcohol) was injected, the reappearance of the dark brown colour was observed. Similarly, in case of 1:1 mixture of $PdCl_2$ and salen, yellow colour disappeared completely after passing oxygen through the solution and reappeared on injecting substrate benzaldehyde,. It is indicative of the fact that after passing molecular oxygen, there is an intermediate complex formation which transfers oxygen to the substrate and finally the catalyst regains its original colour However, no clear peak was observed in UV-visible spectrophotometric studies probably due to the unstable nature of the intermediate complex formed.

The reaction mechanism for the oxidation of organic molecules by the use of metal ions/ complexes in the homogeneous systems has been studied widely (48-50) and the formation of peroxo and oxo complexes was suggested to be responsible for the transfer of oxygen to the substrate (51-53). The formation of the oxo complex and the transfer of oxygen via this route has been suggested by Taqui Khan et al. (49) in the ruthenium (III) complex catalysed oxidation of olefins. Vaska et al. (24) have reported the formation of peroxo and superoxo complexes when dioxygen is covalently bound to the metal centre.

On the basis of the above observation and literature data, a probable reaction mechanism may be suggested as follows:



$$\text{LRu(III) complex} + O_2 \rightleftharpoons \text{LRu(IV)}\overset{\text{O}\text{——}\text{O}}{\qquad\quad}\text{LRu(IV)} \rightarrow \text{LRu(V)} = 0$$

LRu(V) = 0 + Benzylalcohol → Benzaldehyde + LRu(III) complex

where L = Ligand salicyldehyde ethylenediame

Keeping the amount of O_2 constant, the corresponding rate equation may be expressed as

R = k [catalyst] [Benzyl alcohol]

Thus on increasing the concentration of the catalyst at a constant concentration of benzyl alcohol or vice versa, the rate was observed to increase which is in agreement with the above results The results are given in Tables 5.3.1 to 5.3.4.

5.5 References

1. R.A. Sheldon, J Dakka, Catal. Today, **19**, 215, 1994
2. J. Haber in R K.Grasseli, S.T. Oyama, A M.Gaffney and J.E Lyons (Eds) Stud Surf Sci and Catal , **110**, Elsevier, Amsterdam, 1997, p 1
3. G. Strukul, Catalytic oxidation with hydrogen peroxide as oxidant, Kluwer, Dordrecht, 1992, p 2
4 K. Weissermel and H.J.Arpe, Industrielle Organische Chemie, third edition, VCH, Weinheim, 1988
5. P. Gallezot, Catal. Today, **37**, 405, 1997.
6. J.R. Monnier, in R.K Grasseli, S.T Oyama, A M.Gaffney and J E. Lyons (Eds.) Stud. Surf. Sci. and Catal., **110**, Elsevier, Amsterdam, p 135
7. Chem. and Engg News, April 8, 1996, p1
8. M. Besson, G Fleche, P. Fuertes, P. Gallezot, F. Lehmer, Paper presented at the European Meeting, Montpelier, France (1993), Paper abstract in Vol. 2, p 416 of the conference abstract.
9. J. Nikov and K. Paev, Catal Today, **24,** 1995, 41
10. P. Barthe and G Blanchard, French Pat 9012, 519 (1990) assigned to Rhone Poulenc Chimie.
11 I. Matsura and Y. Aoki, JP 05331085 A2 (1996) assigned to Nippon catalytic Chem. Ind., CA 121: 107989, 1996.
12 S. Albonetti, F. Cavani, F. Trifiro, P Venturoli, G Calestani, M Lopez Granades and J L G Fierro, J. Catal , **160**, 52, 1996
13. A. Erdohelyi, K Fodor and F Solymosi, J. Catal., **166**,244, 1997

14. A Rocha Jr., A.L.Chages, L.S.V.S.Sune, M F.S. Lopes, J. Pereira in R K.Grasseli, S T.Oyama, A.M Gaffney, and J.E Lyons (Eds) Stud., Surf. Sci and Catal ,**110**, Elsevier, Amsterdam, 1997, p 1193

15 B.M. Despeyroux, K.Deller and E Peldszus in G. Centi and F Trifiro (Eds) New Developments in selective oxidation, Stud. Surf. Sci and Catal., **55**, Elsevier, Amsterdam, 1990, pp 159-169 and references therein

16 R. Sumathi K Johnson, B. Viswanathan and T.K.Varadarajan, India. J chem , **36(10),** 874, 1997.

17 R.Sumathi, B Viswanathan and T.K. Varadarajan in T.S R. Prasada Rao and G. Murali Dhar (Eds.) Recent Advances in Basic and Applied Aspects of Industrial Catalysis, Stud. Surf. Sci. and Catal., **113**, Elsevier, Amsterdam, 1998, p 937.

18. C.N.Pillai and M. Jayamani, J. Catal., **82**, 485, 1983.

19 G.R.Dube and V S Darshane, J.Chem Soc., Faraday Trans. **88**, 1299, 1992.

20. S. Sueto, S. Nishiyama, S. Tsuruya and M Masai, J. Chem Soc., Faraday Trans., **93(4),** 659, 1997

21 B.B.De, B.B Lohary, S.Sivaram and P.K.Dhal, Macromolecules, **27(6),** 1291, 1994.

22. F.R.Hartley, Supported Metal catalysts, Reidel, Dordrecht, 1986

23. J. Leito, D. Milstein, R L.Abright, J.V Minkiewicz and B.C.Gates, CHEMTECH, Jan 1983, p 46

24. L. Vaska, Chem. Rev., **9**, 175, 1976.

25. V.J.Choy and C.J.O'Connor, Coord. Chem Rev., **9.** 145, 1972-73

26 J.E.Lyons, in R.Ugo (Ed.) Asp. Hom. Catal , **3**, Reidel, Dordrecht, 1977, p1.

27. R A.Sheldon and J K.Kochi, Metal Catalyzed Oxidations of Organic compounds, Academic Press, New York, 1981, Chapter 4 and references therein.

28 M M Taqui Khan, Oxidation Commun , **9**, 10, 1986

29. J.J Bozell, B.R. Hames and D R Dimmel, J Org Chem , **60**, 2398, 1995.

30. M.J Upadhyay, P.K Bhattacharya, P A.Ganeshpure and S Satish, J. Mol. Catal., **88**, 287, 1994

31. W. Nam, R. Ho, J.S.Valentine, J. Am. Chem Soc., **113**, 7052, 1991

32. R.S Drago, J Gaul, A. Zombeck and D K Straub, J. Am. Chem. Soc , **102(3),** 1033, 1980

33 S. Kulkarni, M. Alurkar and A Kumar, Appl. Catal., A General, **142**, 243, 1996

34. R.S.Chandran and W.T.Ford, J chem. Soc , Chem. Commun , 104, 1988.

35. H. Turk and W T.Ford, J Org. Chem , **53**, 460, 1988

36 S. Yamaguchi, M. Inoue and S Enomoto, Chem. Lett., 827, 1985

37. W.F.Brill, US Patent 4558026, 1985 assigned to Halcon.

38 R Neumann and M. Levin-Elad. J. Catal., **166**, 206, 1997.

39. I. Song, J Lee, G. Park and W Lee in R K.Grasseli, S T Oyama, A M.Gaffney and J.E. Lyons (Eds.) Stud Surf. Sci. and Catal., **110**, Elsevier, Amsterdam, 1997, p 1183.

40. M.M Miller and D.C.Sherrington, J., Catal., **152**, 377, 1995.

41 C Jia, F.Jin, M Huang, Y. Jiang, Reactive Polymers, **23**, 33, 1994

42 J.S Do, T C.Chou, J. Appl. Electrochem , **22(10),** 966, 1992

43. D.T.Gokak and R N.Ram, J Mol. Catal., **49**, 285, 1989.

44. M M Taqui Khan, B. Taqui Khan, S. Begum and S Mustafa Ali, J Mol. Catal., 34, 283, 1986.

45 M. Terasawa, K. Kaneda, T Imanaka and S Teranishi, J. Catal , **51**, 406, 1978

46. J.N.Shah, Ph.D Thesis, M.S.University of Baroda, 1991

47. J.N.Shah, D.T.Gokak and R.N.Ram, J. Mol Catal., **60**, 141, 1990

48. S. Seibig and R.Eldik, Inorg. Chem., **36**, 4115, 1997.

49. M M.Taqui Khan, R.A.Prakash, S.D.Bhatt, J. Mol. Catal., **75(1),** 41, 1992.

50. Y.H.Lin, I.D.Williams, P.Li, Appl. Catal. A: General, **150(2),** 221, 1997.

51. A.J.Bailey, W.P.Griffith, S.I.Mostafa and P.A.Sherwood, Inorganic Chem., 32(3), 268, 1993.

52. E.R.Birnbaun., M.W.Grinstaff, J.A.Labinger, J.E.Bercaw and H.B.Gray, J. Mol. Catal., A: Chemical **104,** 119, 1995.

53. J. John, M.K.Dalal, and R.N.Ram, in R.K. Grasseli, S.T.Oyama, A.M.Galfney and J.E.Lyons (Eds.) Stud. Surf. Sci. and Catal., Elsevier, Amsterdam, **110**, 1165, 1997.