CHAPTER IV

RESULT AND DISCUSSION

CONTENTS

4.1 KINETICS OF OXIDATION OF TOLUENE USING POLYMER SUPPORTED Mn (II) AND Ni (II) COMPLEXES

4.2 Introduction

Catalytic Oxidation is the single most important commercial reaction for functionalizing hydrocarbon feed backs (olefins, alkenes and aromatics) to industrially important derivatives[1]. The attack of oxygen on hydrocarbon molecules is the easiest route for functionalization. Selective oxidation process in which hydrocarbon molecules are oxygenated to form alcohols, acids or aldehydes are the basis of modern petrochemical industries[2].

Transition metal ions / complexes were found to be very active as catalyst for oxidation reactions in recent years because of their structural variety. Recently the Schiff base complexes of transition metal ions were observed to be very active as catalyst for oxidation reactions.(3,4) These complexes were found suitable as homogeneous catalyst for the oxidation of hydrocarbons. Several Ruthenium (III) complexes (5,6) have been used for catalytic oxidation of hydrocarbons. The schiff base complexes of transition metal ions were found to be effective catalysts in the hydroxylation of alkanes and epoxidation of olefins(5-8). Nilkov and Paev[9] studied the epoxidation of alkenes using iodosylbenzene as an oxidant in the presence of Mn(II) amide complexes and a number of studies have been carried out for the oxidation, epoxidation reactions which include the oxidation of hydrocarbons using Ru (III) complexes.(10)

However, the major disadvantage of homogeneous catalyst is the problem of separating the very expensive catalysts from the products at the end of the reaction. Moreover, they are thermally unstable, prone to poisoning by oxygen and moisture and corrode the reactor walls when used in a commercial scale.

Application of heterogenized homogeneous catalysts for oxidation reactions is interesting in addition to advantages offered by heterogeneous catalyst. The design and synthesis of cross-linked polymers carrying catalytically active species and also retains activity and selectivity of homogeneous catalysts offers several practical advantage over soluble homogeneous catalysts[11]. In addition to retaining the activity and selectivity of well-defined homogeneous catalysts, the polymeric approach to catalyst design offers an efficient mean for recovery and recycling of expensive catalysts and is amenable for scaling up for continuous industrial processes[11]. 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[12-13]. Thus, catalytic oxidation by polymer-bound catalyst has gained prominence in recent years.

Historically, the need for more selective metal systems capable for direct activation of dioxygen and transfer to suitable substrate prompted inorganic chemists to explore the reactivity of transition metal complexes[14-17]. Development of transition metal complexes as oxidation catalyst also generate a lot of interest[18-19]. Apart from the chemical significances these catalysts offer a number of advantages as described in chapter I. 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. 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. De et al[20] have reported better selectivity of polymer bound Schiff base complexes of Mn(II) for the oxidation of olefins compared to homogeneous analogue. Kulkarni et al[33-34] recently studied the oxidation of cyclohexane to cyclohexanone with molecular oxygen using a polymer supported Schiff base chelated with cobalt palmitate and observed a high yield probably due to significant role played by the polymer support no metal leaching was observed for 100 h. of experiment which shows strong metal binding cobalt (II) pyridine complex bound to the 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 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 studied extensively[1].Supported bimetallic (pd, Bi/C) and trimetallic (Pd, Pt, Bi/C) catalysts were used by Despeyroux et al[15] to oxidize glucose to gluconic acid with high selectivity. 96% selectivity was obtained using a 4% Pd, 1% Pt, 5% Bioncharcoal catalyst. Pt was found to enhance the activity and Bi enhanced the selectivity of Pd catalyst. Catalytic oxidation of alcohols is a useful method for the preparation of aldehydes and ketones. Oxidation of benzyl alcohol 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], where as on metal oxides it undergoes dehydrogenation to yield benzaldehyde and toluene as major products and benzylbenzoate, benzene and methanol in small amounts depending upon reaction conditions[19]. Recently Viswanthan 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 a oxidant. Sweto et al[20] have recently observed high activity of NAZSM-5 supported Cu Catalysts in oxidation of benzaldehyde.

Application of heterogenized homogeneous catalyst for oxidation reactions is interesting as in addition to advantages offered by herterogeneous catalyst, it also retains activity and selectivity of homogeneous catalyst The design and synthesis of cross linked polymers carrying catalytically active species offer several practical advantages over soluble homogenous 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 to scaling up for continuous industrial processes[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 prominence in recent years.

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[24-27]. Platinum group metal complexes, in particular, have received much attention in recent years because of the structural variety and their role in catalytic oxidation reaction[28]. Of the variety of ligands employed for the purpose, the noteworthy examples include porphyrin derivatives, diamines, amino acids, carboxylic acids and Schiff bases.(29-31) Many of these complexes were heterogenized on polymer support and catalytic activity was compared with the heterogenized and homogeneous systems. The product of the reaction tetralon is the raw material for the production of the agro-chemical intermediate 1 napthol. A colloidal catalyst prepared by attaching cobaltphalocyanine tetra-sulfonate (Co Pc Ts) via the anionic sulphate groups to a styrene divinycbenzene co-polymer containing quaternary ammonium ions was used for the oxidation of 2, 6-di-tert-butyl-phenol 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 poly-styrene sulfonic acid resin (Dowex 50 W.H. form) was found to catalyze the oxidation of 2- methylnapthalene with 60% aqueous hydrogen peroxide to give menadione in 55-60% yield at 90-97% conversion[36]. Tellurium bound macromolecular styrene divinylbenzene co-polymer 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 high selectivity and yield Sherrington et al[40] have reported epoxidation of cyclohexene using polybenzimidazole supported Mo(VI) with high activity and no metal leaching was observed upto nine cycles. Jiva et al [41-42] have used polymaleic 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.

Ram et al[60] synthesised Ru(III) complex by sequential attachment of H_2N - CH_2 - CH_2 - NH_2 and $RuCl_3$ to chloromethylated styrene - divinyl benzene co-polymer with 8% cross - linking. The activity of this catalyst was tested for a temperature of the system and also by varying the concentration of substrate and catalyst. The activation energy and entropy was calculated from the kinetic data and probable reaction mechanism was proposed. Ram et al[61] synthesized the polymer supported palladium (II) complex catalyst for oxidation of toluene. The activity was tested by varying parameters such as temperature, concentration of substrate and catalyst. the kinetic data was used to calculate, the activation energy and entropy. The probable reaction mechanism was proposed. Ram and co-workers[62] synthesized Ru (III) complex as catalyst and the activity of this catalyst was tested for oxidation, by varying the parameters such as temperature, substrate and catalyst concentration. From the kinetic data, activation energy and entropy was calculated. The probable mechanism was proposed. Lei Ziqiang et al[63] studied the oxidation of alkylbenzene to aryl alcohol and ketones was accomplished with high selectivity and activity using linear poly styrene (PS) and styrene divinyl benzene co-polymer (DVB) as support for copper (II) complex catalysts The reaction was carried out in presence of molecular oxygen at 110^{0}C Groves and co-workers[64] studied the novel oxidative processes for substrate such as olefins, alkenes aroms and alcs, using metallic prophyrins for salen the complex is having nitrosyl axial ligands and electron withdrawing peripheral substituents are preferred. Weiner, et al[65] reported that poly oxoanion - supported iron (II) complex is significant as well as enroute to the goal of achieving a long lived, catalytic dioxygenase system without the need to worry about catalyst lifetime - limiting ligand oxidation side reactions. Suresh S; Skaria s; and co-workers[66] synthesized a novel polymer supported vanadium (V) and chromium (IV) ions as oxidation catalysts. The variety of oxidation reactions were carried out.

Gu, Fengcai and co-workers[67] reported that N N_bis (Salicylidence) - 1, 3 propylenediiminato cobalt (II) catalyst can co-ordinate and active the molecualr oxygen. It is utilised in synthesis of fine chemicals. The kinectic study was carried out by changing the parameters such as concentraticn of catalyst, the temperature of the system, the time, the velocity of air flow and solvents. The possible mechanism is discussed..

Zhang, et al[68] reported the oxidation of toluene to benzoic acid and oxidation of other aromatic hydrocarbons in presence of cobalt trichloroacetate, manganese trichloroacetate and ammonium bromide as catalyst.

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

4.3 EXPRIMENTAL

MEASUREMENT OF CATALYTIC ACTIVITY FOR OXIDATION REACTION

The oxidation reaction was carried out in a magnetically stirred glass reactor using methanol as the solvent using polymer supported manganese and nickel catalysts and their homeogeneous counterpart. Methanol was chosen as solvent for the oxidation reaction because of better swellability of polymer bound catalyst and miscibility with substrate (as mentioned in chapter 3). The progress of reaction was followed by measuring the uptake of oxygen as a function of time at a constant pressure using a glass manometric appratus. The experimental set up and detailed procedure are describe in chapter 2.

4.4 Analysis of Kinetic Data:

The Kinetic data for the oxidation reaction were obtained in a kinetic regime of a stirring speed of 650rpm at 35^0C. The stoichiometry of the reaction was checked by carrying out a few experiments at constant temperature and oxygen pressure at different concentration of toluene. The initial rate data obtained from oxygen uptake measurements is used to evaluate the Kinetic parameters. The products were analyzed using a gas chromatography 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 the catalysts and substrate concentration, temperature of the system and the nature of the solvent was investigated The order of reaction with respect to the substrate and the catalyst concentration was determined by log-log plot. The values of energy of activation and entropy of activation were calculated using the rate data The results are given in tabular form

4.5 Results and Discussion

4.6 Effect of concentration of Toluene :

Fig. 3a shows that the oxygen uptake with time increases initially slowly followed by a rapid increase and finally approaches the equilibrium. This may be due to the fact that initially a small quantity of surface complex is formed which is insufficient to provide oxygen to the substrate from the slopes of the tangent of the above plot found to increase on increasing the concentration of the substrate. Thus, the rate of oxidation of toluene was found to increase from 0.030 to 0.062 ml min^{-1} as the concentration of toluene varies from $6.72x1U^{-4}$ to $12.8x10^{-4}$ mole l^{-1} at 35^0C using 80PDA Mn(II), (Mn(II) content is $3.14x10^{-5}$mole l). The variation of initial late in case of 8PPOA (Ni(II)), (Ni content is $1.15\times10^{-8}$$mole^{-1}$) is from 0.039 to 0.121 ml min^{-1} as the concentration of toluene varies from $6.72x10^{-4}$ to $12.8x10^{-4}$ mole l^{-1} at 35^0C under the similar conditions. The other results are given in table 3.1. (Ni content is $1.15\times10^{-8}$$mole^{-1}$).

The plot of log (initial rate) against log [Toluene] at fixed concentration of catalyst was found to be linear[52] (fig 3b). The values for the order of reaction calculated from the slope of the above plots were found to be fractional with respect to toluene concentration. The results are given in Table 3.1.

4.7 Influence of catalyst concentration :

The influence of catalyst concentration on the rate of oxidation of toluene for different polymer bound catalyst has been investigated. An increase in the rate of oxidation was observed as the concentration of Mn(II) & Ni(II), increase on the surface of the polymer the results are summarised in Table(3.2).

An enhanced rate of oxidation of toluene was observed from 0.086 to 0.102 ml $mole^{-1}$ as the concentration of Mn(II) was varied from $1.680x10^{-5}$ to 2.686×10^{-5} mole $^{-l}$ in case of 14 OPDA Mn (II) catalyst at 35^0C. at a fixed concentration of toluene ($9.42x10^{-4}$ mole $)^{-1}$. In case of 14PPDA (Ni (II)) the rate of reaction was found to increase from 0.062 to 0.096 $ml.mole^{-1}$ as the concentration of Ni(II) varied from 1.26×10^{-5} to 2.51×10^{-5} ml mole l^{-1} at 35^0C at a fixed concentration of toluene. (9.8×10^{-4} ml mole l^{-1}). The other results are summarized in Table (3.2).

An increase in the rate with amount of the catalyst in the range studied is indicative of the fact that there is no dimerization of metal complex[43] and the Mass transfer effect could be neglected. Similar, results have been given by Taquikhan and co-workers[44-45].

The order of reaction with respect to catalyst concentration was calculated from the plots of log (initial rate) versus log [Catalyst] fig (3c) and was found to be fractional in all cases. Though the reaction was carried out in a chemically controlled 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. The results are summarized in Table 3.2.

4.8 Effect of Temperature on the rate of reactions

The nature of the amount of oxygen uptake at various interval of time was observed to be the same as observed earlier Fig. [3d] the volume of oxygen was found to increase with temperature. The rate of oxidation calculated from the slope of the tangent was found to increase with temperature for all catalysts. Thus, in case of 8 OPDA Mn (II) the rate of oxidation was found to enhance from 0.050 to 0.162 ml.min^{-1}, keeping fixed concentration of substrate (9.80×10^{-4} mole l^{-1}) as the temperature is raised from 30^0C to 45^0C. Similarly, in case of catalyst 8PPDA[Ni(II)], where the metal content is 1.15×10^{-5} ml mole l^{-1}, the enhancement in the rate of oxidation was observed from 0.020 to 0.129 under similar conditions. The other results are given in Table (3.3).

The energy of activation calculated from the slope of the straight line plot of log (initial rate) versus 1/T (Arrhenius plot) was found to be in the range of 40 KJ mole^{-1} to 58 KJ mole^{-1} Table (3.3) indicating that the process is fast. The entropy of activation calculated using the equation:

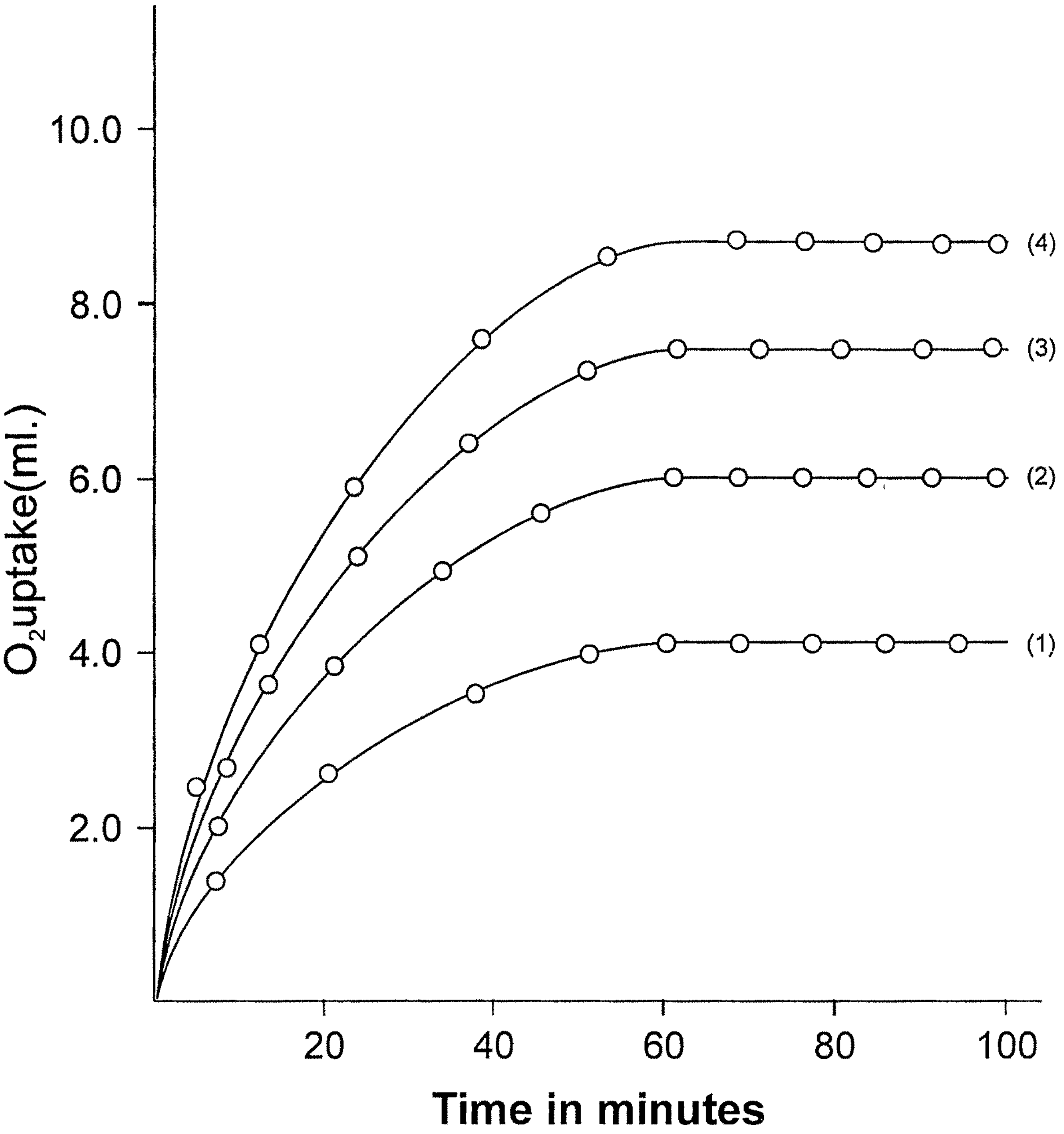


Fig. (3a) Plot of O_2uptake v/s. time for the Catalyst 14OPDA(Mn)II for different concentration of Toluene

[Toluene](mol.l^{-1}x10^{-4})
1) 6.72 2) 9.80 3) 11.5 4) 12.8

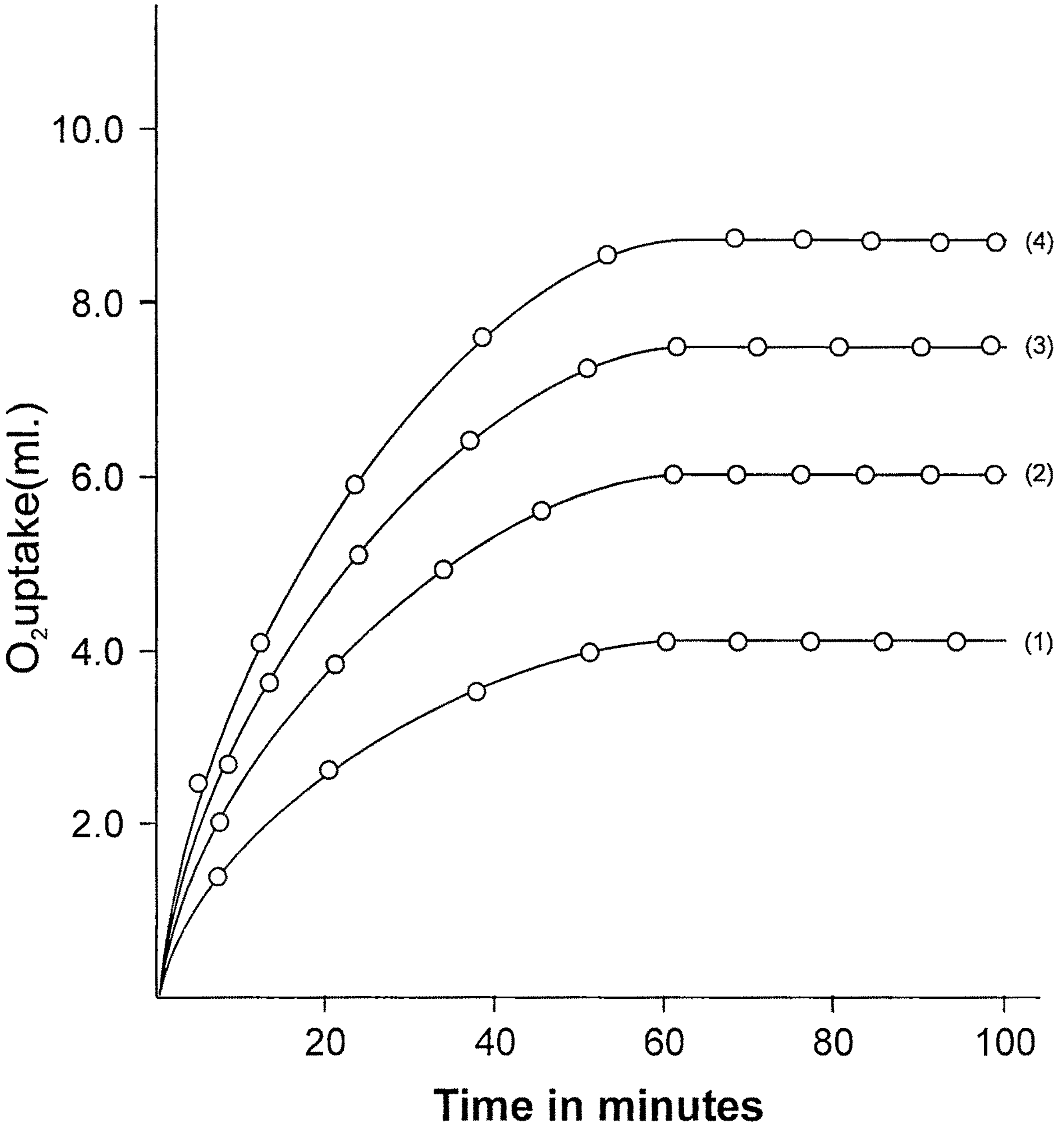


Fig. (3a) Plot of O$_2$uptake v/s. time for the Catalyst 8OPDA(Mn)II for the various amount of the Catalyst

[Catalyst](mol.l^{-1}x10^{-5})
1) 2.35 2) 3.14 3) 3.90 4) 4.70

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

where K is Boltzmann constant; h is Planck's constant; Δs is entropy of activation, E is the energy of activation, T is temperature, k is the rate of reaction and R is constant. It was found to be in the range of $\underline{-164}$ to $\underline{-167}$ eu. The negative value of entropy is indicative of the loss of freedom of motion due to fixation of catalyst molecule on the polymer matrix.

Influence of nature of the solvent

The influence of different solvents on the rate of oxidation of toluene has been studied at 35^0 C using concentration of toluene 9.80×10^{-4} mole 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 solvent character. The rate of reaction for the catalyst 14OPDAMn(II) was found to be 0.094 ml min^{-1} in methanol where as in benzene it was observed to be 0.042 ml min^{-1}. Similar results have been noted while using 8OPDA Ni(II) as catalyst in various solvents. Using methanol as a solvent the rate was noted to be 0.025 ml min^{-1} for the oxidation of toluene at 35^0 C.

A higher catalytic activity in case of polar solvent might be due to the larger swelling which is responsible for more active sites available on the surface. An increase in intra-particle diffusion cannot be ruled out[46-47]. Thus, selection of a better swelling agent is essential to achieve maximum efficiency of polymer-bound catalysts, as shown in the Table 3.4.

Effect of [Toulene] on the rate of Oxidation using polymer supported catalysts at 35^0 C and 1 atms. Pressure.

Volume of Methanol = 20 ml.

Table 3.1

Catalysts	**[Catalysts] mole l^{-1}**	**[Toluene] mole l^{-1} x 10^4**	**Rate of reaction ml. min^{-1}**	**Order of reaction**
14 OPDA Mn (II)	1.93×10^{-5}	6.72	0.079	
		9.80	0.091	0.35
		11.5	0.098	
		12.8	0.105	
14 OPDA Ni (II)	2.23×10^{-5}	6.72	0.071	
		9.80	0.083	0.29
		11.5	0.092	
		12.8	0.108	
14 PPDA Mn (II)	1.63×10^{-5}	6.72	0.067	
		9.80	0.073	0.42
		11.5	0.087	
		12.8	0.102	
14 PPDA Ni (II)	1.63×10^{-5}	6.72	0.054	
		9.80	0.068	0.34
		11.5	0.075	
		12.8	0.079	

Kinetic of oxidation of Toulene at various combination of catalyst anchored on polymer at 35^{0}C and 1atm. Pressure.

Volulme of Methanol = 20ml.

[Toluene] = 9.80 X 10^{-4} mole l^{-1}

Table 3.2

Catalyst	[Catalyst] (mole l$^-$) X 10^5	Rate of reaction (mole l$^-$)	Order of reaction
14 OPDA Mn(II)	1.68	0.086	0.39
	1.93	0.092	
	2.492	0.096	
	2.686	0.102	
14 OPDA Ni (II)	1.68	0.077	
	2.23	0.084	0.29
	2.74	0.098	
	3.35	0.109	
14 PPDA Mn (II)	1.23	0.067	
	1.63	0.073	0.42
	2.04	0.085	
	2.45	0.098	
14 PPDA Ni (II)	1.26	0.062	
	1.67	0.072	0.32
	2.08	0.087	
	2.51	0.096	

Kinetics of oxidation of Toluene at various Temperatures using metal complex catalysts. Volume of Methanol = 20 ml.

[Toluene]= 9.80×10^{-4} mole e^{-1}

Table 3.3

Catalyst	[Catalyst] mole $l^{-1} \times 10^{5}$	Temp. ^{0}C.	Rate of Reaction ml min^{-1}	Energy of Activation (kJ) mole^{-1}	Entropy of Activation (eu)
14OPDA Mn (II)	1.93	30	0.066	54.33	-129.0
		35	0.104		
		40	0.133		
		45	0.145		
14OPDA Ni (II)	2.33	30	0.075	31.21	-166.0
		35	0.082		
		40	0.091		
		45	0.102		
14PP DA Mn (II)	1.63	30	0.052		-165.0
(Schiff Base)		35	0.072	44.68	
		40	0.083		
		45	0.094		
14PP DA Ni (II)	1.67	30	0.046		-167.0
(Schiff Base)		35	0.069	32.02	
		40	0 081		
		45	0.097		

Kinetic of Oxidation of Toluene using various solvents, using polymer supported catalysts at atomospheric pressure

Reaction Temperature = 35^0C

Quantity of Solvent used = 20ml.

[Toluene] = 9.8×10^{-4} mole l^{-1}

Table 3.4

Catalyst	**[Catalyst] mole l^{-1}**	**Solvent**	**Rate of reaction (ml min^{-1})**
14 OPDA Mn(II)	1.93×10^{-5}	Methanol	0.094
		Ethanol	0.083
		THF	0.075
		Benzene	0.042
14 OPDA Ni(II)	2.23×10^{-5}	Methanol	0.083
		Ethanol	0.072
		THF	0.061
		Benzene	0.038
14 PP DA Mn(II)	1.63×10^{-5}	Methanol	0.075
(Schiff Base)		Ethanol	0.055
		THF	0.048
		Benzene	0.020
14 PP DA Mn(II)	1.67×10^{-5}	Methanol	0.068
(Schiff Base)		Ethanol	0.054
		THF	0.041
		Benzene	0 026

Effect of [Toluene] on the rate of Oxidation using polymer supported catalysts at 35^0 C and 1atm. Pressure.

Volume of Methanol = 20 ml.

Table 3.1

Catalysts	[Catalysts] mole l^{-1}	[Toluene] mole $l^{-1} \times 10^4$	Rate of reaction ml. min^{-1}	Order of reaction
8 OPDA Mn (II)	3.14×10^{-5}	6.72	0.060	
		9.80	0.085	0.52
		11.5	0.091	
		12.8	0.093	
8 OPDA Ni (II)	2.36×10^{-5}	6.72	0.055	
		9.80	0.071	0.48
		11.5	0.077	
		12.8	0.110	
8 PPDA Mn (II)	1.79×10^{-5}	6.72	0.043	
(Schiff Base)		9.80	0.062	0.55
		11.5	0.109	
		12.8	0.124	
8 PPDA Ni (II)	1.15×10^{-5}	6.72	0.039	
(Schiff Base)		9.80	0.075	0.41
		11.5	0.081	
		12.8	0.121	

Kinetics of Oxidation of Toulene using effect of [Catalyst] using Metal complex catalysts at 35^0 C and at 1atm. Pressure.

Volume of Methanol = 20 ml.

[Toluene] = 9.80 X 10^{-4} mole l^{-1}

Table 3.2

Catalysts	[Catalysts] mole l^{-1} X 10^5	Rate of reaction ml. min^{-1}	Order of reaction
8 OPDA Mn (II)	2.35	0.054	
	3.14	0.087	0.91
	3.90	0.091	
	4.70	0.098	
8 OPDA Ni (II)	1.77	0.042	
	2.36	0.069	0.65
	3.02	0.087	
	3.58	0.100	
8 PPDA Mn (II)	0.98	0.043	
(Schiff Base)	1.79	0.061	0.61
	1.98	0.074	
	2.18	0.094	
8 PPDA Ni (II)	1.14	0.052	
(Schiff Base)	1.17	0.074	0 52
	1.19	0.088	
	2.5	0.104	

Kinetics of Oxidation of Toulene at Various Temperatures using Metal Complex Catalysts

Volume of Methanol = 20 ml.

[Toluene] = 9.80 X 10^{-4} moles lit^{-1}

Table 3.3

Catalyst	[Catalyst] (mole l^{-1}) X 10^5	Temp. ^{0}C	Rate of reaction ml min^{-1}	Energy of activation kJ $mole^{-1}$	Entropy of activation (eu)
8 OPDA Mn (II)	3.14	30	0.050	57.39	-164.0
		35	0.089		
		40	0.150		
		45	0.162		
8 OPDA Ni (II)	2.36	30	0.042	40.99	-168.0
		35	0.038		
		40	0.075		
		45	0.086		
8 PPDA Mn (II)	1.79	30	0.054	44.96	-168.0
		35	0.063		
		40	0.080		
		45	0.086		
8 PPDA Ni (II)	1.15	30	0.050	40.20	-167.0
		35	0.078		
		40	0.095		
		45	0.129		

Kinetics of oxidation of Toluene using, various solvents, using polymer supported catalysts at atmospheric pressure.

Reaction Temperature = 35^0C

Quantity of Solvent used = 20 ml.

[Tolune] = $9.8 x 10^{-4}$ mole l^{-1}

Table 3.4

Catalyst	**[Catalyst] mole l^-**	**Solvent**	**Rate of reaction ml min^{-1}**
8 OPDA Mn (II)	$3.14 X 10^{-5}$	Methanol	0.091
		Ethanol	0.084
		THF	0.045
		Benzene	0.021
8 OPDA Ni(II)	$2.36 X 10^{-5}$	Methanol	0.072
		Ethanol	0.065
		THF	0.051
		Benzene	0.025
8 PP DA Mn(II)	$1.79 X 10^{-5}$	Methanol	0.070
		Ethanol	0.064
		THF	0.052
		Benzene	0.026
8 PP DA Ni(II)	$1.15 X 10^{-5}$	Methanol	0.075
		Ethanol	0.059
		THF	0.035
		Benzene	0.019

Effect of [Toluene] on the rate of Oxidation using polymer supported catalysts at 35^0 C and 1atm. Pressure.

Volume of Methanol = 20 ml.

Table 3.1

Catalysts	[Catalysts] mole l^{-1}	[Toluene] mole l^{-1} x 10^4	Rate of reaction ml min^{-1}	Order of reaction
6 OPDA Mn (II)	1.57 X 10^{-5}	6.72	0.019	
		9.80	0.054	0.60
		11.5	0.069	
		12.8	0.089	
6 OPDA Ni (II)	2.58 X 10^{-5}	6.72	0.025	
		9.80	0.050	0.38
		11.5	0.071	
		12.8	0.098	
6 PPDA Mn (II)	2.20 X 10^{-5}	6.72	0.032	
(Schiff Base)		9.80	0.055	0.31
		11.5	0.062	
		12.8	0.079	
6 PPDA Ni (II)	2.30 X 10^{-5}	6.72	0.034	
(Schiff Base)		9 80	0.058	0.42
		11.5	0.064	
		12.8	0.071	

Kinetics of Oxidation of Toulene using effect of [Catalyst] using Metal complex catalysts at 35^0 C and at 1atm. Pressure.

Volume of Methanol = 20 ml.

[Toluene] = 9.42 X 10^{-3} mole l^{-1}

Table 3.2

Catalysts	[Catalysts] mole l^{-1} X 10^5	Rate of reaction ml. min^{-1}	Order of reaction
6 OPDA Mn (II)	1.173	0.045	
	1.57	0.056	0.55
	1.96	0.065	
	2.35	0.080	
6 OPDA Ni (II)	2.40	0.037	
	2.58	0.048	0.48
	2.80	0.054	
	3.15	0.059	
6 PPDA Mn (II)	1.65	0.020	
(Schiff Base)	2.20	0.055	0.62
	2.75	0.075	
	3.29	0.086	
6 PPDA Ni (II)	1.82	0.055	
(Schiff Base)	2.30	0.066	0 29
	2.87	0 081	
	3.44	0 92	

Kinetics of Oxidation of Toulene at Various Temperatures using Metal Complex Catalysts

Volume of Methanol = 20 ml.

[Toluene] = 9.80 X 10^{-4} moles l^{-1}

Table 3.3

Catalyst	[Catalyst] mole l^{-1}	Temp. ^{0}C	Rate of reaction ml min.$^{-1}$	Energy of activation kJ mole^{-1}	Entropy of activation (eu)
6 OPDA Mn (II)	1.57 X 10^{-5}	30	0.032		-169.0
		35	0.056	36	
		40	0.070		
		45	0.083		
6 OPDA Ni (II)	2.58 X 10^{-5}	30	0.036	40	-168.0
		35	0.051		
		40	0.065		
		45	0.071		
6 PPDA Mn (II)	2.20 X 10^{-5}	30	0.047	39	-121.0
		35	0.058		
		40	0.068		
		45	0.074		
6 PPDA Ni (II)	2.30 X 10^{-5}	30	0.045	55	-174.0
		35	0.055		
		40	0.073		
		45	0 081		

Kinetics of oxidation of Toluene in various solvents, using Polymer supported catalysts at 35^0 C and 1atm. Pressure.

Voume of Methanol = 20 ml.

Table 3.4

Catalyst	[Catalyst] mole l^{-1}	Solvent	Rate of reaction ml min^{-1}
6 OPDA Mn (II)	1.57 X 10^{-5}	Methanol	0.057
		Ethanol	0.047
		THF	0.035
		Benzene	0.030
6 OPDA Ni(II)	2.58 X 10^{-5}	Methanol	0.055
		Ethanol	0.045
		THF	0.039
		Benzene	0.022
6 OP DA Mn(II)	2.20 X 10^{-5}	Methanol	0.059
		Ethanol	0.043
		THF	0.032
		Benzene	0.019
6 OP DA Ni(II)	2.30 X 10^{-5}	Methanol	0.056
		Ethanol	0.042
		THF	0.032
		Benzene	0.018

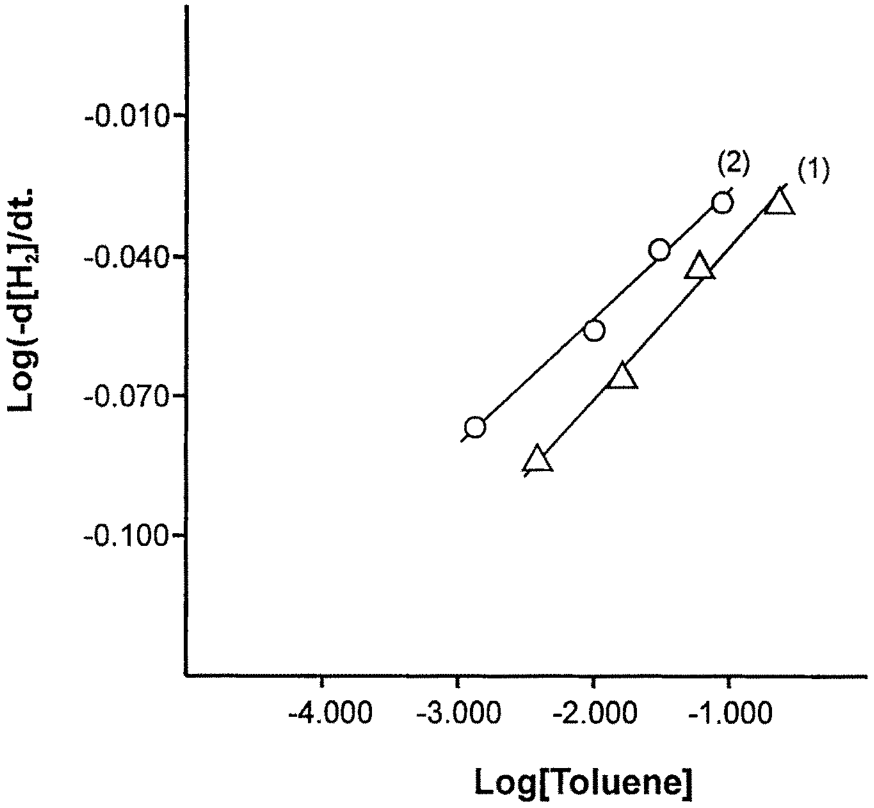


Fig. (36) Plot of Initial rate v/s. Log[Toluene] for Catalyst
(1) 6OPDAMn(II) (2) 6OPDANi(II)

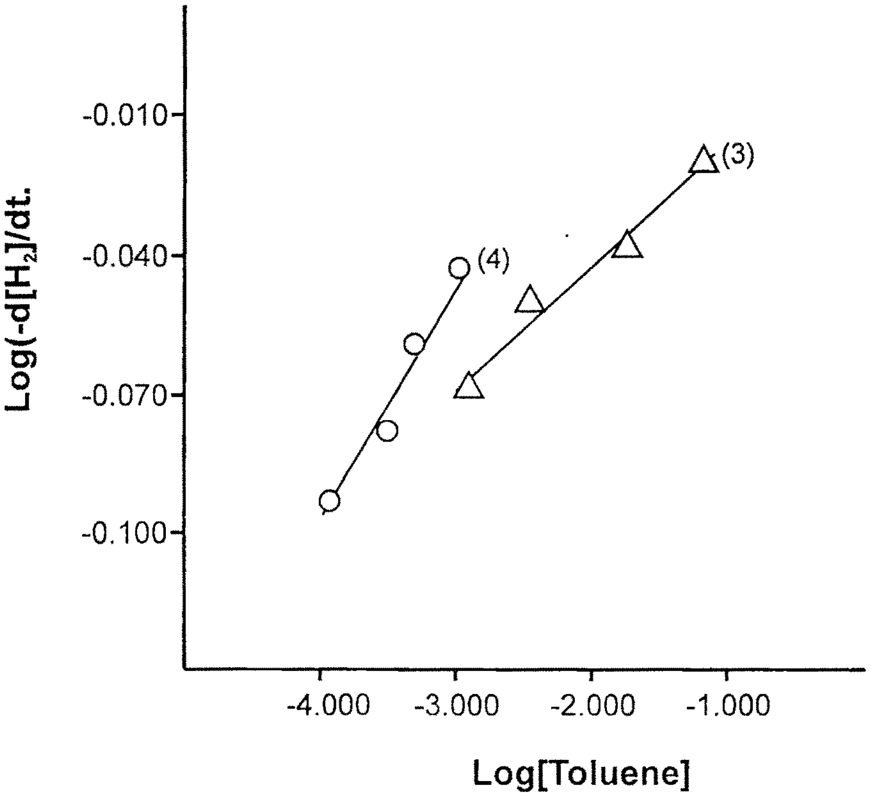


Fig (3b) Plot of Initial rate v/s. Log[Toluene] for Catalyst
(1) 6PPDAMn(II) (2) 6PPDANi(II)

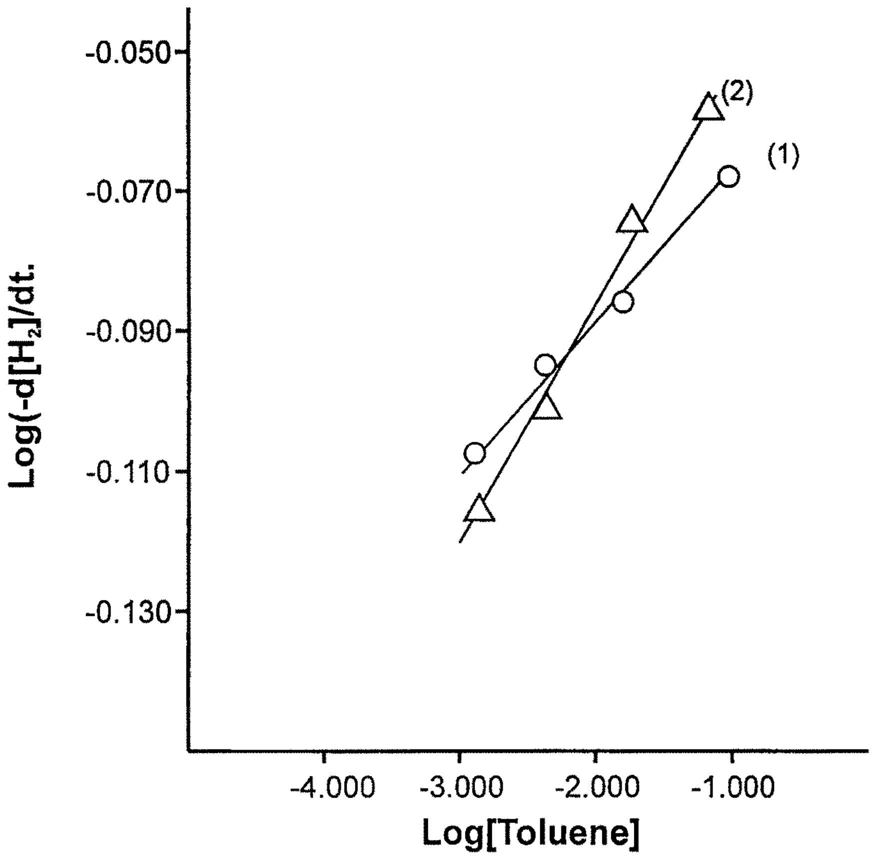


Fig. (3b) Plot of Initial rate v/s. Log[Toluene] for Catalyst
(1) 8OPDAMn(II) (2) 8OPDANi(II)

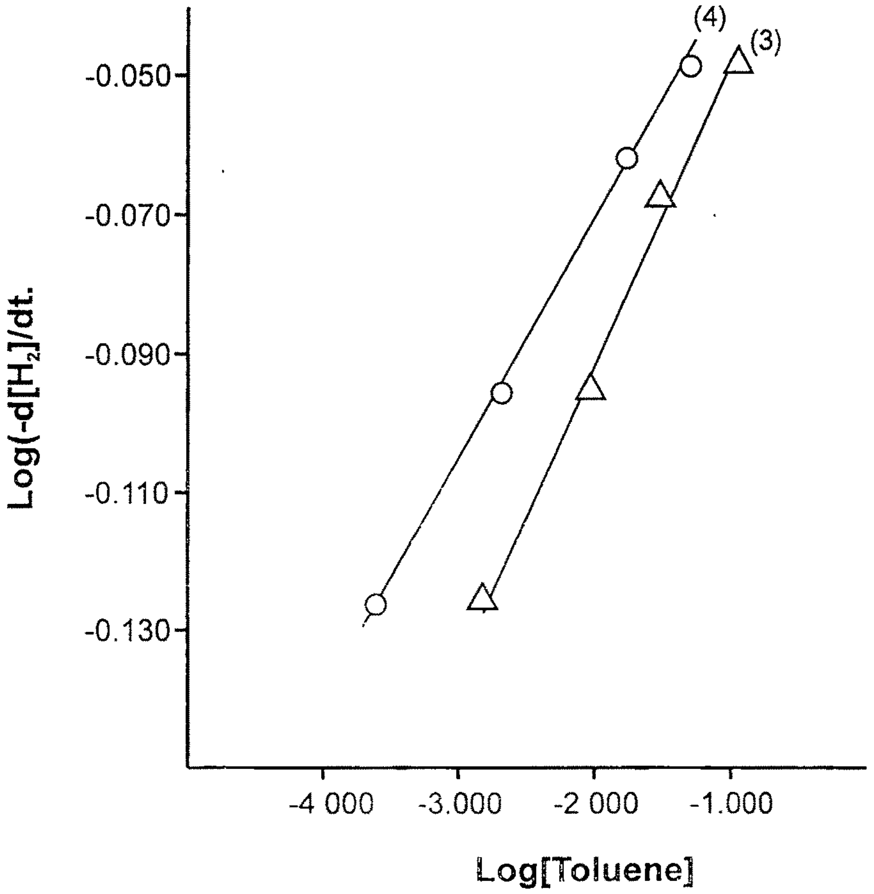


Fig (3b) Plot of Initial rate v/s. Log[Toluene] for Catalyst
(1) 8PPDAMn(II) (2) 8PPDANi(II)

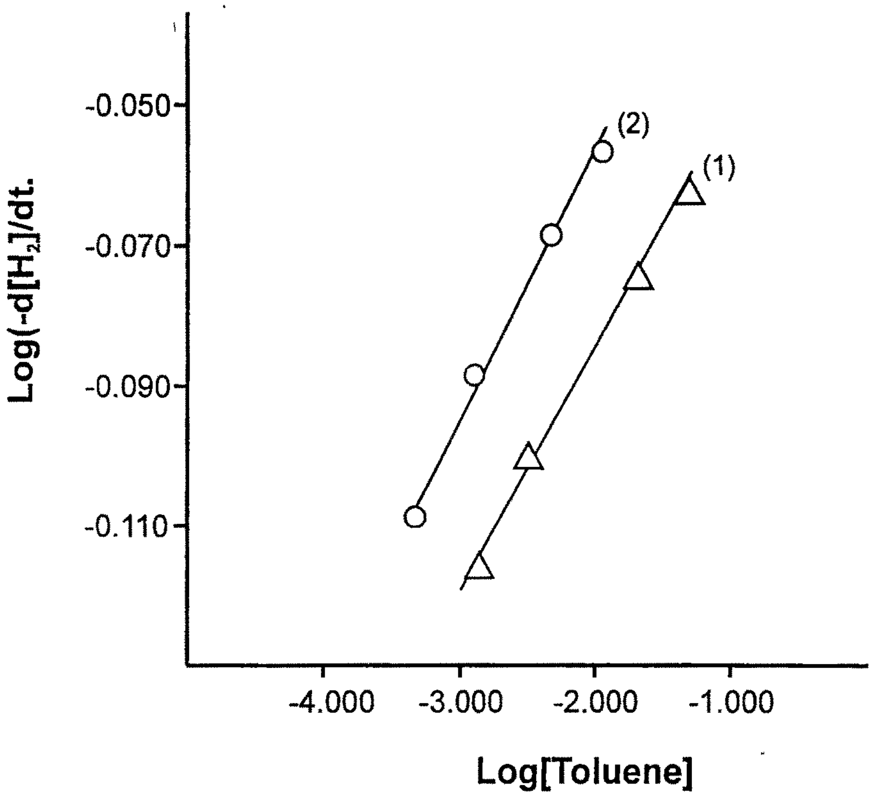


Fig. (3b) Plot of Initial rate v/s. Log[Toluene] for Catalyst
(1) 14OPDAMn(II)
(2) 14OPDANi(II)

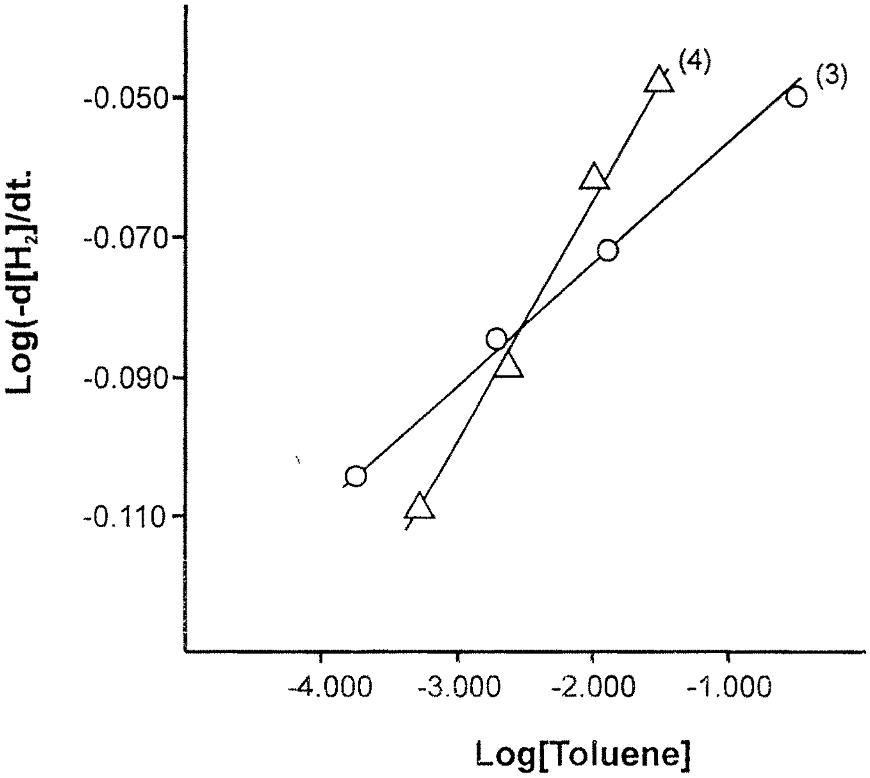


Fig. (5b) Plot of Initial rate v/s. Log[Toluene] for Catalyst
(1) 14PPDAMn(II)
(2) 14PPDANi(II)

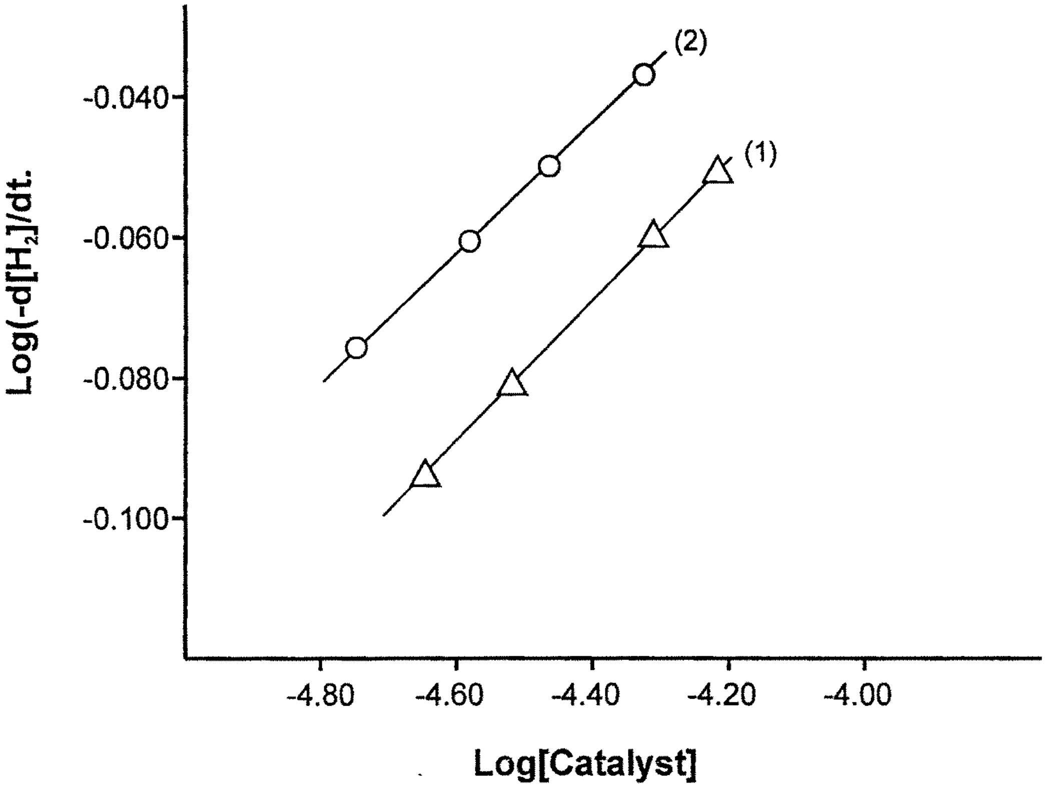


Fig. (3c) Plot of Initial rate v/s. Log[Catalyst] for Catalyst
(1) 6OPDAMn(II)
(2) 6OPDANi(II)

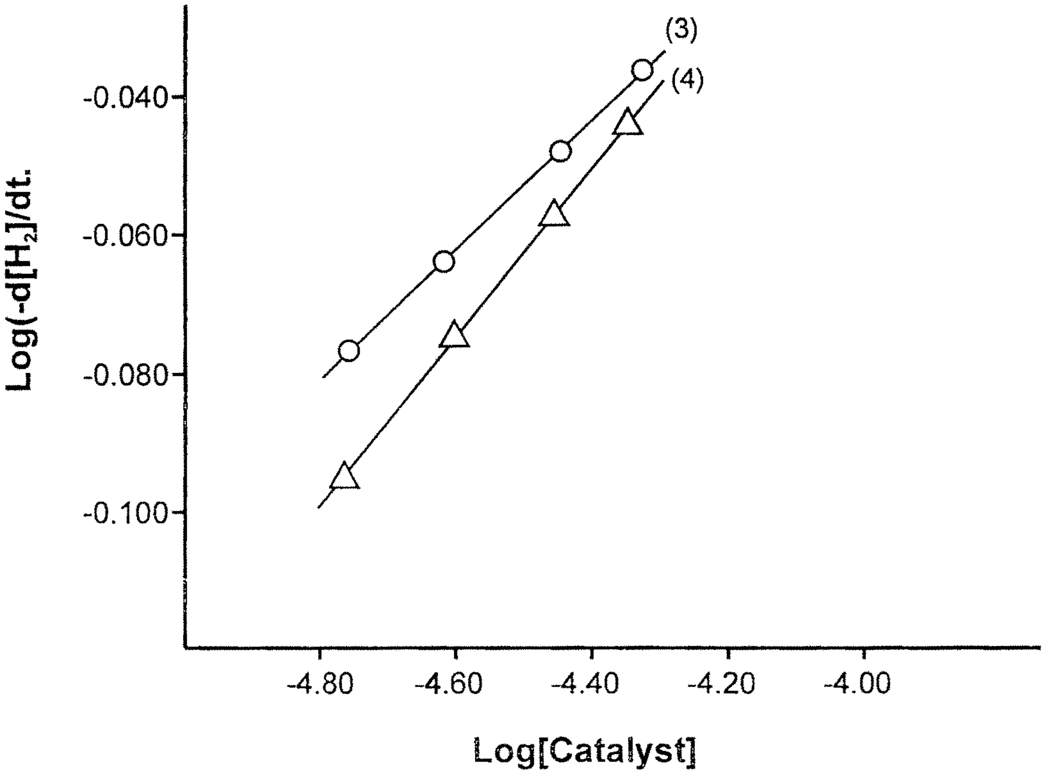


Fig. (3c) Plot of Initial rate v/s. Log[Catalyst] for Catalyst
(1) 6PPDAMn(II)
(2) 6PPDANi(II)

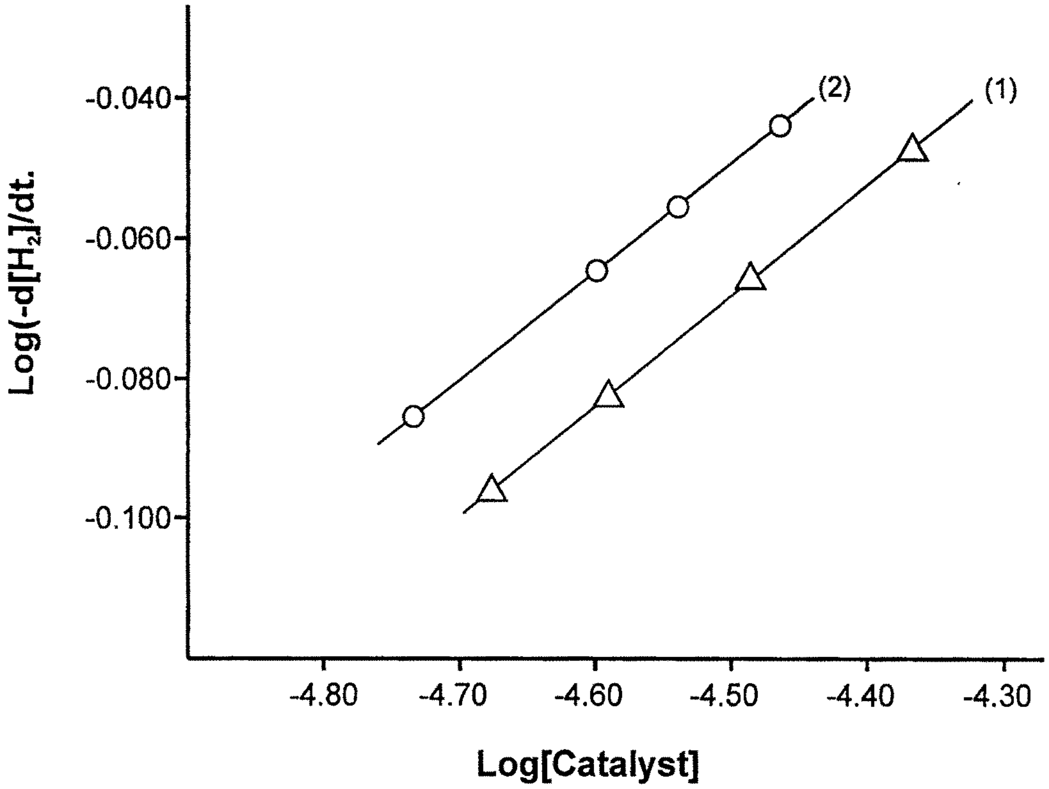


Fig. (3c) Plot of Initial rate v/s. Log[Catalyst] for Catalyst
(1) 8OPDAMn(II)
(2) 8OPDANi(II)

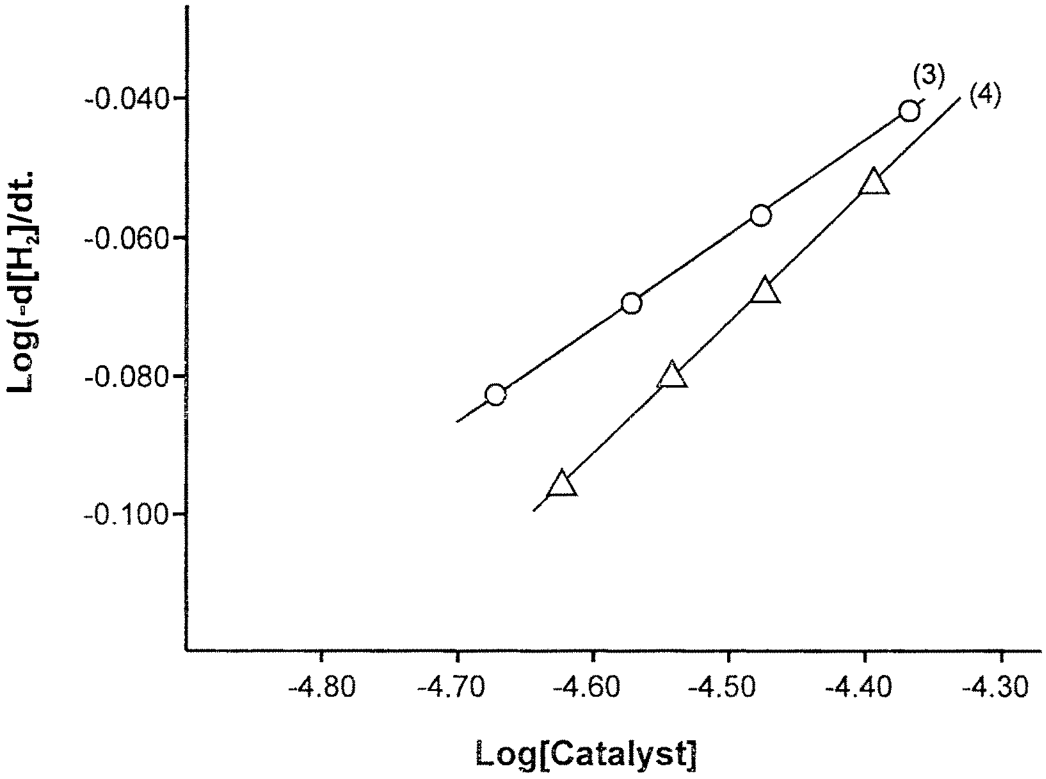


Fig. (3a Plot of Initial rate v/s. Log[Catalyst] for Catalyst
(1) 8PPDAMn(II)
(2) 8PPDANi(II)

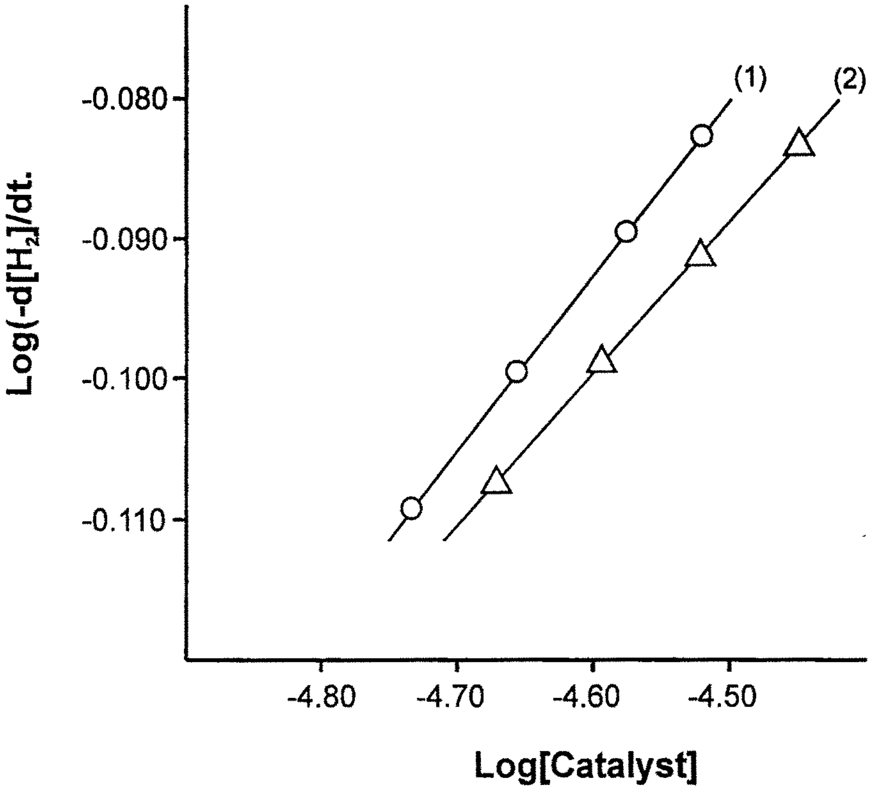


Fig. (3c) Plot of Initial rate v/s. Log[Catalyst] for Catalyst
(1) 14OPDAMn(II)
(2) 14OPDANi(II)

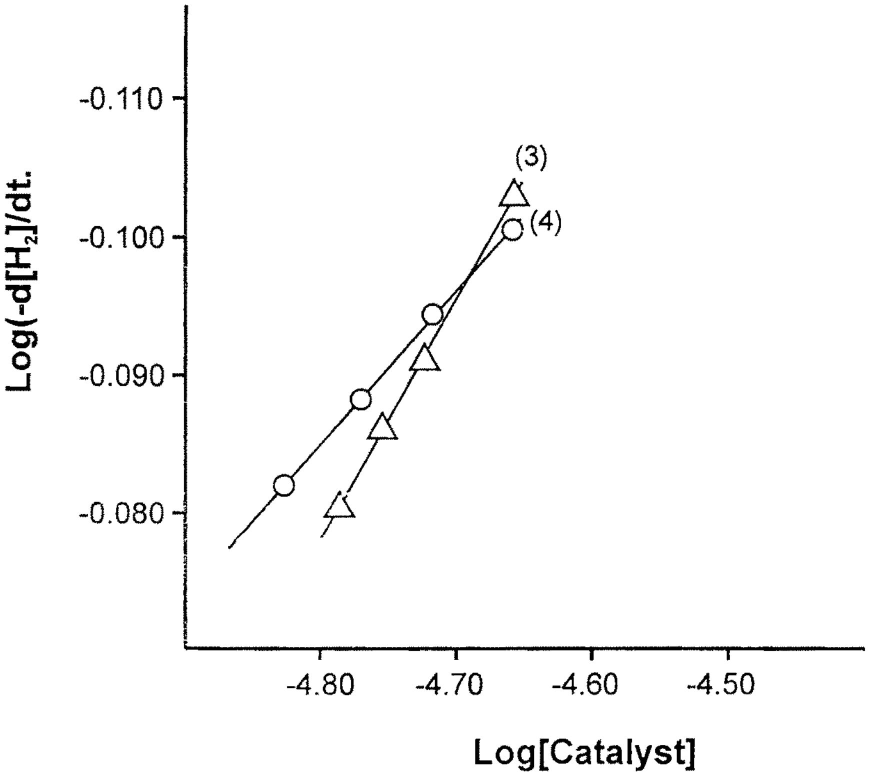


Fig. (3c) Plot of Initial rate v/s. Log[Catalyst] for Catalyst
(1) 14PPDAMn(II)
(2) 14PPDANi(II)

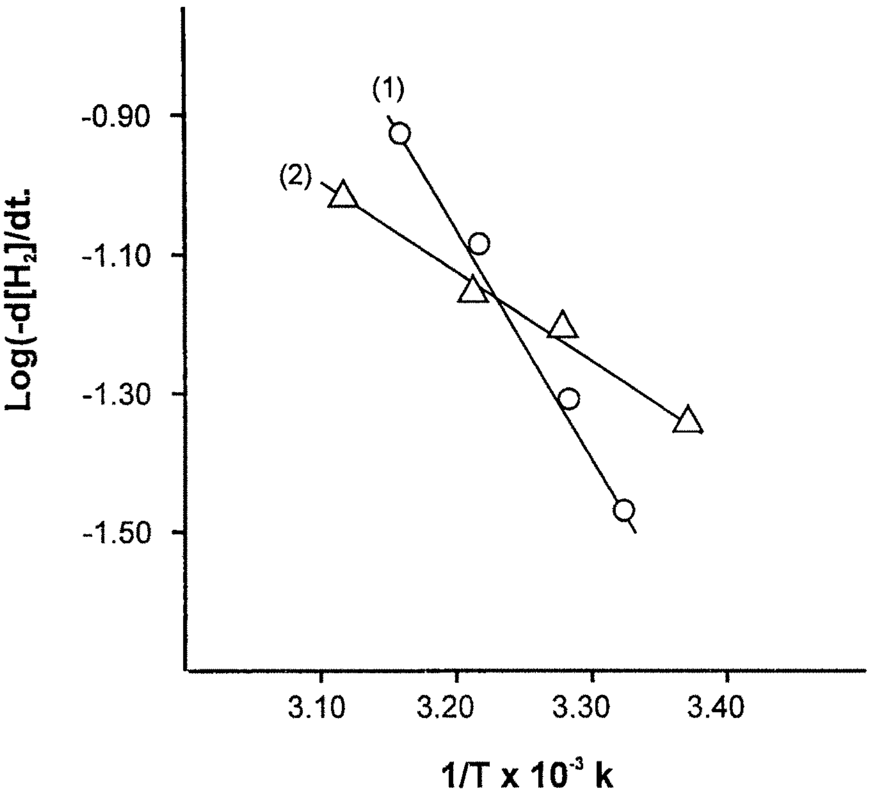


Fig. (3d) Arrhenius Plot of Initial Rate v/s. 1/T for the Catalyst
(1) 6OPDAMn(II) (2) 6OPDANi(II)

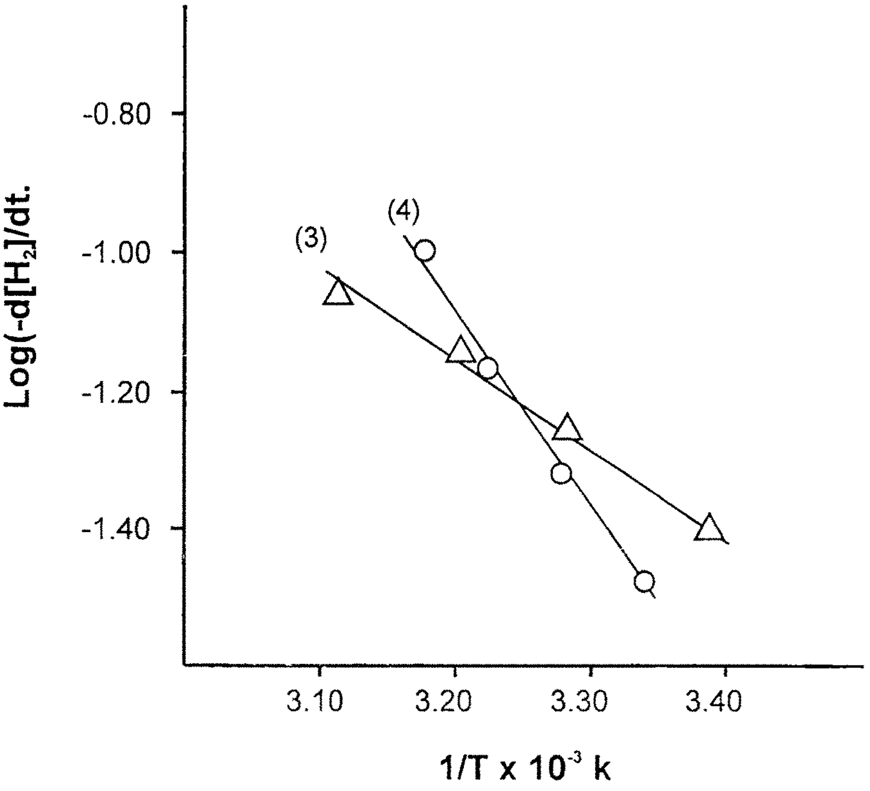


Fig. (3d) Arrhenius Plot of Initial Rate v/s 1/T for the Catalyst
(1) 6PPDAMn(II) (2) 6PDANi(II)

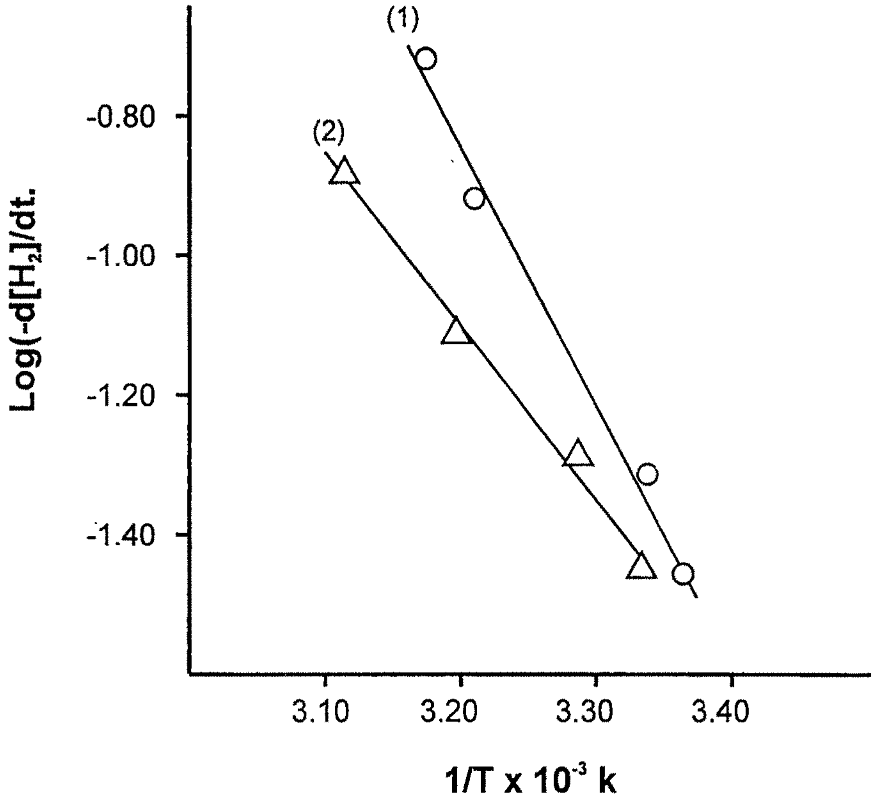


Fig. (3d) Arrhenius Plot of Initial Rate v/s. 1/T for the Catalyst
(1) 8OPDAMn(II) (2) 8OPDANi(II)

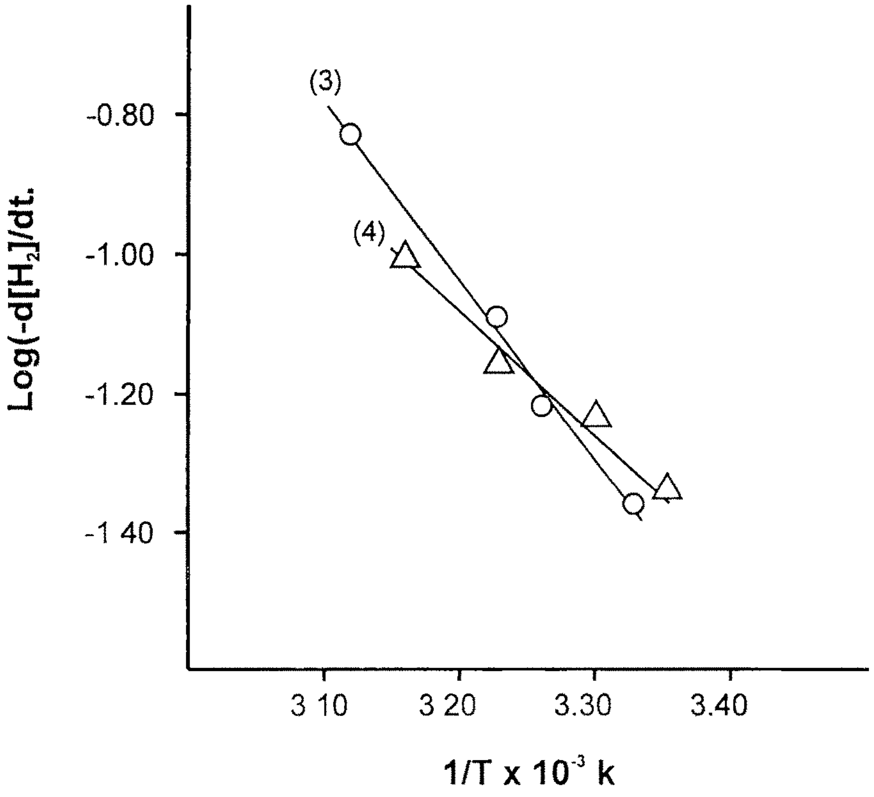


Fig. (3d) Arrhenius Plot of Initial Rate v/s. 1/T for the Catalyst
(1) 8PPDAMn(II) (2) 8PDANi(II)

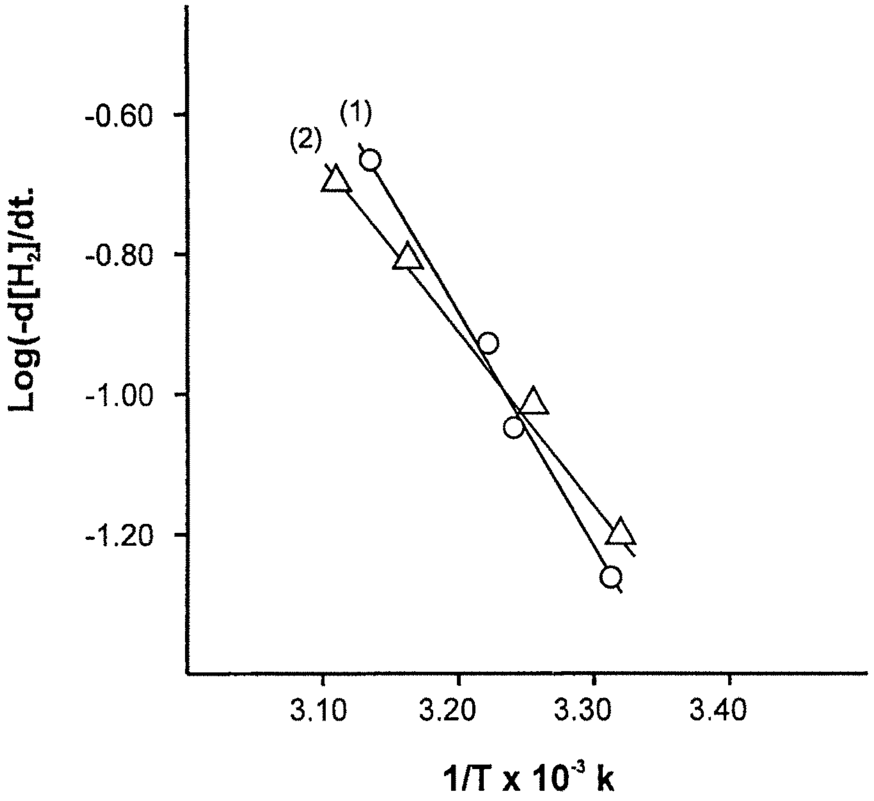


Fig. (3d) Arrhenius Plot of Initial Rate v/s. 1/T for the Catalyst
(1) 14OPDAMn(II) (2) 14OPDANi(II)

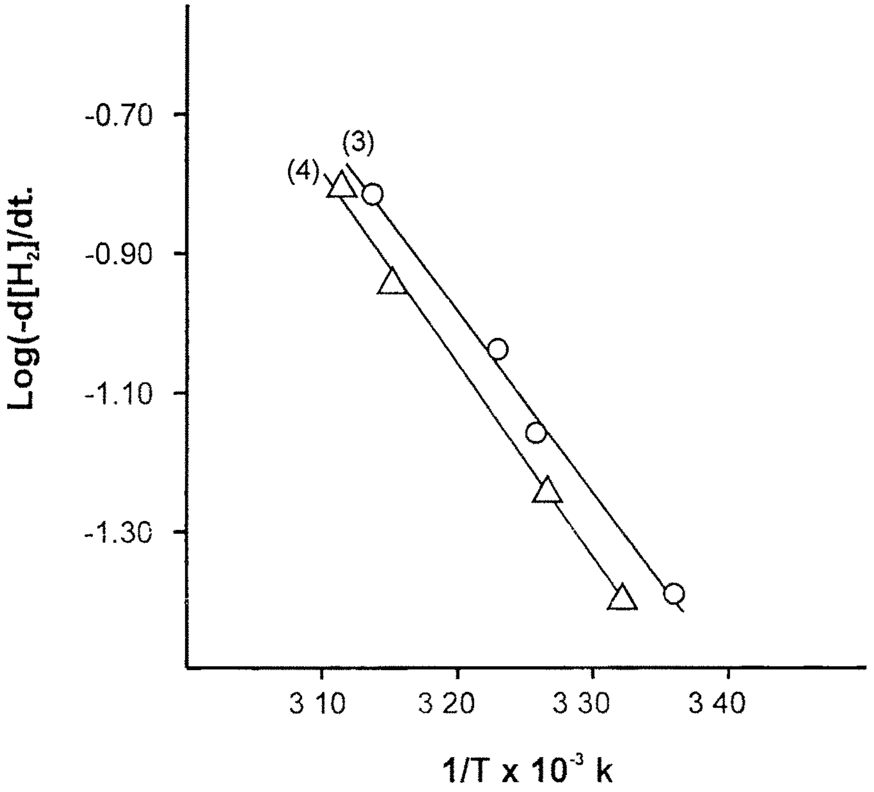


Fig. (3d) Arrhenius Plot of Initial Rate v/s. 1/T for the Catalyst
(1) 14PPDAMn(II) (2) 14PDANi(II)

4.10 HOMOGENEOUS CATALYST

INTRODUCTION

The oxidation of organic compounds by molecular oxygen (dioxygen) has a long history[54]. It was later recognized that these oxidation processes involve the formation of organic peroxides.

Catalysis by metal complexes plays an important role in the control of selectivity, partial oxidation of alkanes, olefins and aromatic hydrocarbons of useful products. Oxidation of ethanol to acetic acid was carried out by Davy, using Pt (Platinum) catalyst in vapour phase. The Celenese process for liquid phase oxidation of n-butane to acetic acid, is still used today. A variety of metal catalysed oxidation has been developed for selective oxidation.

The success of Waker process has led to interest in chemistry of organometallic compounds and homogeneous catalysis. The petro-chemical processes employ homogeneous catalysts in liquid-phase.

Aranjo A.S. and co-workers[53] studied the oxidation of toluene using VAPO – II catalyst The reaction was carried out in a different reactor at 430 - 470^{0}C with varying space velocity. The reaction product were benzaldehyde and benzene, confirmed by the gas chromatography.

Konietzni and co-workers[54] studied the oxidation of Toluene, using AMM-Mn_x Si catalyst and found good activity of the new catalysts The major product is benzaldehyde and is attributed to the homogeneous distribution of 'Mn" in the shape selective environment of the microspores.

El-Mottaleb et al[55] prepared and characterized the complexes of Mn(II), Fe(III) & Cu(II) and three tridentate pyridyl hydrazones. The ligands were prepared via Schiff base concentration of b–chloro–2- hydreazonopyridine with h-formylpyridine The catalytic activity was co-related with the levels acidity of metal centers,created according to the nature of ligand substituents The probable mechanistic implications of catalysed oxidation reactions are discussed

Zhou; Lingping and co-workers[56] studied the oxidative methylation of toluene with methane over Kx, Ky, KM, KzSM-5 and KB zeolites and compared the reactivity.

Muresanu, clandia etal[57] studied the kinetics of toluene by cerium (IV) in sulfuric acid media and reported that an adduct was formed between toluene and Ce(IV) and subsequently under going electron transfer. The main reaction product was benzyl alcohol and benzaldehyde.

Larrondo S and co-workers[58] studied the kinetics of toluene oxidation on $Vsb_{0\,8}\ Ti_{0\,2}\ O_4$.and reported the reaction network involves 3 steps. The partial oxidation of toluene to benzaldehyde, a consecutive oxidation of benzaldehyde to carbon oxides and a parallel oxidation of toluene to carbon oxides. The product distribution was affected by temperature.

Mannepalli Lakshmi[59] carried out the oxidation of toluene with continuous flow of air and reported that benzaldehyde was prepared with 40-50% selectivity. Preferably, the catalyst is selected from salts of (Fe, Mn, Co, Mo, Ni,) and co-catalyst is selected from Mn and Cu Salts.

In the present investigation, the homogeneous metal complexes of Mn(II) and Ni(II) have been used to study the kinetics of oxidation of toluene under mild operating conditions. The influence of various parameters such as concentration of catalyst and substrate, temperature of the system as well as nature of solvent used on the rate of the reaction has been investigated

EXPERIMENTAL

MEASUREMENT OF CATALYTIC ACTIVITY OF OXIDATION OF TOLUENE

The oxidation reaction was carried out in magnetically stirred glass reaction using methanol as the solvent using homogeneous catalysts. Methanol was chosen as solvent for the oxidation reaction because of better miscibility with substrate. (as mentioned in chapter 3). The progress of reaction was followed by measuring the uptake of oxygen as a function of time at constant pressure using a glass manometric apparatus. The experimental set-up and detailed procedure are described in chapter 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^{0}C. The stoichiometry of the reaction was checked by carrying out a few experiments at constant temperature and oxygen pressure at different concentration of toluene. The initial rate data obtained from oxygen uptake measurements is used to evaluate the kinetic parameters.

In each kinetic run the uptake of oxygen was measured as 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 the nature of solvent was investigated.

In the case of homogeneous system, in spite of using a larger concentration of Mn(II) and Ni(II) metal ions as catalyst for above reaction, a lower rate was observed as compared to heterogenised homogeneous system.

The higher rate of catalytic activity of heterogenised homogeneous catalysts is due to lower values of activation energy The activation energy of homogeneous counter part is higher Thus, the rate of reaction is higher in case of heterogenised homogeneous catalyst

Effect of [catalyst] on the rate of oxidation using homogeneous complexes at 35^{0}C at 1 atm. pressure.

In case of change of catalyst concentration the rate of reaction is much more lower compared to heterogenised homogeneous catalyst. The rate of reaction was found to be 0.035 ml min^{-1} with metal concentration 4.02 X 10^{-4} mole l^{-1} and the substrate concentration 9.80 X 10^{-4} . In spite of much higher concentration of metal and substrate the rate is low.

Kinetics of oxidation of toluene at various temperature using metal complex catalysts.

At higher temperature the rate of reaction did not enhanced considerably. At 45^0 C the rate recorded was 0.039 ml min^{-1} which is very low compared to heterogenised homogeneous catalysts.

The values for the energy of activation calculated from the slope of the straight line plot of log (initial rate) against 1/T, the energy of activation was found to be 72.2 kJ mole^{-1} for OPDA Mn(II) and 49.4 kJ mole^{-1} for OPDA Ni(II)

Effect of [Toluene] on the rate of oxidation using homogeneous complexes at 35^{0}C at 1 atm. Pressure.

In case of change of toluene concentration (substrate) the rate of reaction and enhanced from 0.018 to 0 032 (ml minutes^{-1}) as the substrate. concentration enhance from 6.72 x 10^{-4} mole l^{-1} to 12.8 x10^{-4} mole l^{-1} and the metal concentration 3.02 x 10^{-4} (Mn(II)) mole l^{-1} . It is clear that rate of reaction is much slower compared to haterogenised homogeneous catalyst.

Effect of [Toluene] on the rate of Oxidation using homogeneous complexes at 35^{0}C at 1atm. Pressure

Volume of Methanol = 20ml.

Catalysts	[Catalysts] mole l^{-1}	[Toluene] mole l^{-1} X 10^4	Rate of reaction ml min^{-1}	Order of reaction
	3.02 X 10^{-4}	6.72	0.018	
OPDAMn (II)		9.80	0.021	0.45
		11.5	0.032	
		12.8	0.040	
	2.59 X 10^{-4}	6.72	0.017	
OPDANi (II)		9.80	0.020	0.48
		11.5	0.028	
		12.8	0.035	
	2.29 X 10^{-4}	6.72	0.015	
PPDAMn (II)		9.80	0.019	0.51
		11.5	0.027	
		12.8	0.039	
	2.10 X 10^{-4}	6.72	0.012	
PPDANi (II)		9.80	0.016	0.43
		11.5	0.024	
		12.8	0.032	

Effect of [Catalyst] on the rate of oxidation using metal complex catalysts in homogeneous medium at 35^{0}C at 1atm. Pressure

Volume of Methanol = 20ml.

Catalysts	[Catalysts] mole l^{-1} X 10^4	[Toluene] mole l^{-1} X 10^4	Rate of reaction ml. min^{-1}	Order of reaction
	2.21	9.80	0.015	
OPDAMn (II)	3.02		0.018	0.50
	3.45		0.029	
	4.02		0.035	
	1.80	9.80	0.013	
OPDANi (II)	2.59		0.019	0.55
	2.92		0.025	
	3.20		0.032	
	2.12	9.80	0.020	
PPDAMn (II)	2.92		0.025	0.48
	3.29		0 029	
	3.91		0 034	
	1.91	9 80	0 016	
PPDANi (II)	2 25		0.021	0.52
	2 75		0 029	
	3 09		0 032	

Kinetics of oxidation of Toluene at various Temperatures using metal complex catalysts in homogeneous medium.

Volume of Methanol = 20 ml.

[Tolune]= 9.80×10^{-4} mole l^{-1}

Catalyst	[Catalyst] mole l^{-1} x 10^4	Temp. ^{0}C.	Rate of Reaction ml min^{-1}	Energy of Activation kJ $mole^{-1}$	Entropy of Activation (eu)
	3.02	30	0.010	72.2	-110
OPDAMn (II)		35	0.015		
		40	0.025		
		45	0.039		
	2.59	30	0.011	49.4	-95
OPDANi (II)		35	0.014		
		40	0.022		
		45	0.030		
	2.79	30	0.012		-102
PPDAMn (II)		35	0.016	65.5	
		40	0.029		
		45	0.036		
	2.41	30	0.010		-104
PPDANi (II)		35	0.013	60.4	
		40	0.019		
		45	0.028		

4.11 Study of 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 catalyst may lose their activity by leaching of the metal ions from the surface to the solution or reduction to free metal[47-52]. 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 experiment was carried out at 35^{0}C and injecting a known amount of substrate (i.e. 20 ul.). After every cycle the catalyst was separated and washed with various solvents and dried to reuse it. The rate of oxidation was measured as function to time for both fresh and used catalysts. The results are summarized in Table 4.1. No change in the rate of reaction was observed upto 3cycles and after that a decreasing rate was observed. The metal content present on the surface was estimated after the completion of the reaction and the loss of 39% 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.

Table 4.1 : Life cycle study of polymer bound catalysts at 35^{0}C and 1atm. Pressure in 20 ml. Methanol.

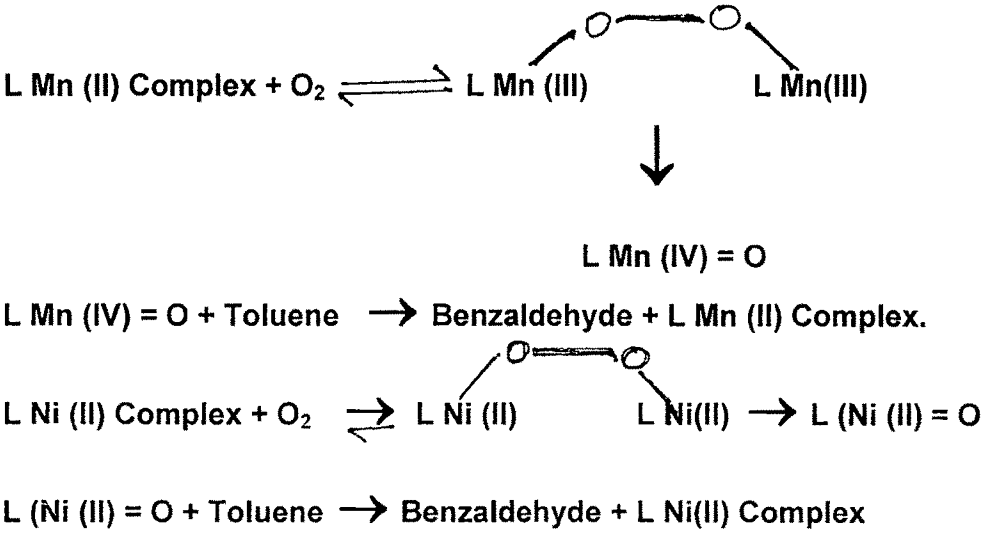
	I	II	III	IV
OPDA Mn(II)	0.040	0.040	0.034	0.030
OPDA Ni(II)	0.035	0.035	0.030	0.022
PPDA Mn(II)	0.039	0.039	0.035	0.032
PPDA Ni(II)	0.036	0.036	0.029	0.025

REACTION MECHANISM :

In the present study the partial pressure of oxygen is kept constant. In all the experiments the solvents and the catalysts were initially saturated with oxygen followed by injection of toluene and thereafter the actual uptake of oxygen was taken. A slight color 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 toluene oxidation in a separate experiment. When metal chloride was mixed with the homogeneous catalyst and oxygen was bubbled through it, a change in color was observed and on injecting the substrate the original colour reappeared. This is indicative of the fact that after passing molecular oxygen, there is and intermediate complex formation which transfers oxygen to the substrate and finally the catalyst regains its original colours. The reaction mechanism for the oxidation of organic molecules by the use of metal ions/complexes in the homogeneous systems have been studied widely (56-58) and the formation of peroxo and oxo complexes were suggested to be responsible for the transfer of oxygen to the substrate (59-61). The formation of the peroxo & superoxo compound and the transfer of oxygen via this route was supported by Vaska et al[62] when dioxygen is covalently bound on the metal center .

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



L Mn (II) Complex + O_2 $\rightleftharpoons$ L Mn (III)—O—O—Mn(III) L $\rightarrow$ L Mn (IV) = O

L Mn (IV) = O + Toluene $\rightarrow$ Benzaldehyde + L Mn (II) Complex.

L Ni (II) Complex + O_2 $\rightleftharpoons$ L Ni (II)—O—O—Ni(II) L $\rightarrow$ L (Ni (II) = O

L (Ni (II) = O + Toluene $\rightarrow$ Benzaldehyde + L Ni(II) Complex

Where L is Ligand (o-Phenylenediamine)

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

$$R = k\,[\text{Catalyst}]\,[\text{Toluene}]$$

Thus, on increasing the concentration of the catalyst at a constant concentration of toluene or vice-versa the rate was observed to increase.

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, Amesterdam, 1997, P.I.
3. G. Strukul, Catalytic Oxidation with hydrogen peroxide as oxidant, Kluwer Dordecht, 1992, P2.
4. K. Weissermel and H.J.Arpe, Industrielle Organnische 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. Gaffnery and J.E.Lyons (Eds.) Stud. Surf. Sci and catal, 110, Elsevier, Amsterdam P.135
7. Chem. and Engg. News, April 18 1996, P,1.
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 Chimo. e
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 Calestins, 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.Cages, L.S.V.S. Sune, M.F.S. Lopes, J.Pereira in R.K.Grasseli, S.T.Oyama, A.M.Gaffriey and J.E.Lyons (Eds.) Stud; Surf; Sci. and Catal,110 Elsevier Amsterdam,1997. P 1193

15. B.M.Despey roux, K.J. Deller and E. Peldszus in G. Centl. And F.Trifiro (Eds) New Developments in selective oxidation, Stud, Surf, Sci and Catal, 55, Elsevier, Amsterdam, 1990, PP159-169 and references there in.

16. R.Sumathi, K.Johnson, B.Vishwanathan and T.K. Varadrakan India, J. Chem 36(10), 874, 1997.

17. R.Sumathi, B. Vishwanathan and T.K. Varadrajan T.S.R. Prasada Rao and Applied Aspects of Industrial Catlysis, Stud., Surf, Sci, and Catal. 113, Elsevier, Amsterdam,1998, P.937

18. C.N. Pillar and J.Jayamani, J.Catal,82, 485, 1983

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

20. S.Sueto, S.Nishiyama, S.Tsuruya and M.Masi, 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.Martley, 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 CJO'Connor, Co-ord Chem Rev. 9, 145, 1972-73

26. J.E.Lyons in R.Ugo(Eds) Asp. Hom. Catal; 3 Reidel, Dordrecht, 1977, P-1.

27. R.A.Sheldon and J.K.Kochi, Metal Catalyzed Oxidation of Organic Compounds, Academic Press, New-York, 1981, Chapter 4 and references.

28. M.M. Taqui Kha, 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

36. S. Yamaguchi; M.Inoue and S.Enomtoto, 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 Grasselli, 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.Jiva; F.Jin, M.Huang, Y.Jiang. Reactiv 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.Tagui Khan, B. Tagui Khan, S.Begum and S.Mustafa Ali J. Mol.Catal; 34, 28, 3, 1986.

45. M.Terasavsa, 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.Seiling and R.Eldik, Inorg. Chem. 36, 4115; 1997.

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

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

51. E.R.Birnbaun; M.W.Grinstaff, J.A.Labinger, J.E.Bercaw and H.B.Gray, J.Mol.Catal; A chemical 104, 119, 1995.

52. 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. And Surf. Sci. and Catal, Elsevier, Amsterdam,110; 1165, 1997.

53. Aranjo A.S. Fernandes V.J., Jr.Arujo, A.S Sune L.S. V S Chagas A.L Rocha, A, O. Jr (Dept. of Chemistry Federal Univ of Rio Grande elonorte, 59078, 970 Natal Brazil) React. Kinet. Catal Left 1999,67Cl), 43-48 (engg) A Kandemiat Kiado

54. Konietzni, Frank; Kolb,Uwe, Dingerdissen, Merier, Wilhelm F, (Max Plank institute for kohen for schung D, 45470. Mulheim on der Ruhr, Germany.

55. El-Mottaleb, M. Ramadan, Abd.(Chemistry Dept., Faculty of Education Tanka University Egypt) Transition Met. Chem. (London) 1998 23(2), 183-189(Eng.) Chapman & Hall.

56 Zhou; Lingping; Lixuaniven; Li,Wei (College of chemistry and Engg. Peking University Beijing, Peap. Rep. Ching 100871)

57. Muresanu Claudia, Balden, Ioan, Bucsa, Crisitina. Faculty of Chemistry and Chmical Engg. "Babis – Bolyai University 3400 cluj. Napoca Rom 45(2), 111-118 (Eng.) Editura Academiei Romane.

58. Larrondo S; Barbaro, A, Irigayen B, Amadeo, N Catal-Today 64(3-4), 179-189(eng. 2001).

59. Kantam, Manne Palli, Lakshmi, Chandary Bayapati Manoranjan, Sreekanth, Rent lavelly, Rao Kottapalli, Kotesware; Naik Kanta Rao, Kumar, Tehlla Prenthap; Eur. Pat Appl. EP-1,088,810.

60. Dalal Mahesh, K.Upadhyay M. Ram R.N. ; J. Mol. Catal, A.Chem 142 (3), 325 - 322 (Eng.) Elsevier Science B.V.

61. Dilip Patel; Dalal Mahesh K; Ram R N. , Stud. Surf. Sci catal 113; 1998

62. John Jacob ; Dalal Mahesh K; Ram R.N. Stud. Surf. Sci. Catal 1997 110 (3rd World Congress on Oxidation catalysis , 1997) 1165 -1171 (Eng.) Elsevier Science B V

63. Lei, Zigiang, Han , Xiangen ; Zhang, Yan; Wang, Rengmin; Cao; Yonghong; Wang, Yrnpu ,Polym. Plast Technol Eng. 38 (1); 159 - 169 ; 1999 (Eng.) ; Marcel Dekker., Inc.

64. Groves John T.; Carofiglio Tommaso Banchio Mercella; Sawve, Antony Pct. Int. Appl. W.O. 9804 , 538 (Cl CO7 D 301/06) 5 Feb. 1998, Us Appl. 760, 849, 5 Dec, 1996. 48 P.P. (Eng.)

65. Weiner, Heiko ; Hoyashi, Yoshinito ; Finake, Richard G. Inorg. Chim. Acta; 291 (1-2) , 426 - 437 ; 1999 (Eng.) Elsevier Science 3A

66. Suresh , S; Skaria, S; Ponarathnam, S., Stud. Surf. Sci Catal 1998 113 (Recent Advances in Basic and Applied Aspects of Industrial Catalysis) 915 - 919 (Eng.)

67. Gu, Fengcai, Wang Jinwing , Liu, Yinfan; Ye Wengiang, Sun, Shrmeri Daxue Xuebao Bianjibu 31 (5) ; 666 – 670

68. Zhang, Xiang - Fushi, Xiao - Tian Hechang Huaxue (4) ; 433 - 437 (Ch) 1998