Oxidation of toluene using polymer anchored Ni(II) complex as catalyst

Kamlesh Gauli [a], R.N. Ram [a,✠], Hemant P. Soni [b,*]

[a] *Chemistry Department, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India*
[b] *Department of Applied Chemistry, Faculty of Technology & Engineering, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat 390001, India*

Abstract

Polymer anchored Ni(II) complex was synthesised by sequential attachment of *O*-phenylenediamine and nickel chloride to chloromethylated styrene-divinyl benzene copolymer with 6% cross-linking. Synthesised catalyst, named 6 OPDA-Ni(II), was characterised by different techniques, such as FTIR, reflectance UV–vis spectroscopy, ESR, 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 toluene to benzaldehyde by varying the temperature of the system as well as the concentration of the substrate and catalyst. The values of energy of activation and entropy of activation have been evaluated from kinetic data. A probable reaction mechanism has been proposed.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Supported catalysts; Heterogeneous catalysis; Homogeneous catalysis; Polymer anchored Ni(II) complexes

1. Introduction

Present days stringent ecological standards require a wide attention to environmental friendly and clean production processes. This service can be very well provided by catalysts with high selectivity. Homogeneous catalysis is practiced since very long time in large-scale oxidation reactions [1,2]. However, problems related to corrosion, plating out on the reactor wall, recovery from the reaction mixture and its reuse are limitations in homogeneous catalytic processes. Most of the problems related with homogeneous catalyst can be solved by supporting the catalyst on the insoluble polymer support and make it heterogenised [3]. Polymer supports used for this purpose are inert, non-toxic, non-volatile, insoluble and often recyclable [4]. Thus, research for viable polymer supported catalysts has gained prominence in industries as well as in chemical laboratories [5]. The behaviour of the supported catalyst under the reactions (temperature, pressure, nature of the reactants and products, etc.) is certainly less well developed area even though these data are

valuable for the conception and development of a fully recyclable catalyst. The main drawback of the supported catalyst is the leaching of metal ion from the surface of support, which can be prevented by using chelating ligands [6]. A number of papers have been published describing supported oxidizing agents as a catalyst for the oxidation of primary and secondary alcohols to aldehydes and ketones [7–10]. We have reported catalytic activity of different heterogenised homogeneous chelated metal complex catalysts for hydrogenation of olefins and oxidation of cyclohexane, toluene and benzyl alcohol [11–15]. Covalently bound multidentate amines could be further modified to prepare polymer bound chelates [16]. Sueto et al. have reported various studies on partial oxidation of benzyl alcohol to benzaldehyde on supported catalysts [17]. Present studies reports synthesis of polymer bound Ni(II)–*O*-phynylenediamine complex and oxidation of toluene with molecular oxygen using this catalyst.

2. Experimental

2.1. Material and equipment

Choloromethylated styrene-divinyl benzene copolymer with 6% cross-linked was provided by Ion Exchange Ltd., Bombay (India). THF, dioxane, methanol and toluene were purified as

---

reported elsewhere [12]. Elemental analysis and TGA were carried out in the laboratory using Column Analyser and a Shimadzu Thermal Analyser DT-30, respectively. UV–vis reflectance spectra of the solid samples were recorded on a Shimadzu's UV-240 spectrophotometer with reference to non-absorbing $BaSO_4$ as a standard. IR spectra were recorded on a Backmann IR-4220. The surface area was determined using Carlo–Erba strumentzione. SEM was done at IIT, Bombay. The swelling studies of the catalyst were carried out using polar and non-polar solvents at a constant temperature. The detailed procedure described earlier [14].

2.2. Synthesis of catalyst

Chloromethylated P(S-DVB) polymer beads were washed in the following sequence: aqueous dioxane, dioxane containing 10% HCl, methanol and finally with distilled water to remove free chloride.

To functionalise the polymer support with the ligand, the chloromethylated polymeric backbone (styrene-divinylbenzene) was treated with appropriate quantity of *O*-phenylenediamine using THF as a solvent at room temperature for 48 h [15]. The beads were washed with deionised water, methanol and dried at 60 °C. The dried beads were refluxed in a solution of *O*-phenylenediamine prepared in benzene for 24 h [16]. The liganded polymer then purified with methanol using soxhlet extraction method and dried at 80 °C. The percentages of C, H and N before and after ligand introduction are given in Table 1.

The functionalised polymer was kept in contact with ethanol for 30 min and an ethanolic solution of $NiCl_2$ (0.5, w/v) was added to it and kept at room temperature for some days. The color of the beads became pale. The catalyst was washed with ethanol and dried in vacuum at 70 °C. The quantity of Ni present on the surface of the polymer was estimated by spectrophotometric method using dimethylglyoxime. This synthesised supported catalyst was named as 6-OPDA-Ni(II).

The unbound (without support) complex of 6-OPDA–Ni(II) was obtained by mixing 1:1 mixture of $NiCl_2$ and *O*-

phenylenediamine in ethanol. The pH of the solution was changed after 2 days and solid product was separated.

2.3. Kinetics of oxidation of toluene

The procedure adopted to investigate the kinetics of oxidation of toluene to benzaldehyde is multipronge. The quantity of oxygen uptake was measured at different intervals of time. The initial rate was calculated from the slope of plot of oxygen uptake against various intervals of time. The detail procedure and experimental set up were described earlier [14]. The products were analysed by the use of gas chromatograph using flame ionisation detector and carbowax column. No side products formed as seen by GC analysis.

3. Results and discussion

3.1. Physical properties

Physical properties of the catalyst 6-OPDA-Ni(II) are given in Table 2(a). A decrease in surface area was observed after loading the metal ion on the polymer support (surface area of the support was 35.21 $m^2\,g^{-1}$ and that of the catalyst was 30.79 $m^2\,g^{-1}$) might be due to blocking of the pores of the polymer support after ligand and metal ion introduction [18,19]. A decrease in swelling is observed as the nature of the solvent changes from polar to non-polar (Table 2b). Methanol was found to be a suitable swelling agent and was therefore employed as a solvent for oxidation of toluene because of better swellability with the catalyst and miscibility with the substrate.

3.2. Morphology of catalyst

The morphology of the catalyst was studied using scanning electron microscope (Fig. 1A and B). A clear change

Table 1
Elemental analysis at the different stages of preparation of catalyst (wt.%)

P	
C	75.38
H	5.93
N	17.50
Q	
C	76.37
H	6.622
N	2.563
R	
C	70.55
H	6.96
N	2.693
Ni	3.81×10^{-4}

P: chloromethylated polymer; Q: after functionalisation by OPDA; R: after complex formation.

Table 2
Physical properties of catalyst 6-OPDA-Ni(II)

(a) Physical properties	
Particle size (mm)	0.5
Surface area (NTP) ($m^3\,g^{-1}$)	30.79
Pore volume ($cm^{-3}\,g^{-1}$)	0.1693
Apparent bulk density ($g\,cm^{-1}$)	0.354
Moisture content (wt.%)	0.521
Elemental analysis (wt.%)	C = 73.45; H = 6.560; N = nil

Solvent	Swelling (mol %)
(b) Swelling studies using different solvents	
Methanol	4.29
Ethanol	3.35
Dichloromethane (DCM)	2.55
N,*N*-Dimethylformamide (DMF)	1.72
Tetrahydrofuran	1.58
Dioxane	1.22
Acetone	1.12
Benzene	1.03
Cyclohexane	0.81
N-Hexane	0.55

in morphology was observed after anchoring the metal complex on the polymer support. An increase in the surface area was observed after anchoring the metal ions, which might be due to functionalisation of polymers with bulky ligand. Successful functionalisation of polymer was confirmed by elemental analysis at different stages of preparation of catalyst.

3.3. Thermal stability of the catalyst

The thermal stability of 6-OPDA–Ni(II) and the support was studied using TG analysis and both were found to be stable upto 150 °C (Fig. 2). Initial weight loss might be due to moisture content whereas degradation of the polymer results in weight loss at high temperature. It was concluded that the catalyst could be used safely upto 130 °C.

3.4. Spectroscopic studies

The UV–vis reflectance spectra of 6-OPDA–Ni(II) (Fig. 3) gave a peak at 350 nm, which might be due to d–d transition of Ni(II). Its homogeneous counterpart also shows a peak at 410 nm, which shows that Ni is present in the +2 oxidation state in both the cases. Various IR frequencies were assigned as $\nu(N–H) = 3442 \, cm^{-1}$, $\nu(C=N) \, 1602 \, cm^{-1}$, $\nu(Ni–N) = 208 \, cm^{-1}$ and $\nu(Ni–Cl) = 247 \, cm^{-1}$ which confirm the formation of the metal complex on the surface of the polymer (Figs. 4 and 5). The g value obtained from the ESR study was found to be
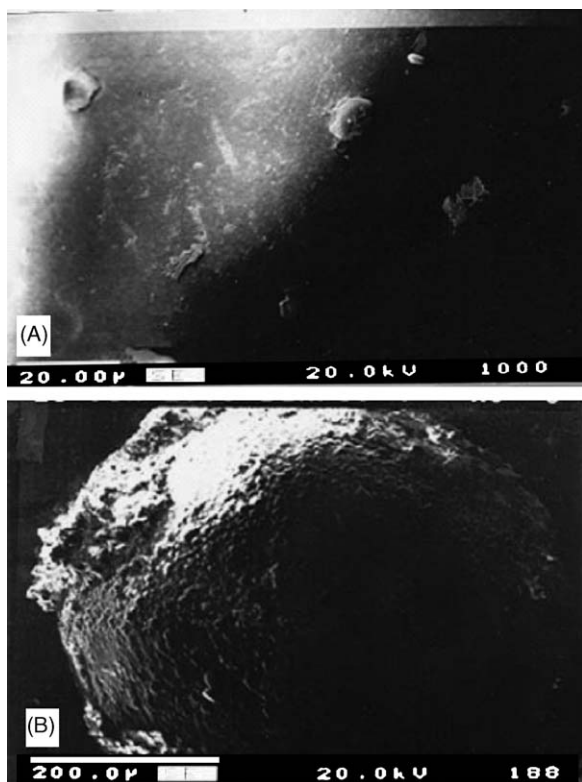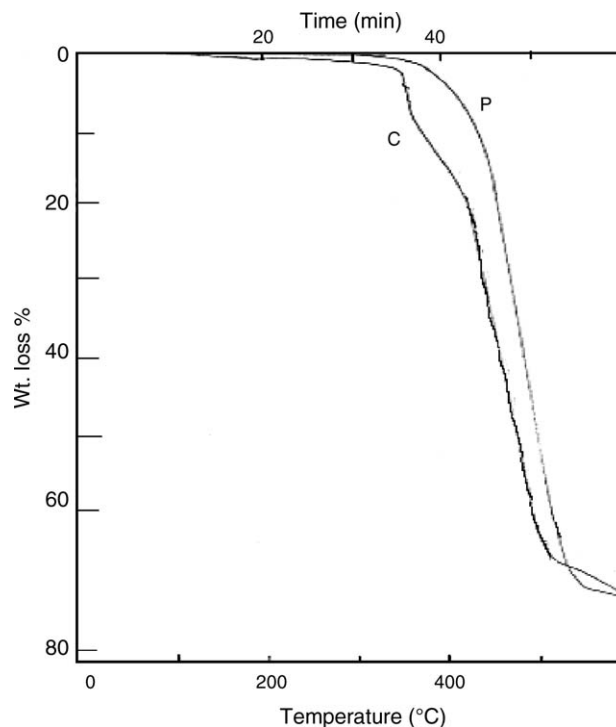

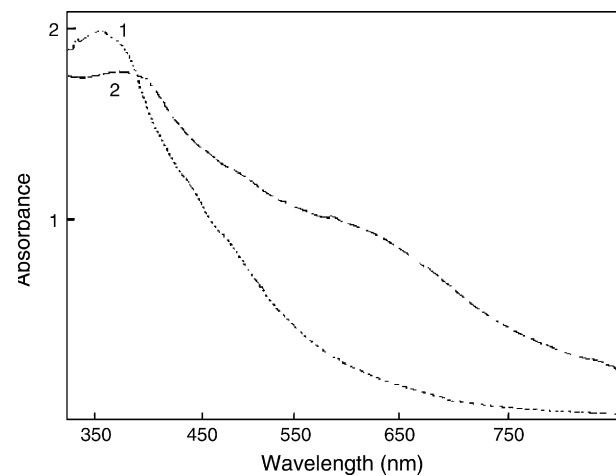Fig. 2. TGA curves for the polymer support (P) and the catalyst (C).

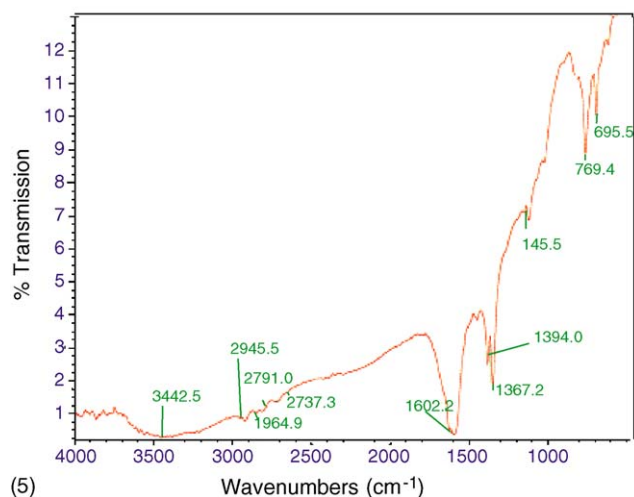Fig. 3. UV–vis spectrum of 6-OPDA–NiCl$_2$ (1) with support and (2) without support.

2.0054, which shows Ni is present in low spin +2 oxidation state (Fig. 6).

Based on the spectroscopic evidence, the following structure of the catalyst is proposed:

Fig. 1. Scanning electron micrograph of (A) polymer support and (B) catalyst on the support.
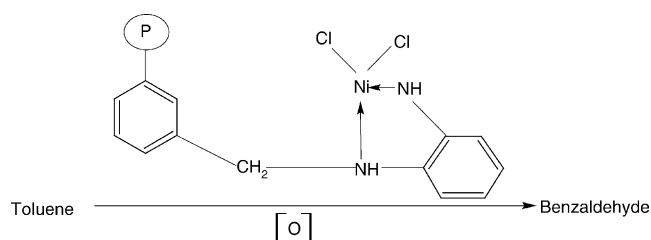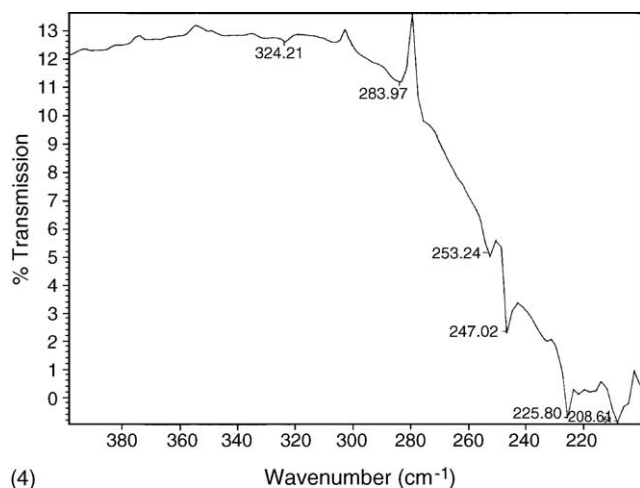
Figs. 4 and 5. FTIR Spectrum of 6-OPDA-Ni(II) catalyst.

3.5. Oxidation of toluene

The influence of the various parameters on the rate of oxidation of toluene by using supported catalyst was studied (Table 3)

and the same study was also carried out by using homogeneous unbound metal complex (Table 4). A very small change was found in oxygen uptake indicating lower catalytic activity in the homogeneous system than that at support on the polymer.

3.6. Effect of toluene concentration

The effect of toluene concentration on the rate of oxidation was determined in the range of 6.72×10^{-3} to 12.8×10^{-3} mol L^{-1} at a constant catalyst concentration of 2.59×10^{-5} mol L^{-1} at 35 °C and 1 atm pressure (Table 4). A linear increase in rate of reaction was found with increase in catalyst concentration, which indicates that there is no dimerisation of metal complex in the range of studied and mass transfer effect could be neglected. It was observed that the rate of oxidation varies linearly with substrate concentration. The order of reaction calculated from the linear plot of log(initial rate) versus log[toluene] was fond to be fractional (plot was not given). A linear plot of 1/rate versus 1/[toluene] for the supported catalyst (Fig. 7) shows that the rate of oxidation of toluene, R, is related to the concentration of toluene [S], by the relationship $1/[R] = a \cdot 1/[S] + b$, where a and b are slope and intercept of the linear plot, respectively.

3.7. Effect of catalyst concentration

The influence of the concentration of the catalyst on the rate of oxidation of toluene was investigated over the range of 1.17×10^{-5} to 2.35×10^{-5} mol L^{-1} of Ni(II) at 35 °C, 1 atm pressure and a substrate concentration 9.42×10^{-3} mol L^{-1} (Tables 3 and 4). The order of reaction obtained from the plot of log(initial rate) versus log[catalyst] was found to be fractional with respect to catalyst concentration. The reason might be due to the non-availability of catalytic sites or due to the lack of swelling of the catalyst and stearic hindrance because of complex nature of catalyst.
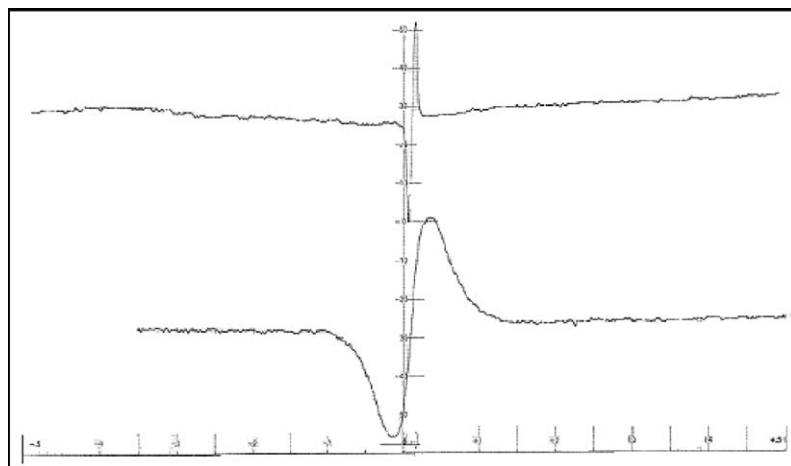

Fig. 6. ESR spectrum of 6-OPDA-Ni(II) catalyst.

Table 3
Summary of the kinetics of oxidation of toluene using polymer supported Ni(II) complex

[Catalyst] (mol L^{-1}) × 10^{-5}	[Toluene] (mol L^{-1}) × 10^{-3}	Temperature (°C)	Rate (mL min^{-1})	Energy of activation E_{act} (kJ mol^{-1})	Entropy of activation (EU)	Order of reaction
2.40	9.42	35	0.037			0.48
2.58			0.048			
2.80			0.054			
3.15			0.059			
1.57	9.80	30	0.036			
		35	0.051	40	−169.0	
		40	0.065			
		45	0.071			
2.58	6.72	35	0.025			0.38
	9.80		0.050			
	11.5		0.071			
	12.8		0.098			

Volume of methanol = 20 mL; pressure = 1 atm.

Table 4
Summary of the kinetics of toluene oxidation using homogeneous 6-OPDA–Ni(II) complex at 35 °C and 1 atm pressure

Temperature (°C)	[Ni(II)] (mol L^{-1}) × 10^{-5}	[Toluene] (mol L^{-1}) × 10^{-3}	Rate of reaction (mL min^{-1})	Energy of activation (kJ mol^{-1})	Entropy of activation (EU)	Order of reaction
30	2.59	9.80	0.11	72.2	−110	
35			0.14			
40			0.22			
45			0.30			
35	2.59	9.80	0.13			0.55
	2.92		0.19			
	3.20		0.25			
	2.12		0.32			
35	2.59	6.72	0.17			0.48
		9.80	0.20			
		11.5	0.28			
		12.8	0.35			

3.8. Effect of temperature

The kinetics of oxidation of toluene were also studied at various temperatures in the range of 30–45 °C, keeping all the parameters constants and the rate was found to be dependent on temperature. The energy of activation calculated from the Arrhenius plot (Fig. 8) was found to be 40 kJ mol^{-1}.

3.9. Reaction mechanism

The reaction mechanism for oxidation with molecular oxygen by metal ion/complex in homogeneous medium is studied widely and the formation of peroxo and oxo complexes was suggested to be responsible for transfer of oxygen to substrate [20,21]. On the basis of experimental results as well as evidence from literature, a probable mechanism can be suggested.
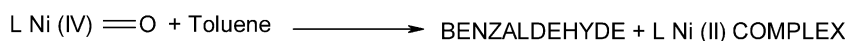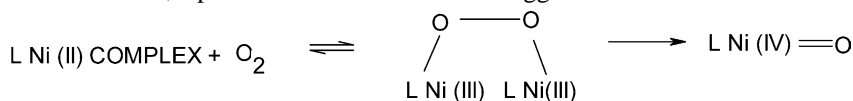
where L is the ligand (O-phenylenediamine). The crrosponding rate equation can be expressed as:

$$R = K[\text{catalyst}][\text{toluene}]$$

where R is initial rate and K is rate constant.

3.10. Life cycle of catalyst

In order to test stability of the polymer supported 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. Results are summarised in Table 5. It was found that maximum rate of reaction was maintained for

L Ni (II) COMPLEX + O$_2$ ⇌ [O—O / L Ni (III) L Ni(III) \] ⟶ L Ni (IV) ═O

L Ni (IV) ═O + Toluene ⟶ BENZALDEHYDE + L Ni (II) COMPLEX

Table 5
Life cycle study of polymer anchored catalyst at 35 °C and 1 atm pressure using 20 mL methanol

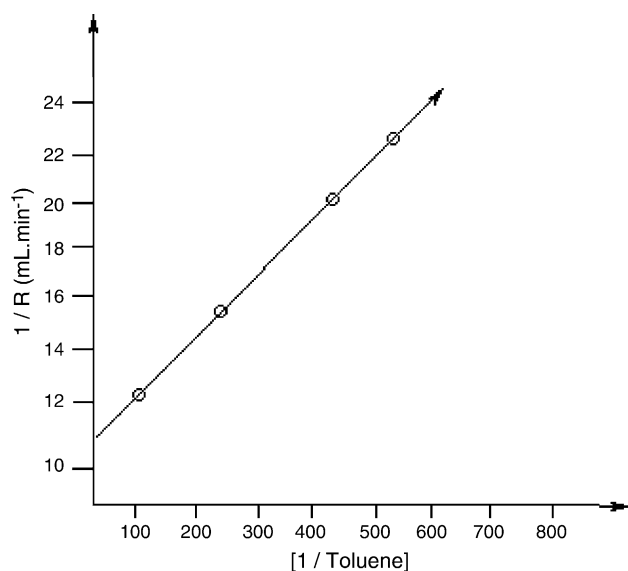| [Ni] (mol L^{-1})× 10^{-5}	[Toluene](mol L^{-1})× 10^{-3}	Time (min)	Rate of reaction (mL min^{-1})	
			Fresh catalyst	Used catalyst
2.58	9.80	90	0.45	0.45
		180	0.45	0.45
		270	0.45	0.42
		360	0.40	0.40

Fig. 7. Plot of 1/rate vs. 1/[tolueue] for the catalyst 6-OPDA-Ni(II).

about 3.5 h for fresh catalyst 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.
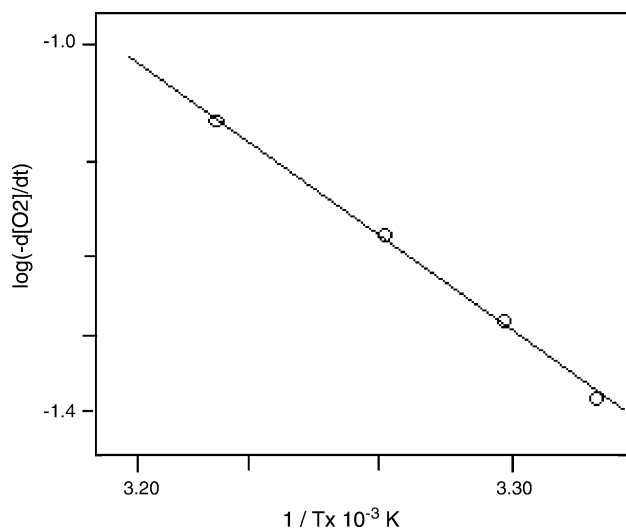
4. Conclusion

The Ni(II) *O*-phenylenediamine complex was successfully heterogenised using the P(S-DVB) copolymer. Elemental analysis, IR, UV–vis, ESR, TGA and SEM confirmed the attachment and formation of the metal complex on the polymer matrix. A probable structure of the catalyst is proposed. This catalyst was found to be active for oxidation of toluene to benzaldehyde. The energy of activation was found to be 40 kJ/mol, which indicates that the reaction is fast. The recycling efficiency of 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 toluene to benzaldehyde than homogeneous counter part. The formation of oxo complex and the transfer of oxygen via this route might be responsible for the reaction.

References

[1] G. Strukul, Catalytic Oxidation with Hydrogen Peroxide Oxidant, Kluwer, Dordrecht, 1992.
[2] F. Quignard, A. Choplin, in: J. Mc Cleverty, A. Mayer, J. Thomas (Eds.), Comprehensive Coordination Chemistry, vol. II, Elsevier Ltd., 2004, pp. 445–470 (Chapter 9).
[3] F. Ciardelli, A. Altomare, G. Conti, G. Arribas, B. Memdez, A. Ismayel, Macromol. Symp. 80 (1994) 29.
[4] S. Schlick, E. Bortel, K. Deyrek, Acta Polym. 47 (1996) 1.
[5] M.M. Miller, D.C. Sherrington, J. Catal. 152 (1995) 368.
[6] L.H. Pignolet, Homogeneous Catalysis with Metal Phosphine Complexes, Pleneum, New York, 1983.
[7] M. Majid Heravi, N. Farhangi, Ind. J. Chem. (B) 433 (B(2)) (2004) 430–431.
[8] L.J. Dong, Z.L. Yun, W.L. Zhou, Monatshefte fuer chemie 135 (1) (2004) 31–34.
[9] L.J. Dong, W. Miao, Z.L. Yun, F.Z. Gang, Catal. Comm. 4 (12) (2003) 647–649.
[10] M. Mohhmmad Hashemi, D. Ghazanfari, M. Akhbari, Monatsheftefuer Chemie 135 (7) (2004) 793–797.
[11] M.K. Dalal, R.N. Ram, Eur. Polym. J. 33 (9) (1997) 1495.
[12] D.R. Patel, M.K. Dalal, R.N. Ram, J. Mol. Catal. A Chem. 109 (1996) 141.
[13] J. John, M.K. Dalal, D.R. Patel, R.N. Ram, J. Macromol. Sci. Pure Appl. Chem. A 34 (3) (1997) 489.
[14] D.T. Gokak, B.V. Kamath, R.N. Ram, J. Appl. Polym. Sci. 35 (1988) 1523.
[15] J.N. Shah, R.N. Ram, J. Mol. Catal. 83 (1993) 67.

Fig. 8. Arrhenius plot for the polymer anchored catalyst.

[16] R.S. Drago, J. Gaul, A. Zombeck, D.K. Staub, J. Am. Chem. Soc. 102 (3) (1980) 1032.

[17] S. Sueto, S. Nishiyama, S. Tsuruya, M. Masai, J. Chem. Soc. Faraday Trans. 93 (4) (1997) 659.

[18] P. Sarkar, P.K. Pania, S.K. Majumdar, J. Ind. Chem. Soc. 65 (1988) 117.

[19] A.S. Aranjo, V.J. Fernandes Jr., A.S. Arujo, React. Kinet. Catal. Left 67 (1) (1999) 43–48.

[20] M.M. Taquikhan, Ch. Shreelatha, S.A. Mirza, G. Ramcharaiah, S.H.R. Abdi, Inorg. Chim. Acta 154 (1988) 103.

[21] J. John, M.K. Dalal, R.N. Ram, Stud. Surf. Sci. Catal. 110 (1997) 1165.