

***LIST OF PUBLICATIONS***

1. **Dilip R. Patel**, M. K. Dalal and R. N. Ram\*  
“ Preparation, characterization and catalytic activity of polymer supported Ru(III) complexes.”  
Journal of molecular catalysis A: Chemical 109(1996)141-148.
2. Jacob John, **Dilip R. Patel**, M. K. Dalal and R. N. Ram\*  
“ Preparation, properties and catalytic application of polymer bound Ru(III) complexes.”  
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3. **Dilip R. Patel** and R. N. Ram\*  
“ Hydrogenation of nitrobenzene using polymer anchored Pd(II) complexes as catalyst ”.  
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4. **Dilip R. Patel**, M. K. Dalal and R. N. Ram\*  
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## Hydrogenation of nitrobenzene using polymer anchored Pd(II) complexes as catalyst

Dilip R. Patel, R.N. Ram \*

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Vadodra 390 002, India

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### Abstract

Polymer anchored metal complex catalysts of Pd(II) were synthesized using styrene-divinyl benzene (PS-DVB) co-polymer of two different crosslinking (2% and 8%) by sequential attachment of chloromethyl group, bidentate ligand and treating the functionalized polymer with the metal chloride solution. The supports and the catalysts were characterized using conventional techniques as well as the spectroscopic methods such as UV-Vis reflectance, IR and DTA-TG analysis. Other physico-chemical properties such as bulk density, moisture content, surface area by BET method and swelling of the catalysts in different solvents have also been studied. The morphology of the catalysts was seen using scanning electron microscope. A probable structure of the catalyst formed on polymer matrix was proposed on the basis of the above studies. The synthesized catalysts were tested for their catalytic activity for the hydrogenation of nitrobenzene as a model reaction. The influence on the rate of various factors such as the amount of catalysts, concentration of the substrate and temperature of the system has been studied. The recycling efficiency of catalysts has also been studied. © 1997 Elsevier Science B.V.

**Keywords:** Styrene-divinyl benzene, Chloromethylation, Hydrogenation, Polymer support, Catalysts.

### 1. Introduction

Transition metal complexes have been used extensively for hydrogenation in homogeneous system probably due to high selectivity under mild operating condition [1-4]. The major disadvantage of the above catalysts is the problem of separation from the reaction system. The difficulties could be avoided if these catalysts were heterogenized on solid supports by covalent bonding. A number of studies have been made while supporting the metal complexes either on inorganic oxides or on polymers and

an enhanced activity was observed [5-7]. The main problem however is the leaching of the metal complexes by using monodentate or nonchelating ligands. Very few papers have been published where bidentate ligands have been used to synthesize the chelated metal complexes on the surface which were found to be coordinatively stable with higher activity [8-11].

An attempt has been made in the present study to synthesize Pd(II) complex of *L*-2-amino butanol containing N and O as donor atoms anchored on poly-styrene-divinylbenzene (PS-DVB) copolymer and to investigate the catalytic activity for hydrogenation of nitrobenzene to aniline which is an intermediate for dyes and

\* Corresponding author. Fax: +91-265-328422.

drugs.

## 2. Experimental

### 2.1. Materials and equipment

All chemicals used were purified as described earlier [12]. 2-amino butanol was distilled before use.  $\text{PdCl}_2$  (obtained from Sisco Research Laboratories, Bombay) was used without purification. 2% Styrene-divinyl benzene (XAD-2) copolymer was obtained from fluke AG and chloromethylated (PS-DVB) 8% cross linked (chlorine content 17.5%) was obtained as a gift sample from Ion Exchange (India) Bombay. Ultraviolet spectra of the anchored catalysts were recorded on a Shimadzu W-240 instrument using  $\text{BaSO}_4$  as standard. IR spectra were recorded on a Beckmann IR 4220. Elemental analyses of the polymers as well as the catalysts were carried out in our laboratory using Coleman analyzer. Surface area of the catalysts was determined by BET method using Carlo-Erba 1800 at liquid nitrogen temperature. The Thermal behavior of the catalysts was studied by DTA-TG analyzer (Shimadzu DT30). Scanning electron micrographs were recorded on a jeol JSM T-300 to investigate the morphology of the catalyst. Swelling studies of the catalysts were carried out using polar as well as non-polar solvents at a constant temperature.

### 2.2. Synthesis of the catalysts

2% cross linked XAD-2 was purified before use and chloromethylated by HCl, HCHO and 1,2 dichloroethane. The detailed procedure for purification as well as for chloromethylation is described earlier [13]. The chloride ion estimated was found to be 6% [14]. In order to enhance the activity of chloromethylated polymer beads, it was treated with NaI solution prepared in acetone dioxane mixture (3:1), purified by Soxhlet extractor using acetone as a solvent and dried for 10 h at 80°C [15]. In order

to anchor the ligand, 25 g of purified beads were refluxed with 10 ml of 2-amino butanol and 180 ml THF used as a solvent for 48 h. The loading of 2-aminobutanol on polymer matrix was confirmed by estimating nitrogen using Coleman analyzer. The results are given in Table 3.

25 g of liganded polymer was kept in contact with 80 ml ethanol for 30 min for swelling purpose. To this 20 ml of ethanolic solution of  $\text{PdCl}_2$  (0.25% w/v) was added through an addition funnel slowly for a period of 30 min. The reaction mixture was initially refluxed for 6 h and then was allowed to stir intermittently for seven days at room temperature. The beads were finally filtered, washed with ethanol, dried in vacuum at 70°C for 24 h and stored in vacuum desiccator. Palladium content was estimated by refluxing a fixed amount of polymer anchored catalyst with conc. HCl (AR) followed by spectrophotometric method using nitroso-R-Salt. The detailed method of analysis is given elsewhere [16].

### 2.3. Nomenclature

The catalysts are designated by the general formula NPML where N: Percent cross link, P: Copolymer of Styrene divinyl benzene, M: Metal atom and L: Ligand.

Catalyst X = 2PPd(II)2AB, Catalyst Y

= 8PPd(II)2AB.

### 2.4. Hydrogenation reaction

The hydrogenation reaction was carried out at atmospheric pressure in a magnetically stirred glass reactor using methanol as a solvent. The progress of the reaction was followed by measuring the uptake of hydrogen gas as a function of the reaction time at constant pressure using a glass manometer. The detailed experimental set up and procedure are described elsewhere [17].

### 3. Results and discussion

#### 3.1. Characterization of the catalysts

Physical properties of the supports and catalysts are given in Table 1. A decrease in surface area was observed after functionalization as also after loading the metal ions which might be due to the blocking of the Pores of the polymer support as well as the steric hindrance. Swelling studies of the catalysts were carried out using both polar and non-polar solvents. The polar

Table 1

Physical properties of the anchored catalysts

Physical properties	Catalyst X	Catalyst Y
Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	0.36 (0.42)	0.08 (0.04)
Surface area ( $\text{m}^2 \text{g}^{-1}$ )NTP	174.17 (330.0)	33.95 (37.37)
Apparent bulk density ( $\text{g cm}^{-3}$ )	0.42	0.47
Moisture content (wt%)	1.32	3.85

Values mentioned in parentheses indicate data for supports.

solvents were found to be good swelling agent.

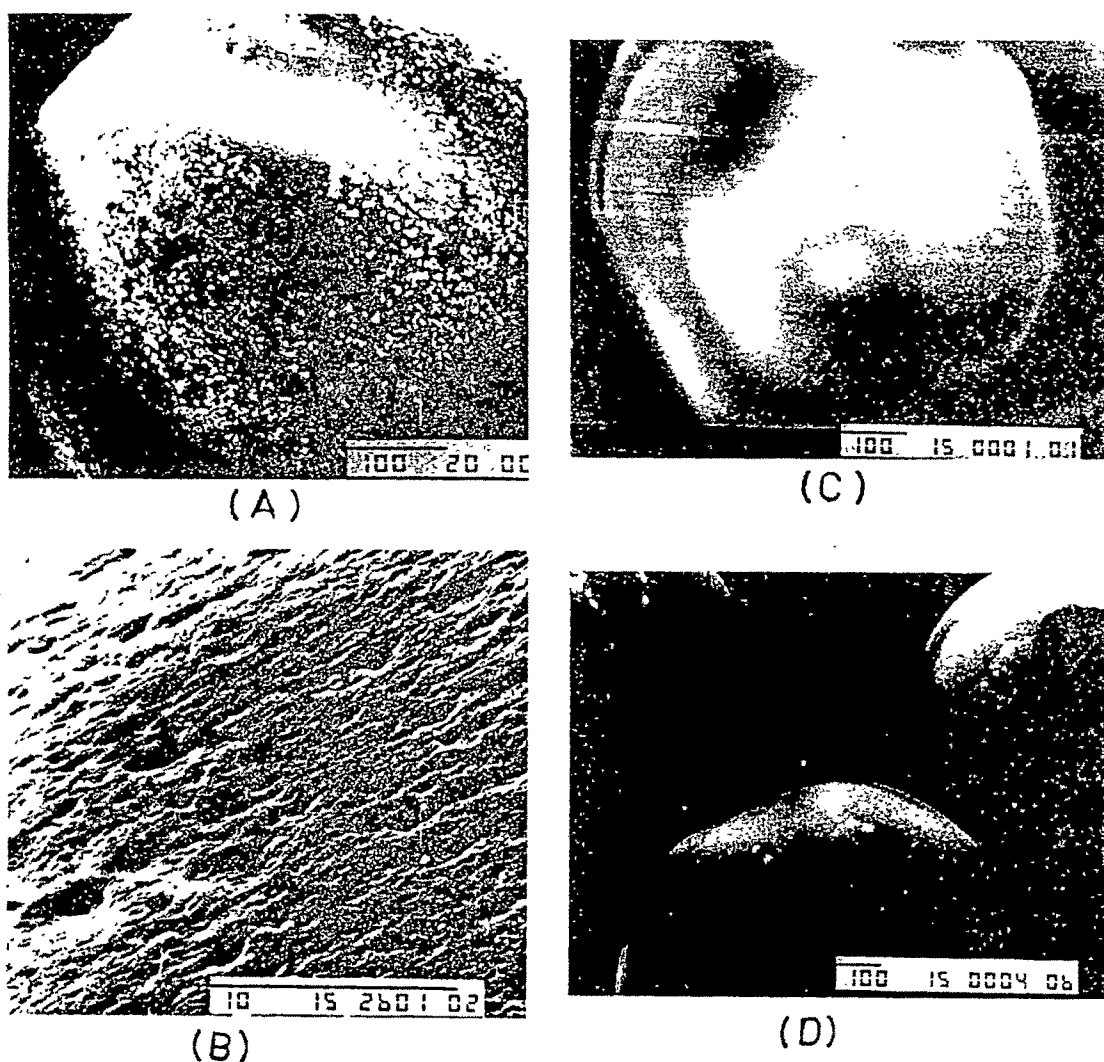


Fig. 1. Scanning electron micrographs of polymer supports and catalysts (A) 2% crosslinked polymer, (B) 8% crosslinked polymer, (C) Catalyst X, (D) Catalyst Y

Table 2  
Swelling studies of polymer anchored catalysts in various solvents

Solvent	Catalyst X (mol%)	Catalyst Y (mol%)
Water	4.12	4.08
Methanol	1.91	1.90
Ethanol	1.45	1.44
Dioxane	1.01	0.81
<i>N,N'</i> -dimethyl formamide	0.88	0.67
Acetone	1.05	0.93
Tetrahydrofuran	0.92	0.85
Benzene	0.93	0.75
Cyclohexane	0.70	0.54
<i>n</i> -heptane	0.44	0.38

Table 3  
Elemental analysis of catalysts X and Y in (wt%)

Catalyst	P	Q				R				Pd (g/g) × 10 <sup>4</sup>
	C	H	Cl	C	H	Cl	C	H	Cl	N
X	80.94	7.46	6.08	68.82	6.21	2.38	5.17	3.41	1.25	5.0
Y	72.95	5.93	1.58	8.87	1.93	6.85	6.37	0.93	2.62	7.5

P: After chloromethylation, Q: After ligand introduction, R: After complexation

This might be due to the hydrogen bonding between the solvents and the catalysts. The results are shown in Table 2.

Elemental analyses of chloromethylated polymer, liganded polymer and anchored catalysts show the anchoring of the metal ions on to the functionalized polymer (Table 3). The anchoring of the metal complex on the polymer was further confirmed by IR and ultra-violet reflectance spectroscopy. The various IR frequencies for these catalysts are given below.

A broad peak at 372 nm for catalyst X and 376 nm for catalyst Y obtained by UV-Vis reflectance spectroscopy is indicative of the d-d transition of Pd(II). A change in morphology of the catalysts from the support is observed by the use of scanning electron microscope which indicates that the ligand as well as the metal ions both are attached to the polymer matrix. The micrographs are given in Fig. 1.

The DTA-TG analyses show that the catalysts and supports both are stable up to 120°C. The results are given for catalyst Y (Fig. 2). However a weight loss was observed around

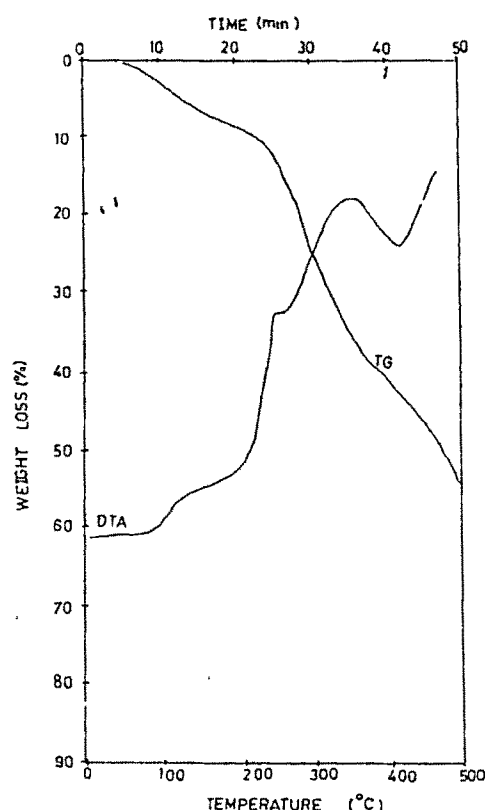


Fig. 2. DTA-TGA curves for catalyst Y.

100°C. This could be due to the moisture content. After 120°C the weight loss might be due to degradation of the polymer. This reveals that the catalysts could be used safely up to 100°C.

Based on the spectroscopic studies probable structure of the synthesized catalyst could be proposed as shown in Scheme 1.

### 3.2. Hydrogenation reaction

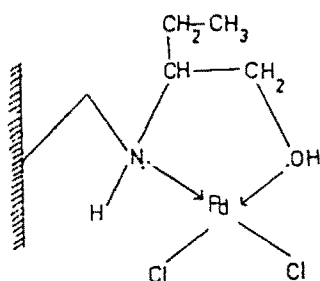
The kinetics of hydrogenation of nitrobenzene was investigated for both catalysts X and Y. The rate of hydrogenation reaction was calculated from the slope of the volume of H<sub>2</sub> uptake as a function of time. A summary of the results are given in Tables 4 and 5. The influ-

\* Table 3

Elemental analysis of catalysts X and Y in (wt%).

Catalyst	P			Q			R			Pd (g/g) × 10 <sup>4</sup>
	C	H	Cl	C	H	N	C	H	Cl	
X	80.94	7.46	6.00	84.68	8.26	1.23	85.11	7.34	1.12	5.50
Y	72.95	5.93	1.11	85.88	7.19	1.36	85.63	7.07	1.25	5.25

P: After chloromethylation, Q: After ligand introduction, R: After complexation



Scheme 1

studied. The recycling efficiency has also been seen.

### 3.3. Effect of nitrobenzene concentration

The concentration of nitrobenzene for catalyst X and Y was varied from  $4.83 \times 10^{-3}$  to  $19.4 \times 10^{-3}$  mol/l at  $35^\circ\text{C}$  and 1 atm.  $\text{H}_2$  pressure using a fixed amount of the catalyst i.e.  $2.58 \times 10^{-5}$  mol/l Pd(II) content for both the catalysts. On increasing the concentration of

ence of various parameters on the rate was

Table 4  
Summary of the kinetics of hydrogenation of nitrobenzene for catalyst X in methanol at atmospheric pressure

Concentration of catalyst in mol/l $\times 10^5$	[nitrobenzene] mol/l $\times 10^3$	Temperature ( $^\circ\text{C}$ )	Volume of methanol (ml)	Rate of reaction (ml min $^{-1}$ )
2.58	9.72	35	20	0.136
3.23				0.142
3.87				0.170
4.52				0.175
2.58	4.83	35	20	0.100
	9.72			0.136
	14.5			0.141
	19.4			0.144
2.58	9.72	30	20	0.090
		35		0.136
		40		0.150
		45		0.157

Table 5  
Summary of the kinetics of hydrogenation of nitrobenzene for Catalyst Y in methanol at atmospheric pressure

Concentration of catalyst in mol/l $\times 10^5$	[nitrobenzene] mol/l $\times 10^3$	Temperature ( $^\circ\text{C}$ )	Volume of methanol (ml)	Rate of reaction (ml min $^{-1}$ )
2.58	9.72	35	20	0.153
3.23				0.177
3.87				0.200
4.52				0.220
2.58	4.83	35	20	0.141
	9.72			0.153
	14.5			0.172
	19.4			0.194
2.58	9.72	30	20	0.145
		35		0.153
		40		0.182
		45		0.203

nitrobenzene the initial rate was found to increase for both the catalysts (Table 4). The order of reaction calculated from the slope of the linear plot (plots are not given) of the log (initial rate) vs. log [nitrobenzene] was found to be 0.10 and 0.32 for catalyst X and Y respectively, which indicates that the reaction is of fractional order with respect to the catalyst.

### 3.4. Effect of the amount of the catalyst

The influence of the amount of catalyst on the rate of reaction was studied over the range of  $2.58 \times 10^{-5}$  to  $4.52 \times 10^{-5}$  mol/l Pd(II) present on the surface of catalyst at constant nitrobenzene concentration of  $9.72 \times 10^{-3}$  mol/l at 35°C keeping 1 atm.  $H_2$  pressure. On increasing the quantity of the catalyst, an enhancement in the rate was observed (Tables 4 and 5). The slope of the linear plot of log (initial rate) against log (amount of the catalyst) was found to be 0.541 and 0.666 for catalysts X and Y respectively which shows that the reaction follows fractional order. Although the reaction was carried out in a chemically controlled regime choosing a suitable swelling agent, the observed fractional order might be due to the inaccessibility of the catalytic sites and steric hindrance.

### 3.5. Effect of temperature

The rate of hydrogenation of nitrobenzene was carried out using both the polymer anchored Palladium complexes at various temperatures in the range 30–45°C. The results are summarized in Tables 4 and 5. The rate of the reaction was found to be dependent on the temperature of the system. The energy of activation calculated from the slope of the straight line plot of log(initial rate) vs.  $1/T$  (Fig. 3) was found to be 1.83 and 4.02 kcal/mol respectively for catalysts X and Y. Thus lower the energy of activation indicates the higher activity of the catalyst. The values for the entropy of activation calculated from the kinetic data were

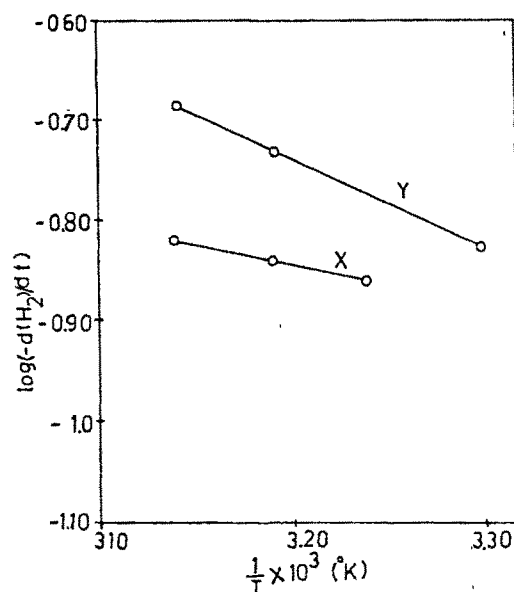


Fig. 3 Plot of  $\log(-d[H_2]/dt)$  against  $1/T$

found to be  $-66.75$  and  $-59.41$  eu respectively for catalyst X and Y. The decrease in entropy corresponds to a considerable loss of freedom due to fixation of the catalyst molecule on the polymer matrix [18].

From Tables 4 and 5, it is seen that the catalytic activity of catalyst Y is higher than catalyst X though the anchoring of the metal ions were found to be less. This may be due to the dispersion of the metal ions on the surface which is responsible for higher catalytic activity. Similar results have also been reported by Huang and He [19] in the hydrogenation of olefins by polymer supported colloidal Palladium catalysts. The dispersion of the metal ions can also be seen on the basis of SEM (Fig. 1).

### 3.6. Recycling efficiency of the supported catalysts

The polymer anchored catalysts can lose its activity by loss of Palladium which is brought about by leaching of the metal complex from the support. To check whether the above phenomenon occurs in this system or not, the recy-

Table 6

Recycling efficiency of catalysts X and Y for hydrogenation of nitrobenzene at 35°C and 20 ml methanol at 1 atm  $H_2$  pressure. Concentration of catalyst:  $2.58 \times 10^{-5}$  mol/l. Concentration of nitrobenzene:  $9.72 \times 10^{-3}$  mol/l. Total time for reaction, 10 h

Time (min)	Rate of reaction ( $ml\ min^{-1}$ )
Catalyst X	
60 (60)	0.136 (0.126)
125 (120)	0.134 (0.104)
195 (185)	0.133 (0.093)
250 (255)	0.076 (0.083)
Catalyst Y	
60 (60)	0.153 (0.153)
120 (125)	0.153 (0.153)
185 (185)	0.151 (0.150)
245 (250)	0.143 (0.141)

Values mentioned in parentheses indicate data for used catalyst.

clung efficiency of the catalysts was carried out by doing some experiments over a period of 10 h. A known quantity of nitrobenzene was injected successively and the rate of reaction was measured each time. The duration between the two introduction was the time required to complete hydrogenation of the nitrobenzene plus 30 min. The results are given in Table 6. It was observed that the rate decreases in case of catalyst X whereas it remains almost constant in case of catalyst Y. The decrease in rate might be due to loss of metal ions from the surface in the reaction system. The loss of the metal ions was found to be more in case of catalyst X. (i.e., from  $5.50 \times 10^{-5}$  g to  $4.25 \times 10^{-5}$  g in one cycle). On the basis of the above results, it could be concluded that 8% cross-linked catalyst has higher stability than 2% cross-linked polymer supported catalyst, thereby a higher catalytic activity. The dispersion as well as the distribution of the metal ions may be higher at 8% of polymer due to its higher hardness (Table 6) indicating thereby an enhanced catalytic activity.

#### 4. Conclusion

Polymer supported metal complex catalysts synthesized using 2-amino butanol as ligand

were found to be active for hydrogenation of nitrobenzene to aniline. The catalysts were observed to be stable  $\sim 100^\circ\text{C}$  on the basis of DTA-TG analyses. A probable structure of the catalyst has been suggested by the use of the modern techniques. The entropy of activation was calculated using the rate data. The catalytic activity of catalyst Y was found to be higher than the catalyst X. This could be due to dispersion of more metal ions on the surface of the polymer. The recycling efficiency of the catalysts indicates that the rate is almost constant up to three cycles for both the catalysts.

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OXIDATION OF TOLUENE USING POLYMER SUPPORTED  
PALLADIUM (II) COMPLEX AS CATALYST

Dilip R.Patel, Mahesh K.Dalal and R.N.Ram\*

Chemistry Department, Faculty of Science,  
M.S.University of Baroda, Baroda -390002. India.

ABSTRACT :

Polymer supported Palladium(II) complex catalyst was synthesised using chloromethylated styrene-divinyl benzene copolymer as a support by sequential attachment of glycine and a metal salt solution. It was characterized using various methods such as IR, UV-Vis, ESR, DTA-TGA, SEM and surface area measurement. Swelling studies, moisture content and bulk density have also been investigated. The catalytic activity of the catalyst was tested for the oxidation of toluene. The effect on it of various parameters has been seen. The recycling efficiency has also been studied.

INTRODUCTION

Transition metal complexes, zeolites, biomimetic catalysts have been widely used for various oxidation reactions of industrial and environmental importance [1-3]. However, few heterogenized polymeric catalysts have also been applied for such purpose. Mild condition oxidation catalyzed by polymer anchored complexes is attractive because of reusability and selectivity of such catalysts. Earlier we have reported synthesis of cobalt and ruthenium-glycine complex catalysts and their application in olefin hydrogenation [4-5]. In present study, we report synthesis of the palladium-glycine complex on the surface of the styrene-divinylbenzene copolymer by sequential attachment of glycine and

metal ions and investigation of oxidation of toluene to benzaldehyde which has been widely used as fine chemicals as well as an intermediate in dyes and drugs.

#### EXPERIMENTAL

*Materials and equipment* : 8% cross-linked chloromethylated styrene-divinyl benzene copolymer donated by Ion exchange (India) Ltd., was washed with mixture of water and dioxane (1:1), dioxane and HCl (10%), methanol and finally with distilled water. All the chemicals and solvents were purified as described earlier [6].  $\text{PdCl}_2$  supplied by SRL, Bombay was used as such. Elemental analysis was carried out in our laboratory using Coleman analyser unit. UV-Visible reflectance spectrum of the solid sample was recorded on Shimadzu UV-240 and infrared spectrum on Beckmann IR 4220. ESR spectrum was scanned on Breaker ESP-300K band spectrophotometer. Surface area was determined using Carlo-Erba 1800 and DTA-TGA on Shimadzu DT-30. Scanning electron micrographs were recorded on a Jeol JSM T-300.

*Synthesis of the catalyst* : Chloromethylated polymer beads were treated with NaI solution prepared in acetone-dioxane mixture (3:1). It was purified by the use of soxhlet extractor and refluxed with glycine used as a ligand for 48 h in a mixture of acetone, THF and water (1:1:1). The anchoring of glycine on polymer was confirmed by nitrogen analysis and was found to be 2.00%. 20g functionalized polymer was kept in contact with 80 ml of ethanol for 30 min. in a round bottom flask for swelling purpose. 100 ml ethanolic solution of  $\text{PdCl}_2$  (0.25% W/V) prepared separately was added to the reaction vessel slowly and kept for 7

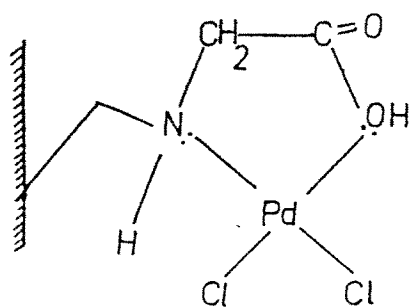
days at room temperature. Finally the beads were filtered, washed with ethanol and dried in vacuum at 70°C. The metal content present on the surface was estimated by refluxing the catalyst (0.2g) with concentrated HCl (A.R.) for 24 h. The concentration was measured by spectrophotometric method using nitroso-R-salt as complexing agent. The procedure in detail is described elsewhere [7].

*Oxidation reaction* : The kinetics of oxidation of toluene was studied at atmospheric pressure by measuring oxygen uptake using a glass manometric apparatus. The detailed procedure and experimental setup are described elsewhere [4,8].

## RESULTS AND DISCUSSION

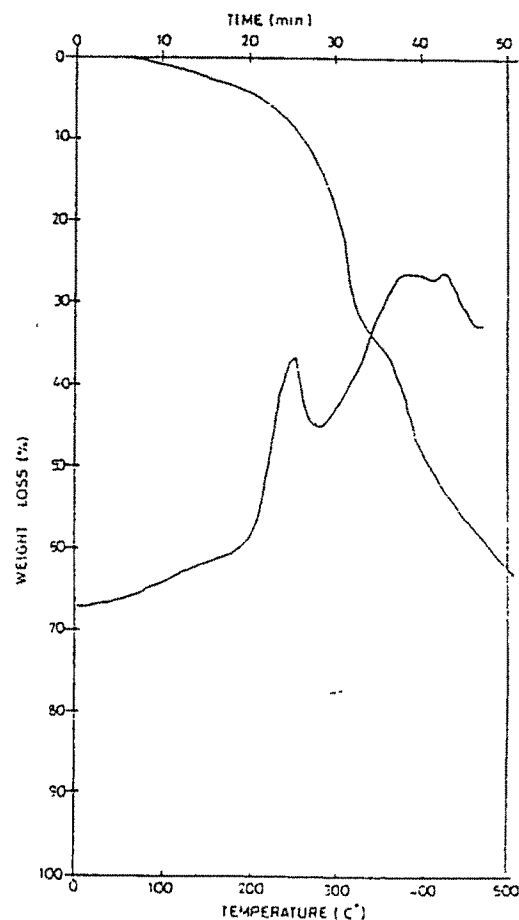
*Characterization of the catalyst* : Physical properties of the catalyst and support are given in Table 1(a). A decrease in surface area was observed after functionalization and anchoring of metal ions which might be due to the blocking of the pores of the polymer support as well as the steric hindrance. Table 1(b) shows the swelling of the catalyst in various solvents. An increase in swelling was observed from non-polar to polar solvents. Water was found to be a good swelling agent but methanol was chosen as a solvent for the reaction system because of good swelling as well as the miscibility of the reacting system. Elemental analyses of the catalyst and the support at different stages indicate the anchoring of the ligand and the metal ions. The results are shown in Table 2. A change in morphology observed by the use of scanning electron micrograph indicate the presence of metal ions and the ligand on the surface of support. DTA curve

indicates a change in thermal stability at 150°C, however a weight loss was observed by the use of TG analysis (Fig.1). The weight loss below 100°C could be due to the moisture content and after that it might be due to degradation of the polymer. On the basis of this it could be inferred that the catalyst could be used below 100°C safely. The UV-visible reflectance spectra of the polymer bound palladium complex gave broad peak at 372 nm, which may be due to d-d transitions of Pd(II). The inactive ESR spectrum of the palladium complex indicates that Pd is present in +2 oxidation state. The mode of anchoring of metal ion on the polymer matrix was also confirmed by Infrared spectra. The various IR frequencies obtained at 232  $\text{cm}^{-1}$  for Pd-Cl, 286  $\text{cm}^{-1}$  for Pd-O, 530  $\text{cm}^{-1}$  for Pd-N and 3400  $\text{cm}^{-1}$  for N-H stretching are indicative of the mode of anchoring of the metal ions on the surface of the polymer. Based on the spectroscopic studies a probable structure of the catalyst has been suggested (scheme 1).



(Scheme 1.)

Fig.1 : DTA-TGA curves  
of the supported catalyst



*Oxidation reaction* : In order to investigate the catalytic activity of the prepared catalyst, the oxidation of toluene was chosen as a model reaction. The influence on the rate of various parameters such as the temperature, amount of the catalyst and the concentration of the substrate was studied. The results are given in Table 3.

*Effect of toluene concentration* : The reaction was carried out by varying the concentration of toluene from  $4.31 \times 10^{-3}$  M to  $17.2 \times 10^{-3}$  M at  $35^{\circ}\text{C}$  and 1 atm  $\text{O}_2$  pressure using a fixed amount of the catalyst i.e.  $6.25 \times 10^{-5}$ g of Pd present on the surface. The rate was found to increase with an increase in the concentration of toluene (Table 3). The order of reaction calculated from the slope of the linear plot of  $\log(\text{initial rate})$  Vs  $\log[\text{toluene}]$  was found to be 0.357 which is indicative of the fractional order.

*Effect of catalyst concentration* : The rate of the oxidation was studied, by varying the amount of catalyst from  $6.25 \times 10^{-5}$ g to  $10.93 \times 10^{-5}$ g of Pd(II) at  $35^{\circ}\text{C}$  and 1 atm pressure with a constant substrate concentration of  $8.62 \times 10^{-3}$ M and an increase in the rate was observed (Table 3). The order of reaction calculated from the linear plot of  $\log(\text{reaction rate})$  Vs  $\log[\text{catalyst}]$  was found to be 0.571 with respect to catalyst concentration. Although the reaction was carried out in a chemically controlled regime choosing a suitable swelling agent, the observed fractional order might be due to the inaccessibility of the catalytic sites and steric hindrance.

*Effect of Temperature* : The effect of temperature on the rate of oxidation was studied over a range of 30-45°C at a catalyst concentration of  $6.25 \times 10^{-5}$ g of Pd, substrate concentration of  $8.62 \times 10^{-3}$ M and 1 atm. pressure. The rate of reaction was found to be dependent on temperature. The energy of activation calculated from the slope of the plot of log (initial rate) against  $1/T$  (Fig.2) was found to be 8.6 Kcal/mole. On the basis of rate and energy of activation, the entropy of activation was calculated by the use of the following equation.

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

The value was found to be -39.5 eu. This indicates the loss of freedom due to catalyst molecules on the polymer matrix.

*Influence of solvents* : The study of the kinetics of the oxidation of toluene was investigated by the use of four different solvents and an enhanced activity was observed as the polarity of

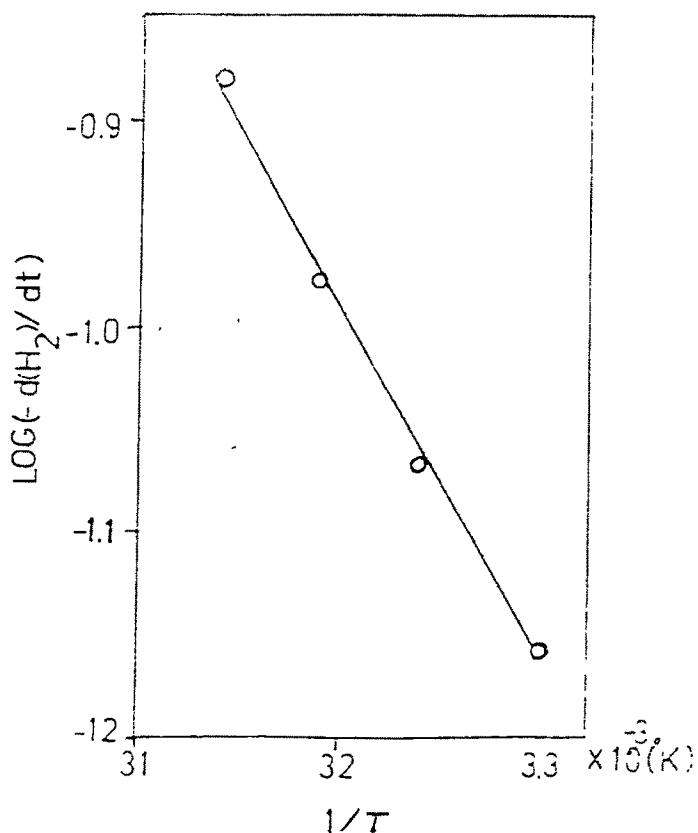


Fig.2 :  
Arrhenious  
plot of the  
supported  
catalyst.

the solvent increased. This might be due to increased swelling of the catalyst and hence the availability of more metal ions on the surface which is responsible to catalyse the reaction.

*Recycling efficiency* : The recycling efficiency of the catalyst was also studied for fresh as well as for the used catalyst. The experiment was carried out for 10 h. In each experiment  $8.62 \times 10^{-3} \text{M}$  (20 ml) of the substrate was injected. The rate of oxidation was measured as a function of time for both used and fresh catalyst. It was observed that the maximum rate of reaction was maintained for 4 cycles, after which the rate decreased slowly (Table 4).

#### CONCLUSION

Polymer supported Pd(II)-glycine complex was found to be stable upto  $150^{\circ}\text{C}$  on the basis of DTA-TG analyses. A change in morphology of the catalyst is indicative of anchoring the ligand as well as the metal ions on the surface of polymer. The catalytic activity of the catalyst was tested for oxidation of toluene under various conditions. The recycling efficiency of the catalyst shows that the catalyst is quite active upto three cycles and after that a decrease in rate was observed.

#### ACKNOWLEDGEMENT

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Table 1(a) Physical properties of the support and catalyst.

Physical property	Catalyst	Support
Pore volume ( $\text{cm}^3\text{g}^{-1}$ )	0.063	0.04
Surface area ( $\text{m}^2\text{g}^{-1}$ ) NTP	27.00	37.37
Apparent bulk density ( $\text{gcm}^{-3}$ )	0.48	
Moisture content (Wt%)	2.25	

Table 1(b) Swelling studies of the supported catalyst in different solvents.

Solvent	Swelling (mol%)
Water	2.73
Methanol	2.03
Ethanol	1.50
Dioxane	1.15
N-N' Dimethyl formamide	1.00
Acetone	0.91
Tetrahydrofuran	0.90
Benzene	0.74
Cyclohexane	0.44
n-heptane	0.41

Table 2 Elemental analysis of the supported catalyst at different stages of preparation (in wt%).

X			Y			Z			
C	H	Cl	C	H	N	C	H	N	Pd(g/g)
78.38	5.93	17.50	78.50	7.16	2.00	61.35	6.25	1.74	6.25 $\times 10^{-4}$

X : Chloromethylated Polymer; Y : After ligand introduction and

Z : After complexation.

Table 3 Summary of the kinetics of oxidation of toluene for supported catalyst.

Amount of Catalyst on the surface Pd(II) in $\text{g} \times 10^5$	[Toluene] $\text{M} \times 10^3$	Temperature ( $^{\circ}\text{C}$ )	Volume of methanol (ml)	Rate of reaction ( $\text{ml} \cdot \text{min}^{-1}$ )
6.25	8.62	35	20	0.085
7.81				0.125
9.37				0.138
10.93				0.150
6.25	4.31	35	20	0.071
	8.62			0.085
	12.90			0.106
	17.20			0.151
6.25	8.62	30	20	0.069
		35		0.085
		40		0.104
		45		0.131

Table 4 Recycling studies of the supported catalyst at  $35^{\circ}\text{C}$  and 20 ml methanol of 1 atm pressure.

Amount of catalyst :  $6.25 \times 10^{-5} \text{g Pd}$ .  
 Concentration of Toluene :  $8.62 \times 10^{-3} \text{M}$ .  
 Total time for reaction : 10 hours.

Time (min.)	Rate of reaction ( $\text{ml} \cdot \text{min}^{-1}$ )
60	0.061 (0.061)
120	0.061 (0.061)
180	0.061 (0.061)
240	0.056 (0.054)
300	0.051 (0.050)

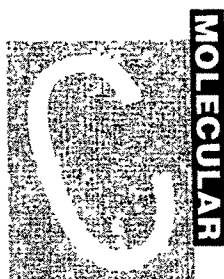
Values mentioned in parentheses indicate data for used catalyst.

Table 5 Effect of solvent on the rate of oxidation of toluene at 1 atm. pressure and  $35^{\circ}\text{C}$  temperature.

Amount of catalyst :  $6.25 \times 10^{-5} \text{g Pd}$ ; [Toluene] :  $8.62 \times 10^{-3} \text{M}$ .

Solvent	Methanol	Ethanol	THF	Benzene
Rate of reaction ( $\text{ml} \cdot \text{min}^{-1}$ )	0.085	0.075	0.055	0.050

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## Preparation characterization and catalytic activity of polymer supported Ru(III) complexes

Dilip R. Patel, Mahesh K. Dalal, R.N. Ram \*

*Chemistry Department, Faculty of Science, M S University of Baroda, Baroda-390 002, India*

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## Preparation characterization and catalytic activity of polymer supported Ru(III) complexes

Dilip R. Patel, Mahesh K. Dalal, R.N. Ram \*

*Chemistry Department, Faculty of Science, M. S. University of Baroda, Baroda-390 002, India*

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### Abstract

Chloromethylated styrene–divinyl benzene copolymer with different types of cross-link was treated with glycine for the introduction of the ligand. The polymer modified with ligand was kept in contact with  $\text{RuCl}_3$  to form the metal complex on the surface of the polymer. The catalysts thus prepared were characterised by techniques such as IR, UV–Vis reflectance spectroscopy and DTA–TG analysis. Other physico-chemical properties such as surface area, moisture content, bulk density and swelling were also studied. The morphology of the catalysts was observed by scanning electron microscope. The catalysts were tested for the hydrogenation of nitrobenzene as a model reaction. The influence of various parameters such as concentration of catalyst and substrate, temperature and different solvents on the rate of the reaction has been studied.

**Keywords:** Poly(styrene–divinyl) benzene, Hydrogenation, Nitrobenzene; Ruthenium; Polymer supported catalyst; Supported catalysts

### 1. Introduction

Transition metal complexes have successfully been used as homogeneous catalysts in a variety of chemical reactions. Immobilization of the homogeneous catalysts on insoluble supports and study of its catalytic behaviour has gained prominence in recent years [1–3]. The main advantage of polymer-supported metal complexes is their easy recovery and reuse after a particular process. The organic polymer support can induce specific control over the catalytic and complexing ability of the ligand [4]. Many researchers have studied and compared the behaviour of ruthenium complex catalysts in homogeneous and heterogenized states mainly be-

cause of their high catalytic activity at mild operating conditions [5–8]. Earlier we have reported the polymer-supported cobalt complex of glycine for hydrogenation [9]. Here we investigate the synthesis of the polymer-supported ruthenium–glycine complex and study the kinetics of the hydrogenation of nitrobenzene to aniline.

### 2. Experimental

#### 2.1. Materials and equipment

Acetone, dioxane, methanol, nitrobenzene, THF were purified by published procedures [10]. Glycine was recrystallised. Aluminium chloride was purified by sublimation.  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$

\* Corresponding author. Tel (+91-265) 328122

(Johnson Matthey, New Jersey) was as used received. XAD-2 was obtained from Fluka AG. Chloromethylated P(S-DVB), 8% cross-linked (chlorine 17.5%), was a gift from Ion Exchange (India) Ltd., Bombay.

UV–Visible reflectance spectra of the prepared catalysts were recorded on a Shimadzu UV-240 instrument using  $\text{BaSO}_4$  as a standard. Elemental analyses were carried out in our laboratory using a Coleman analyser unit. Infrared spectra were recorded on a Beckmann model IR-4220. The surface area was determined using a Carlo Erba model 1800. Scanning electron micrographs were taken on a JEOL JSM T-300 and DTA–TG on Shimadzu DT-30 under a nitrogen atmosphere. Swelling of the catalysts in polar as well as non-polar solvents was examined at constant temperature. The detailed procedure has been described earlier [9].

## 2.2. Synthesis of the catalysts

XAD-2 was washed with distilled water, a water–ethanol mixture (1:1), and finally with ethanol. Any adsorbed material was removed by extracting the polymer in Soxhlet apparatus using ethanol–benzene mixture for a period of 10 h. It was chloromethylated with HCl and HCHO using  $\text{AlCl}_3$  as a catalyst [11]. The above polymer was washed in sequence using a water:dioxane mixture (50:50), water:dioxane + 10% HCl, methanol, and finally distilled water until free chloride ion was removed. The chloride was estimated by a reported method [12] and the content was found to be 6%. In another set of experiments, 8% cross-linked chloromethylated styrene–divinyl benzene was used as the support. The other procedure was the same as described above. In this case the chlorine content was found to be 17.5%.

## 2.3. Introduction of glycine into the polymer support

The chloromethylated P(S-DVB) resin was kept in contact with NaI prepared in acetone–

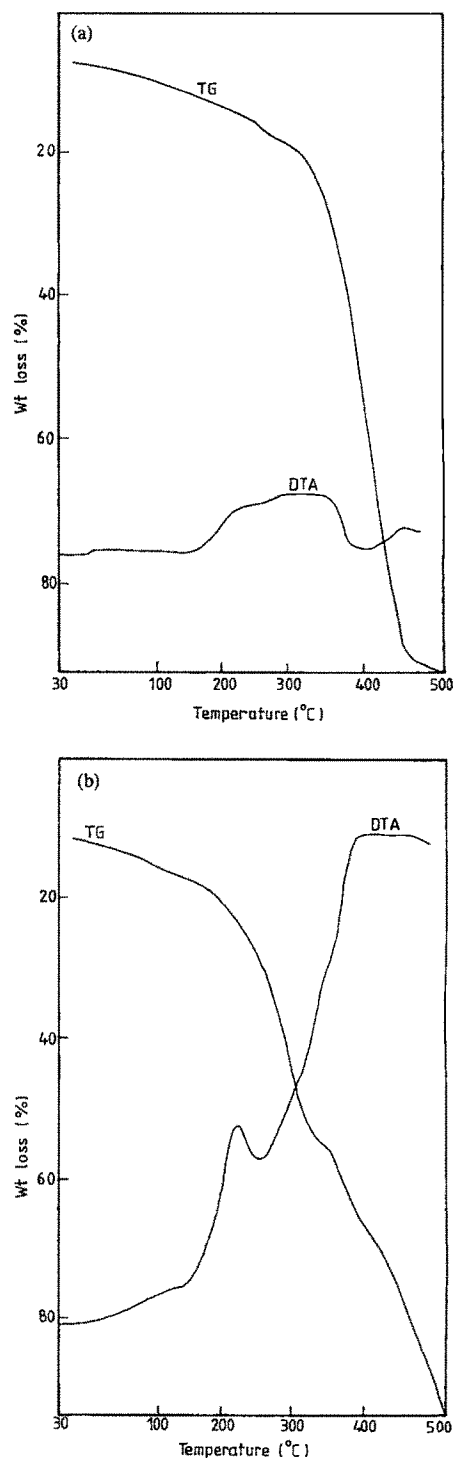


Fig. 1 DTA–TG curves for (a) catalyst A and (b) catalyst B

Table 1  
Physical properties of the supported catalysts

Physical properties	Catalysts	
	A	B
Apparent bulk density ( $\text{g cm}^{-3}$ )	0.38	0.48
Moisture content (wt%)	0.61	2.23
Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	0.46	8.25
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	222.06	40.40

dioxane mixture (3:1), to enhance the activity of the surface, for 4 days. It was purified by Soxhlet extraction using acetone as solvent and dried at 60–70°C for 8 h. The polymer beads thus processed were refluxed with a solution of glycine prepared in acetone–THF–water (1:1:1) for a maximum period of 48 h. and finally the polymer was washed with tetrahydrofuran [13]. The loading of glycine on the polymer was confirmed by the percentage of N which was found to be 1.08% for catalyst A and 2.01% for catalyst B.

#### 2.4. Attachment of metal ion to polymers modified with ligand

The polymers modified with ligand were kept in contact with 100 ml ethanol for 30 min. in a round bottom flask. An ethanolic solution of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (0.25% w/v) was placed in an addition funnel fitted to the reaction vessel. The solution was added to the reaction vessel for a period of 30 min. The reaction was kept for seven days at room temperature. The beads were filtered and washed thoroughly with ethanol. The supported catalysts thus obtained were dried in vacuum at 70°C for 24 h. The metal content was determined by refluxing a

fixed amount of catalyst with conc. HCl (AR) for 3 h and then estimating the metal concentration in a solution by spectrophotometric method after complexation with nitroso-R salt [14].

#### 2.5. Nomenclature

The catalysts thus prepared are designated by the general formula NPML, where, N = percent cross-link, P = copolymer of styrene–divinyl benzene, M = metal atom, L = type of ligand.

The following 2 catalysts were prepared: catalyst A = 2 PRu(III)Gly, catalyst B = 8 PRu(III)Gly.

#### 2.6. Kinetics of hydrogenation

The kinetics of the hydrogenation of nitrobenzene was carried out at atmospheric pressure by measuring hydrogen uptake using a glass manometric apparatus. The detailed procedure and experimental set-up are described elsewhere [15]. The initial rate was calculated from the slope of the tangent of the plot of hydrogen uptake against time.

### 3. Results and discussion

Physical properties of the supported catalysts are given in Table 1. A decrease in surface area was found while immobilizing the ligand and the metal ions on the polymer support. This may be due to blocking of the pores after supporting the ligand and the metal ions. Similar studies have been made by Ram et al. [9] earlier and a decrease in surface area was found.

Table 2  
Elemental analysis and metal loading at different stages of preparation <sup>a</sup> (wt%)

Catalyst	P			Q			R			
	C	H	Cl	C	H	N	C	H	N	Ru (g/g)
A	80.94	7.46	6.00	86.36	6.77	1.08	87.45	6.71	< 1	$4.50 \times 10^{-4}$
B	68.95	5.93	17.50	54.76	5.96	2.01	58.22	5.66	1.82	$6.75 \times 10^{-4}$

<sup>a</sup> P = after chloromethylation; Q = after ligand introduction, R = after complex formation

Elemental analysis at the different stages of preparation of catalysts are shown in Table 2. Attachment of ligand and complex formation of the polymer are confirmed from elemental analysis. The loading of glycine and subsequently that of metal ion is less in the case of catalyst A having low degree of cross-linking than catalyst B having a higher degree of cross-linking. This may be explained in terms of a high degree of functionalisation of the polymer used for the preparation of catalyst B. Swelling of the supported catalyst in various polar and non-polar solvents were carried out (Table 3) and polar solvents were found to be good swelling agents; this may be due to the hygroscopic nature of the polymer used as support [9].

### 3.1. Thermal stability of the catalyst

The polymers used as support were found to be stable up to 135°C. However the supported

Table 3  
Swelling of the supported catalysts (mol-%)

Solvent	Catalyst	
	A	B
water	4.91	3.71
methanol	1.20	1.83
ethanol	1.40	1.35
acetone	0.98	0.96
THF	0.90	0.85
n-heptane	0.67	0.36

catalysts were less stable (Fig. 1). The initial weight loss below 100°C might be due to moisture content and that above 100°C due to degradation of polymer. Therefore, the catalyst could be used safely in the range 80–90°C.

The change in the morphology of the supported catalysts was observed from scanning electron micrographs (Fig. 2). Change in the porous texture and shape of polymer beads has been found after loading the metal complex.

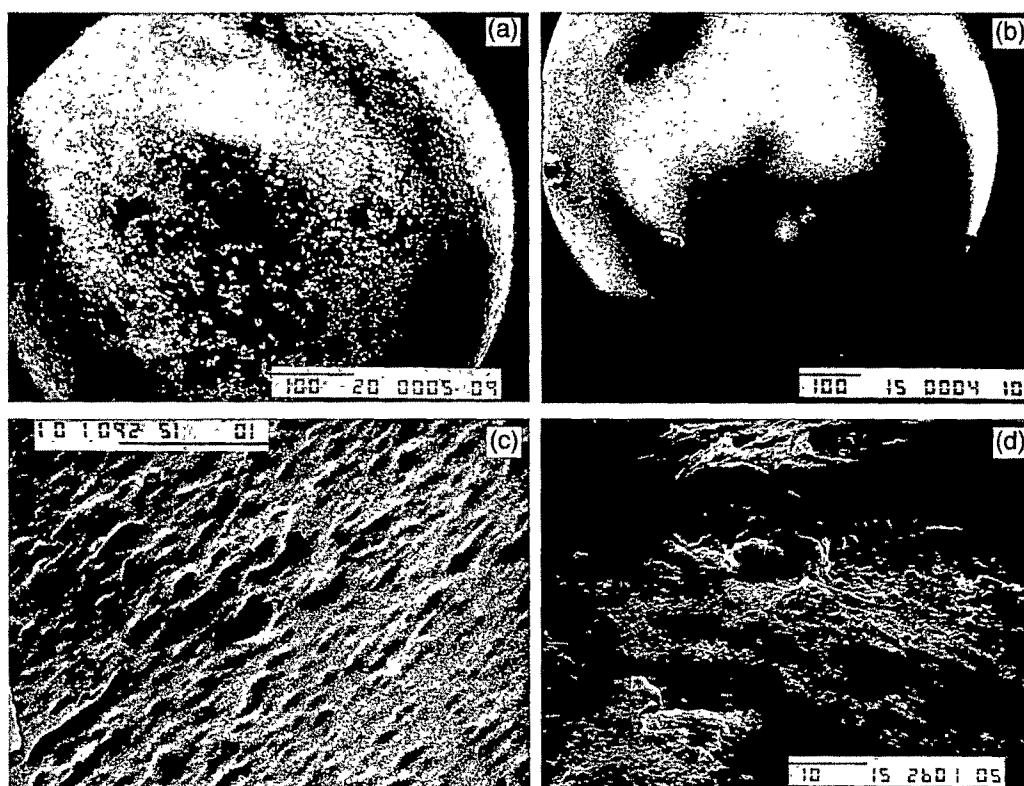


Fig. 2 Scanning electron micrograph of: (a) 2% styrene-divinyl benzene; (b) catalyst A, (c) 8% styrene divinyl benzene; (d) catalyst B

Such changes are also revealed in the surface area measurements.

The UV–Visible reflectance spectra of the supported catalysts gave peaks at 375 and 385 nm for catalyst A and B respectively which

might be due to d–d transitions of Ru(III). The formation of metal complex on the polymer support was confirmed by infrared spectral studies. The various IR frequencies are shown below.

	(N–H) cm <sup>-1</sup>	(Ru–N) cm <sup>-1</sup>	(Ru–Cl) cm <sup>-1</sup>	(C=O) cm <sup>-1</sup>
Catalyst A	2968	264	215 229	1604
Catalyst B	3371	279	231 250	1675

On the basis of the spectroscopic data, a probable structure of the catalyst is as shown in Scheme 1.

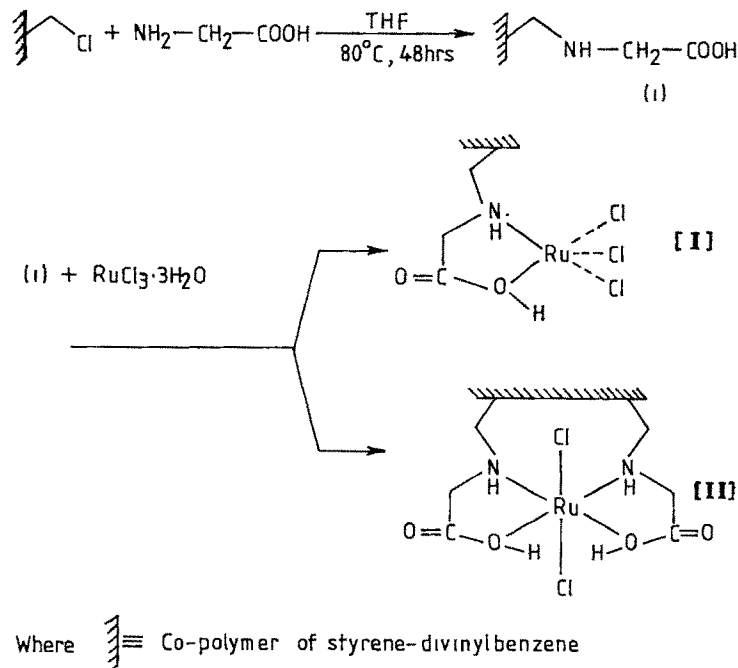
### 3.2. Hydrogenation reaction

The kinetics of hydrogenation of nitrobenzene was investigated for both the catalysts. The rate of hydrogenation was calculated from the

slope of the plots of volume of H<sub>2</sub> absorbed at STP as a function of time. The results are given in Tables 4 and 5. The influence of the various parameters on the rate of hydrogenation is discussed on the basis of experimental observation.

### 3.3. Effect of nitrobenzene concentration

The influence of nitrobenzene concentration on the rate of reaction was studied in the range



Scheme 1

Table 4

Summary of the kinetics of hydrogenation of nitrobenzene by catalyst A in 20 ml methanol at atmospheric pressure

[Ru] (mol $\times 10^5$ )	[Nitrobenzene] (mol l $^{-1}$ ) $10^3$	Temp ( $^{\circ}$ C)	Rate of reaction (ml min $^{-1}$ )
0.45	3.25	35	0.11
0.56			0.13
0.67			0.16
0.78			0.18
0.45	1.62		0.08
	3.25		0.11
	4.87		0.14
	6.50		0.18
0.45	3.25	30	0.08
		35	0.11
		40	0.13
		45	0.21

of  $1.63 \times 10^{-3}$  to  $6.50 \times 10^{-3}$  mol l $^{-1}$  at 35 $^{\circ}$  and 1 atm H $_2$  pressure using catalyst concentration of  $0.45 \times 10^{-5}$  M for catalyst A and  $0.67 \times 10^{-5}$  M for catalyst B and a linear increase in the rate was observed (Tables 4 and 5). This infers that the metal complexes present on the surface are monomeric. The order of reaction calculated from the linear plot of log (initial rate) against log [Nitrobenzene] was found to be 0.50 for catalyst A and 0.80 for catalyst B. The straight line plot (Fig. 3) of 1/Rate vs. 1/[sub-

Table 5

Summary of the kinetics of hydrogenation of nitrobenzene by catalyst B in 20 ml methanol at atmospheric pressure

[Ru] (mol $\times 10^5$ )	[Nitrobenzene] (mol l $^{-1}$ ) $10^3$	Temp ( $^{\circ}$ C)	Rate of reaction (ml min $^{-1}$ )
0.45	3.25	35	0.12
0.67	1.63	35	0.09
0.84			0.10
1.00			0.14
1.17			0.17
0.67	1.63	35	0.09
	2.44		0.10
	3.25		0.13
	4.07		0.15
	4.90		0.28
0.67	1.63	30	0.06
		35	0.09
		40	0.12
		45	0.14

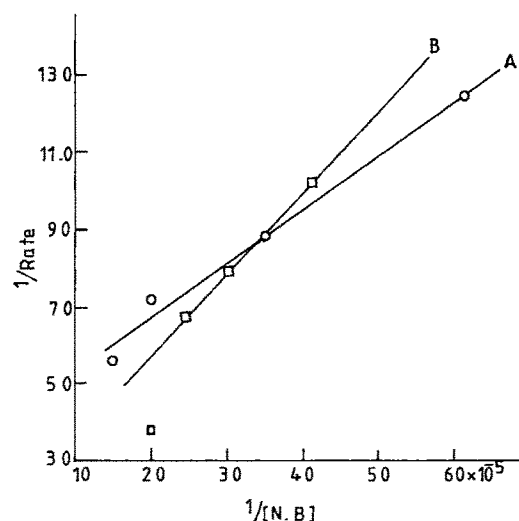


Fig. 3 Plot of 1/Rate vs. 1/[Nitrobenzene] for catalysts A and B.

strate] indicates the relation between the rate and the concentration of the substrate.

#### 4. Effect of catalyst concentration

A linear increase in the rate of hydrogenation with an increase in concentration of catalyst was found when the quantity of the catalyst was varied from  $0.45 \times 10^{-5}$  to  $0.78 \times 10^{-5}$  M for catalyst A and from  $0.67 \times 10^{-5}$  to  $1.17 \times 10^{-5}$  M for catalyst B, at a constant nitrobenzene concentration of  $3.25 \times 10^{-3}$  and  $1.63 \times 10^{-3}$  mol l $^{-1}$ , respectively (Tables 4 and 5). The order of the reaction with respect to catalyst concentration calculated from the slope of the linear plot of log (initial rate) vs. log [catalyst] (plots are not given) was 0.83 and 0.35 for catalyst A and B, respectively. The fractional order might be due to non-availability of catalytic sites, less swelling of the catalyst as well as steric hinderance [16].

#### 5. Effect of temperature

The kinetics of the hydrogenation of nitrobenzene was studied in the temperature range

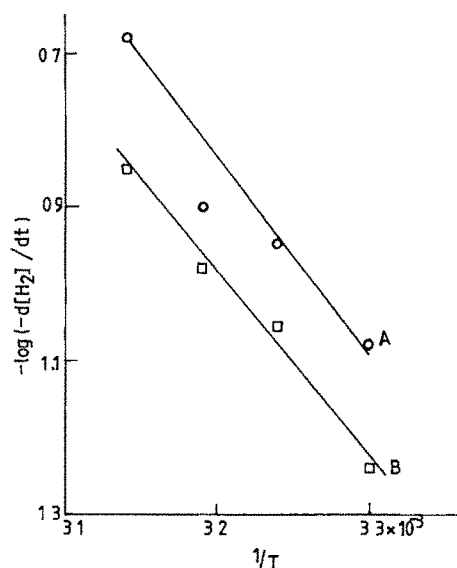


Fig. 4. Arrhenius plots for catalysts A and B.

of 30–45°C for both the catalysts at a constant concentration of the substrate and a fixed amount of the catalysts A and B. The rate of the reaction was found to be dependent on temperature of the system. The values for the energy of activation calculated from the slope of the plot of  $\log [-d[H_2]/dt]$  vs.  $1/T$  were found to be 49.85 and 44.67 kJ mol<sup>-1</sup> for catalyst A and B, respectively (Fig. 4). On the basis of the above, it could be concluded that the catalyst B is having higher catalytic activity than catalyst A.

Table 6

Effect of solvents on the hydrogenation of nitrobenzene at 35°C and 1 atm pressure using 20 ml of solvent

Solvent	Rate of reaction <sup>a</sup> (ml min <sup>-1</sup> )	
	Catalyst A	Catalyst B
methanol	0.11	0.09
ethanol	0.08	0.06
THF	0.06	0.05
benzene	0.06	0.05

<sup>a</sup> For catalyst A [Ru] =  $2.22 \times 10^{-5}$  mol, [Nitrobenzene] =  $3.25 \text{ (mol l}^{-1}\text{)} \times 10^3$ . For catalyst B, [Ru] =  $3.34 \times 10^{-5}$  mol, [Nitrobenzene] =  $1.63 \text{ (mol l}^{-1}\text{)} \times 10^3$ .

## 6. Effect of solvent

Various polar and non-polar solvents were introduced to study the kinetics of the hydrogenation of nitrobenzene at 35°C. The rate was found to decrease from a polar to a non-polar solvent (Table 6). This indicates that the rate of hydrogenation depends on the swelling of the catalyst and hence the availability of the active sites present on the surface.

## 7. Conclusion

On the basis of the energy of activation values, it could be concluded that the catalyst B has higher catalytic activity than A. This might be due to large amount of metal complexes dispersed and exposed to the reaction system though the swelling of the catalyst is less at higher percentage of cross-linking.

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