

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

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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.  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$

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(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-

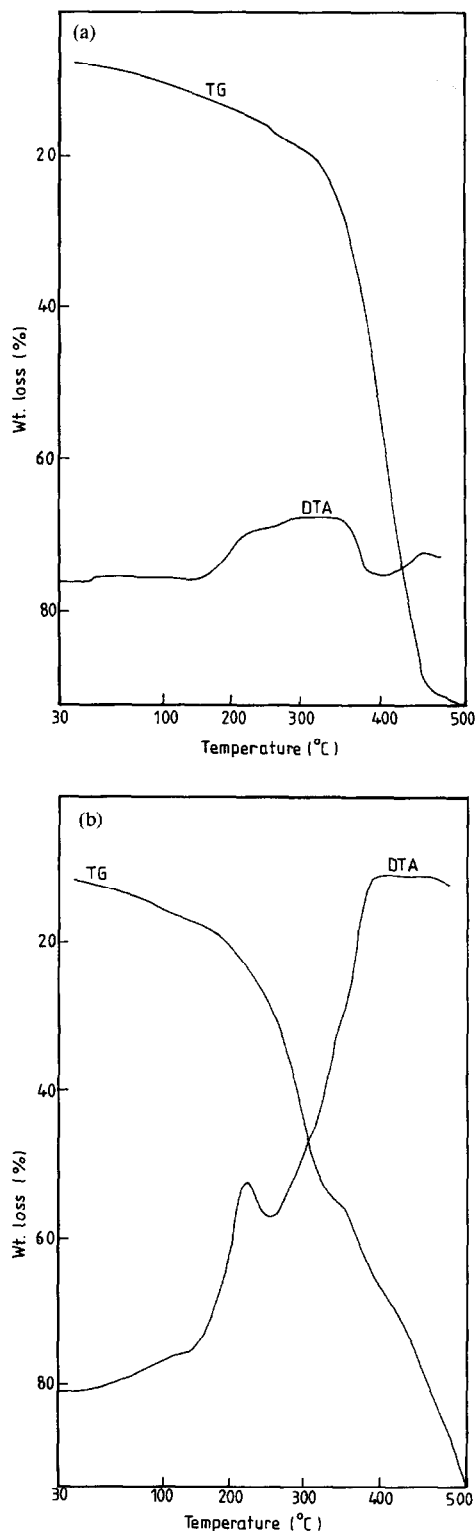


Fig. 1. DTA-TG curves for (a) catalyst A and (b) catalyst B.

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
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.

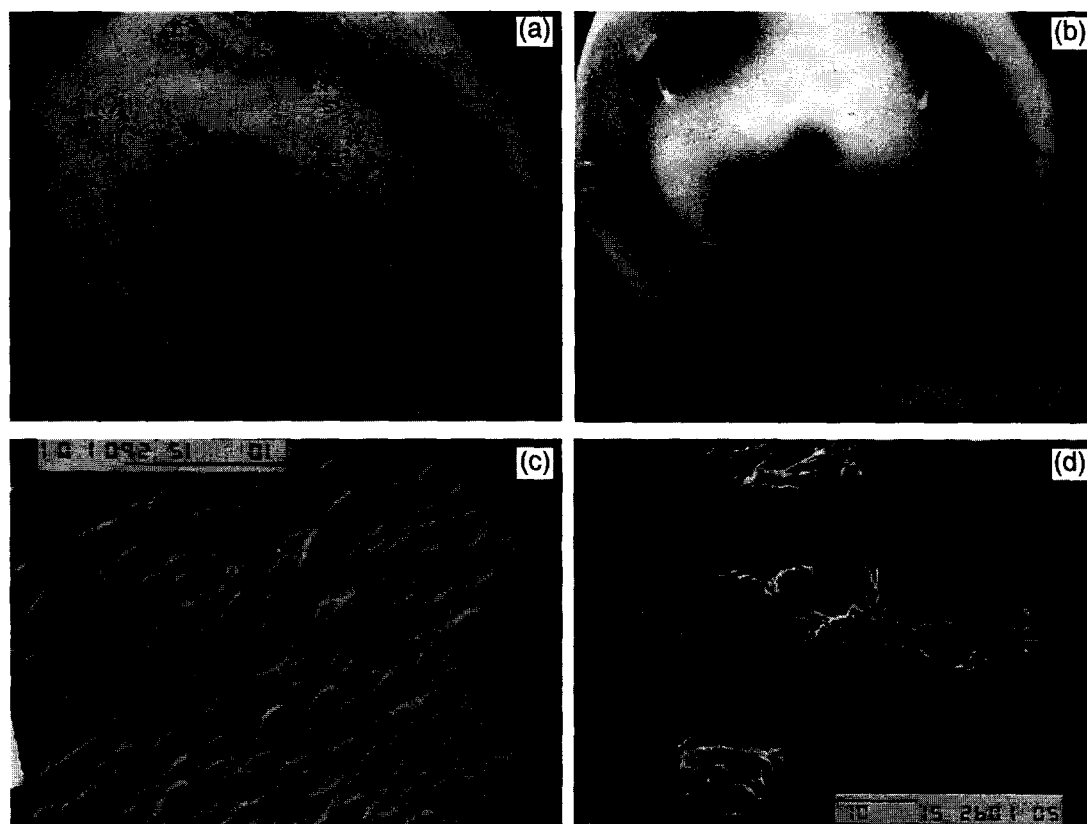


Fig. 2. Scanning electron micrograph of: (a) 2% styrene–divinyl benzene; (b) catalyst A; (c) 8% styrene divinyl benzene; (d) catalyst B.

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.

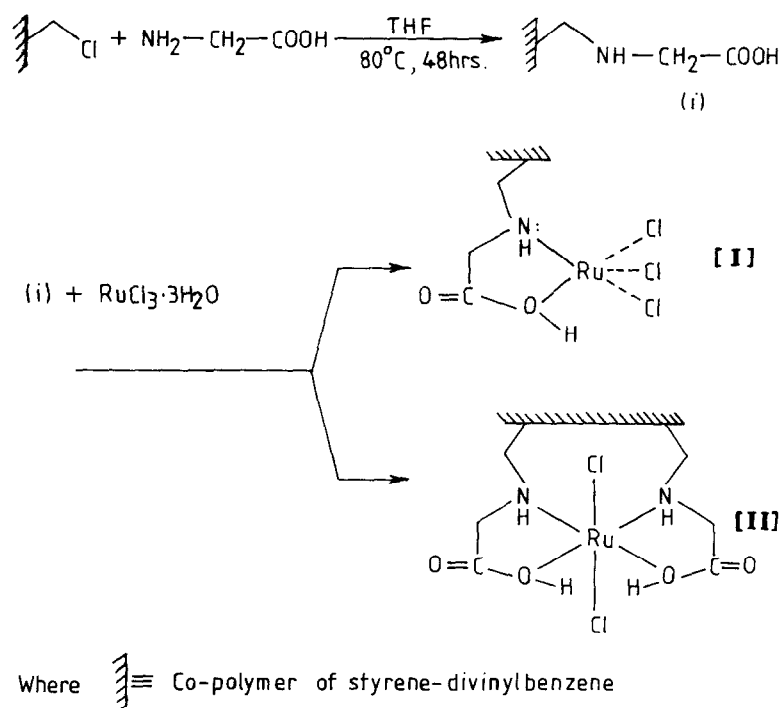
### 3.2. Hydrogenation reaction

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 $l^{-1}$ ) $10^6$	Temp ( $^{\circ}C$ )	Rate of reaction (ml $min^{-1}$ ) $10^2$
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  $1.63 \times 10^{-6}$  to  $6.50 \times 10^{-6}$  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 $l^{-1}$ ) $10^6$	Temp ( $^{\circ}C$ )	Rate of reaction (ml $min^{-1}$ $\times 10^2$ )
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

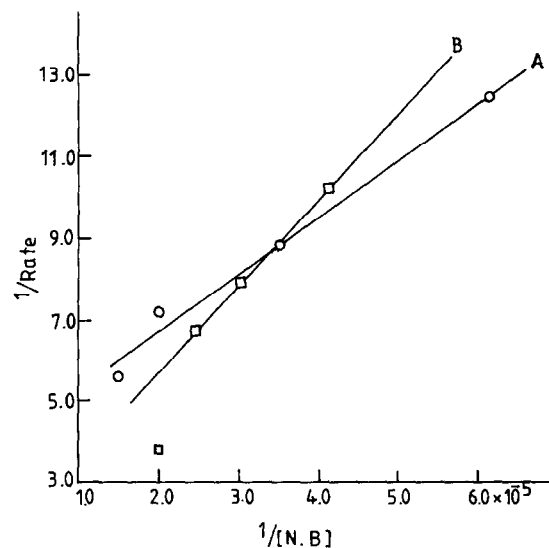


Fig. 3. Plot of  $1/Rate$  vs.  $1/[Nitrobenzene]$  for catalysts A and B.

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  $3.25 \times 10^{-6}$  and  $1.63 \times 10^{-6}$  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

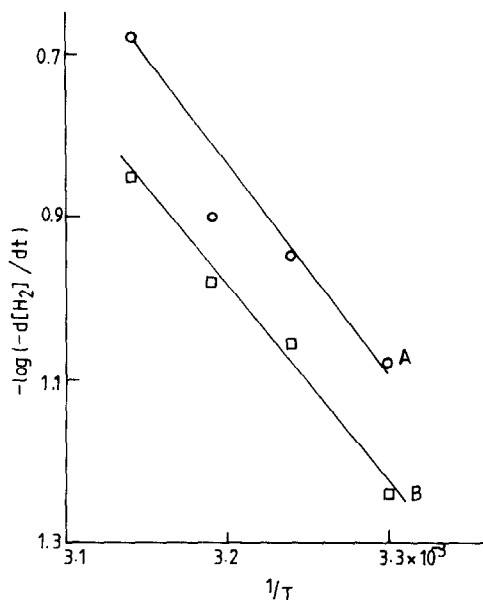


Fig. 4. Arrhenius plots for catalysts A and B.

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  $\text{kJ mol}^{-1}$  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> ( $\text{ml min}^{-1} \times 10^2$ )	
	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  $[\text{Ru}] = 2.22 \times 10^{-5}$  mol,  $[\text{Nitrobenzene}] = 3.25$  ( $\text{mol l}^{-1}$ ) $10^6$ . For catalyst B,  $[\text{Ru}] = 3.34 \times 10^{-5}$  mol,  $[\text{Nitrobenzene}] = 1.63$  ( $\text{mol l}^{-1}$ ) $10^6$ .

## 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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