

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, Vadodara 390 002, India

Received 13 June 1997; accepted 3 September 1997

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. © 1998 Elsevier Science B.V.

Keywords: Styrene–divinyl benzene; Chloromethylation; Hydrogenation; Polymer support; Catalysis

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

* Corresponding author. Fax: +91-265-792508.

activity for hydrogenation of nitrobenzene to aniline which is an intermediate for dyes and drugs.

2. Experimental

2.1. Materials and equipment

All chemicals used were purified as described earlier [12]. 2-amino butanol was distilled before use. PdCl₂ (obtained from Sisco Research Laboratories, Bombay) was used without purification. 2% Styrene–divinyl benzene (XAD-2) copolymer was obtained from Fluka 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 UV-240 instrument using BaSO₄ 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), puri-

fied 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 PdCl₂ (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 concentrated 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 solvents were found to be good swelling agent. 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

Table 1
Physical properties of the anchored catalysts

Physical properties	Catalyst X	Catalyst Y
Pore volume (cm ³ g ⁻¹)	0.36 (0.42)	0.08 (0.04)
Surface area (m ² g ⁻¹) N TP	174.17 (330.0)	33.95 (37.37)
Apparent bulk density (g cm ⁻³)	0.42	0.47
Moisture content (wt%)	1.32	3.85

Values mentioned in parentheses indicate data for supports.

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

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 H₂ uptake as a function of time. A summary of the results are given in Tables 4 and 5. The influence of various parameters on the rate was studied. The recycling efficiency has also been seen.

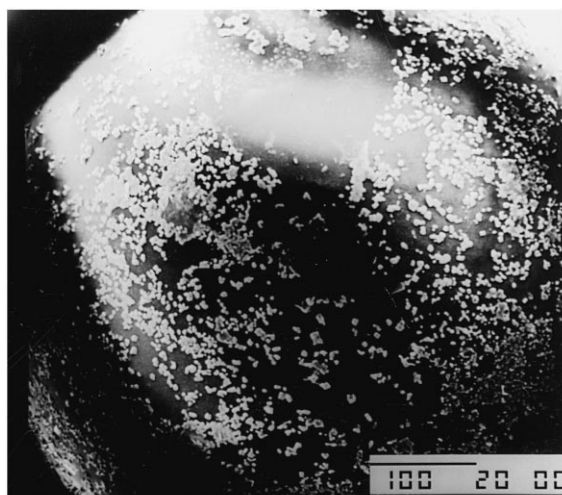
3.3. Effect of nitrobenzene concentration

The concentration of nitrobenzene for catalyst X and Y was varied from 4.83×10^{-3} to 19.4×10^{-3} mol/l at 35°C and 1 atm. H₂ pressure using a fixed amount of the catalyst i.e. 2.58×10^{-5} mol/l Pd(II) content for both the catalysts. On increasing the concentration of 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

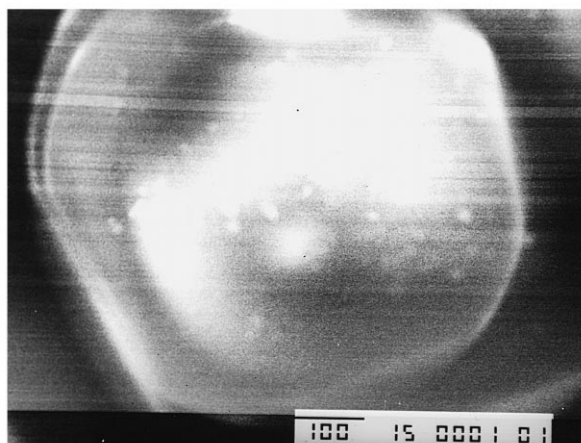
Table 3
Elemental analysis of catalysts X and Y in (wt%)

Catalyst	P			Q			R			Pd (g/g) $\times 10^4$
	C	H	Cl	C	H	N	C	H	N	
X	80.94	7.46	6.0	84.68	8.26	1.23	85.11	7.34	1.12	5.50
Y	72.95	5.93	17.5	85.88	7.19	3.68	85.63	7.09	3.26	2.75

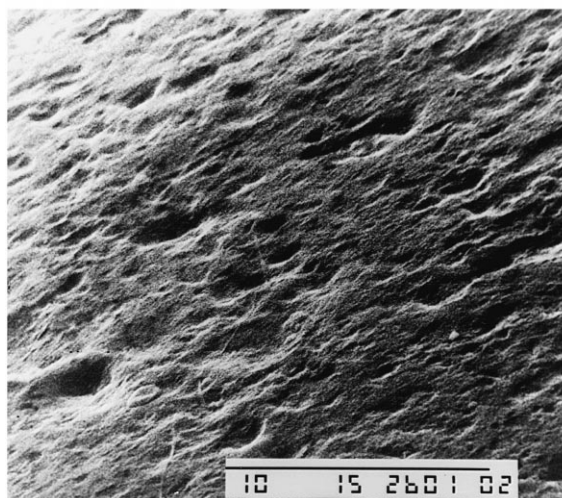
P: After chloromethylation Q: After ligand introduction R: after complexation.



(A)



(C)



(B)



(D)

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

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 substrate.

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 2.58×10^{-5} to 4.52×10^{-5} mol/l Pd(II) present on the surface of catalyst at constant nitrobenzene concentration of 9.72×10^{-3} mol/l at 35°C keeping 1 atm. H₂ 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 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 activ-

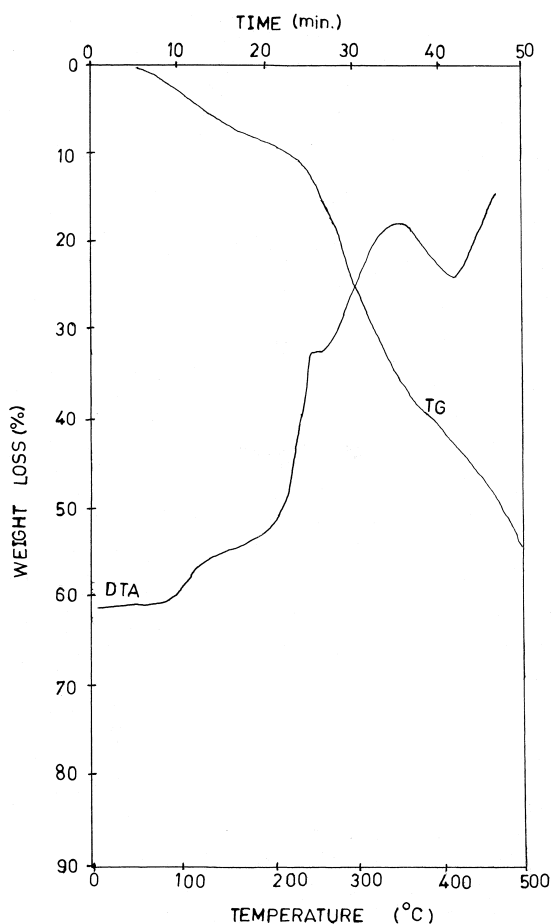
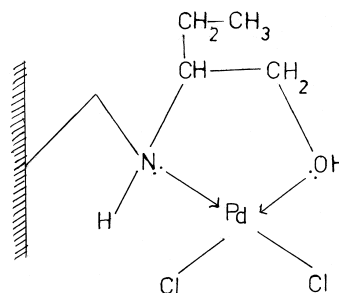


Fig. 2. DTA-TGA curves for catalyst Y.



Scheme 1.

Table 4

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

Concentration of catalyst (mol/l × 10 ⁵)	[nitrobenzene] (mol/l × 10 ³)	Temperature (°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

ity. 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 recycling 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

Table 5

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

Concentration of catalyst (mol/l × 10 ⁵)	[nitrobenzene] (mol/l × 10 ³)	Temperature (°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

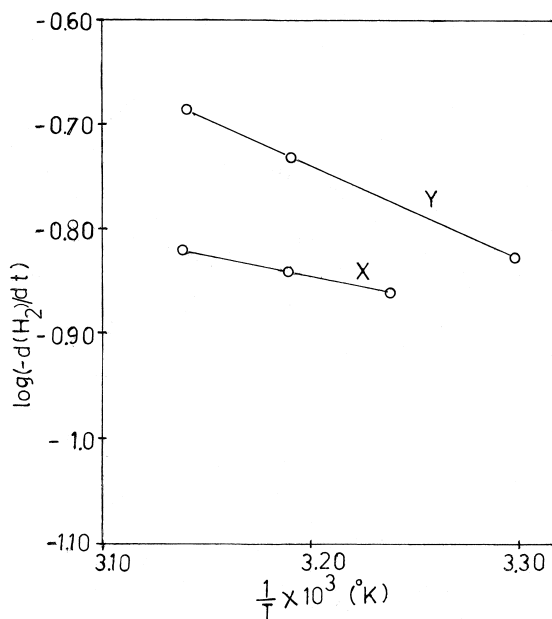


Fig. 3. Plot of $\log(-d[H_2]/dt)$ against $1/T$.

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 5.50×10^{-5} g to 4.25×10^{-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

Table 6

Recycling efficiency of catalysts X and Y for hydrogenation of nitrobenzene at 35°C and 20 ml methanol at 1 atm. H₂ pressure. Concentration of catalyst: 2.58×10^{-5} mol/l. Concentration of nitrobenzene: 9.72×10^{-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.

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.

Acknowledgements

Thanks are due to Professor A.C. Shah, Head, Chemistry Department, Catalysis group (R&D) I.P.C.L. Baroda as also to Ion exchange (India) Limited for providing the chloromethylated sample of Styrene divinyl benzene.

References

- [1] A.M. Trzeciak, J.J. Ziolkowski, *J. Mol. Catal.* 88 (1994) 13.
- [2] L.H. Pignolet, *Homogeneous Catalysis with metal phosphine complexes*, Plenum Press, New York, 1983.
- [3] N. Kameda, R. Igarashi, *J. Mol. Catal.* 92 (1994) 257.
- [4] R. Skoda Folder, L. Kollar, *J. Mol. Catal.* 101 (1995) 37.
- [5] S. Huang, B. He, *J. React. Poly.* 23 (1994) 1.
- [6] A. Biffis, B. Corain, *J. Appl. Catal.* 124 (1995) 355.
- [7] R.T. Smith, R.K. Ungar, *Organometallics* 2 (1983) 1138.
- [8] M.M. Mdleleni, R.G. Rinker, *J. Mol. Catal.* 89 (1994) 283.
- [9] J.N. Shah, R.N. Ram, *J. Mol. Catal.* 77 (1992) 235.
- [10] D.R. Patel, M.K. Dalal, R.N. Ram, *J. Mol. Catal.* 109 (1996) 141.

- [11] A. Syamal, M.M. Singh, *React. Polym.* 21 (1993) 45.
- [12] B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell (Eds), *Vogel's textbook of practical Organic Chem.* Elbs longmann London, 1978.
- [13] J. John, R.N. Ram, *Polym. Int.* 34 (1994) 369.
- [14] A.I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd ed., Longmann, London, 1975.
- [15] R.S. Drago, J. Gaul, A. Zombeck, D.K. Straub, *J. Am. Chem. Soc.* 102 (1980) 1033.
- [16] A.K. Singh, M. Katyal, R.P. Singh, *J. Ind. Chem. Soc.* 53 (1976) 691.
- [17] D.T. Gokak, R.N. Ram, *J. Mol. Catal.* 49 (1989) 285.
- [18] K. Kaneda, T. Imanaka, *Trends Org. Chem.* 2 (1991) 109.
- [19] S. Huang, B. He, *React. Polym.* 23 (1994) 11.