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Polymer anchored palladium(II)-diaminopropane complexes: synthesis and catalytic behaviour

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Abstract

Styrene-divinylbenzene copolymer with 5% and 15% cross linked were synthesised by suspension polymerization, chloromethylated and treated with 1,2-diaminopropane for the introduction of the ligand. The polymer beads modified with ligand was kept in contact with $PdCl_2$ to form the metal complex on the surface of the polymer. The catalysts thus prepared were characterized by various techniques such as FTIR, reflectance UV–vis spectroscopy, SEM, EPR, TGA and ESCA. Physico-chemical properties such as moisture content, bulk density, surface area by BET method and swelling with different solvents were studied. The catalytic activity of synthesised catalysts was tested for hydrogenation of cyclohexene as a model reaction. Kinetic studies were carried out by varying different parameters. Energy of activation as well as entropy of activation was calculated. The recycling efficiency of the catalysts was also studied. A probable reaction mechanism was proposed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polymer anchored catalysts; Hydrogenation of cyclohexene; Pd(II) complexes; 1,2-Diaminopropane; Kinetics of hydrogenation; Reaction mechanism

1. Introduction

Chemically bonding metal complexes to an insoluble solid is one of the popular methods to overcome problems of homogeneous catalysis [1]. Catalysts prepared in this way, regarded as heterogenized catalysts have created large interest in recent past [2–6]. Many researchers have studied and compared the behaviour of transition metal complexes as catalysts in homogeneous and heterogenized state, mainly because of their higher catalytic activity under mild operating conditions [7,8]. Earlier, we have reported immobilization of various metal complexes on organic polymer [9–13]. The present study deals with synthesising chelated palladium metal complex on a polymeric support and investigating its catalytic behaviour for the hydrogenation of cyclohexene.

2. Experimental

2.1. Materials and equipments

Styrene, divinylbenzene (DVB), dioxane, methanol and cyclohexene were purified according

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to published methods [14]. 1,2-diaminopropane and 1,2-dichloroethane were distilled before use. Aluminium chloride was distilled by sublimation. $PdCl_2$ (Lobachemie, Bombay) was used as such.

Elemental analyses and TGA were carried out in our laboratory on a Coleman analyzer and a Shimadzu thermal analyzer DT-30 respectively. Surface area of the supports as well as the catalysts was measured using Carlo-Erba strumentzione 1800. Ultraviolet spectra of the solid samples were recorded on a Shimadzu UV-240 spectrophotometer with reference to a non-absorbing $BaSO_4$ as standard and liquid samples in methanol. FTIR spectra were recorded on a Perkin-Elmer 1720 (USA). EPR spectra were scanned on Bruker ESP-300 K band spectrometer using a 100 kHz field modulation. EPR experiments were conducted on powdered sample at 298 K in N_2 atmosphere. ESCA was recorded on VG model ESCA-3 mark II (UK) with the Al K_α and Mg K_α as radiation sources. SEM were recorded on a Jeol scanning microscope model JSM T-300. Swelling studies of the catalysts were carried out using various polar and non-polar solvents at a constant temperature. The detailed procedure has been described earlier [13].

2.2. Synthesis of polymer anchored catalysts

Styrene/divinylbenzene copolymer with 5% and 15% cross linked were synthesised by the suspension polymerization technique using benzoyl peroxide as an initiator [13]. The polymer beads were then washed with distilled water, water–ethanol mixture (1:1), ethanol and finally soxhlet extracted with ethanol/benzene (1:1) mixture for 10 h. The polymer beads were chloromethylated with HCl, paraformaldehyde, acetic anhydride and 1,2-dichloroethane as solvent using $AlCl_3$ as a catalyst [15]. The elemental analysis shows the percentage of C, H and Cl as 75.98, 7.24 and 9.8 for 5% cross linked polymer and 82.41, 7.32 and 8.9 for 15% cross linked polymer. In order to introduce the ligand,

a solution of 1,2-diaminopropane in ethanol was refluxed with above beads for 4 h and kept at room temperature for 48 h with occasional stirring, filtered, washed with 0.5 M NaOH and then with deionized water and dried at 70°C. The loading was confirmed by elemental analyses which shows N% as 2.22 for 5% cross linked polymer and 2.12 for 15% cross linked polymer. The functionalised beads were kept in contact with ethanolic solution of $PdCl_2$ for 7 days. The experimental procedure for anchoring the metal ion is reported elsewhere [9]. The metal content was determined by refluxing metal containing polymer beads with conc. HCl (AR) for 24 h and then estimating the metal concentration in the solution by a spectrophotometric method after complexation with nitroso-R salt [16].

2.3. Nomenclature

Catalysts thus prepared were named as NPML where N = % cross linked, P denotes copolymer of styrene divinylbenzene, M = Metal (Pd) and L = Ligand (1,2-diaminopropane).

Following 2 catalysts were prepared
Catalyst A = 5PPd(II)DAP
Catalyst B = 15PPd(II)DAP

2.4. Kinetics of hydrogenation

The kinetics of hydrogenation of cyclohexene was studied at atmospheric pressure by measuring hydrogen uptake using a glass manometric apparatus. The detailed procedure and experimental set up are described elsewhere [13]. It was found from the GC analysis that the amount

Table 1
Physical properties of the catalysts A and B

Physical properties	Catalyst A	Catalyst B
Apparent bulk density (g ml^{-1})	0.49	0.46
Moisture content (wt.%)	1.51	1.22
Surface area (m^2 g^{-1})	8.82 (9.78)	26.97 (27.93)
Pore volume (ml g^{-1})	0.217 (0.212)	0.40 (0.43)

Values for polymer support are given in parenthesis.

Table 2
Elemental analyses at different stages of catalyst preparation (in wt.%)

Catalyst	a			b			c			
	C	H	Cl	C	H	N	C	H	N	Pd
A	75.98	7.24	9.8	71.23	7.33	2.22	71.11	7.18	2.09	4.35×10^{-2}
B	82.41	7.32	8.9	75.11	7.36	2.12	74.98	7.08	1.89	3.9×10^{-2}

a = After chloromethylation; b = after ligand introduction; c = After complex formation.

of H_2 absorbed was directly proportional to cyclohexene converted, i.e., no side product was formed. The initial rate was calculated from the slope of the plot of the H_2 uptake at various interval of time.

3. Results and discussion

3.1. Characterisation of the catalysts

Physico-chemical properties of the supported catalysts are given in Table 1. A decrease in surface area observed after loading the metal ions on to the polymer support might be due to the blocking of pores of polymer support after introducing the ligand and the metal ions. Similar results have also been reported earlier [11–13]. Elemental analysis at different stages of preparation of the catalysts is indicative of the successful functionalization of the polymer (Table 2). Maximum swelling observed in water may be due to hydrogen bonding of water with amino groups. Methanol was chosen as a sol-

vent for the hydrogenation reaction because of its swellability with the catalyst and miscibility with the substrate. A decrease in swelling was observed as the nature of the solvent changes from polar to non-polar as also on increasing degree of cross linking of polymer support reflecting rigidity of the catalyst [8,13] (Table 3). Change in the morphology of catalysts was seen using scanning electron microscope. The micrographs are given for the catalyst B and its support 15% cross-linked P(S-DVB) in Fig. 1. It was observed that the beads are porous and the texture changes with the change in degree of

Table 3
Swelling studies using different solvents

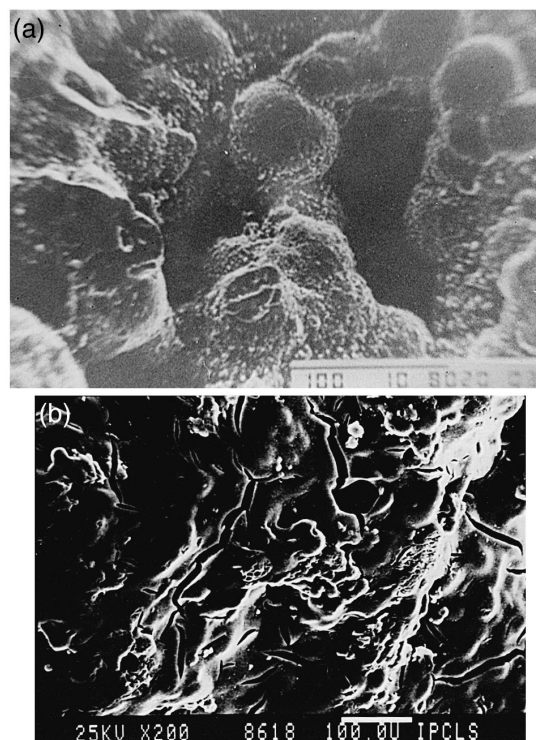| Solvent	Swelling (mol%)	
	Catalyst A	Catalyst B
Water	0.711	0.658
Methanol	0.596	0.592
Ethanol	0.388	0.362
Dioxane	0.122	0.116
DMF	0.112	0.103
Acetone	0.101	0.092
THF	0.094	0.084
Benzene	0.079	0.060
n-heptane	0.039	0.031

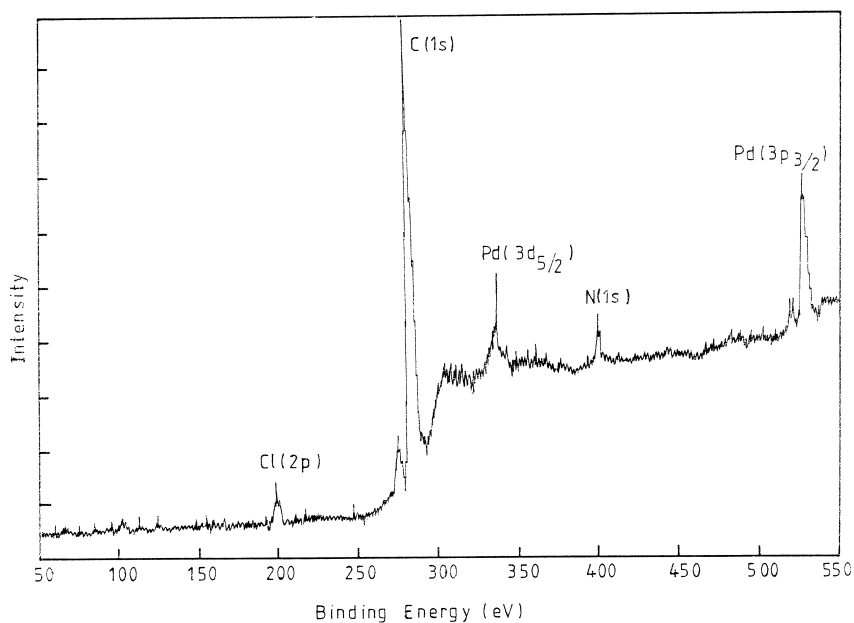Fig. 1. SEM of (a) P(S-DVB) 15% cross-linked (b) catalyst B.

Fig. 2. ESCA spectrum of catalyst B.

cross linking of polymer. The UV–visible reflectance spectra of both catalysts show d–d transition of Pd(II) at 210 and 340 nm for catalyst A and at 245 and 340 nm for catalyst B. In case of homogeneous complex, the absorption maxima occurred at 340 nm indicating the presence of Pd(II) in the same oxidation states both in homogeneous and heterogeneous systems. The EPR spectrum of the unbound Pd complex was found to be inactive confirming
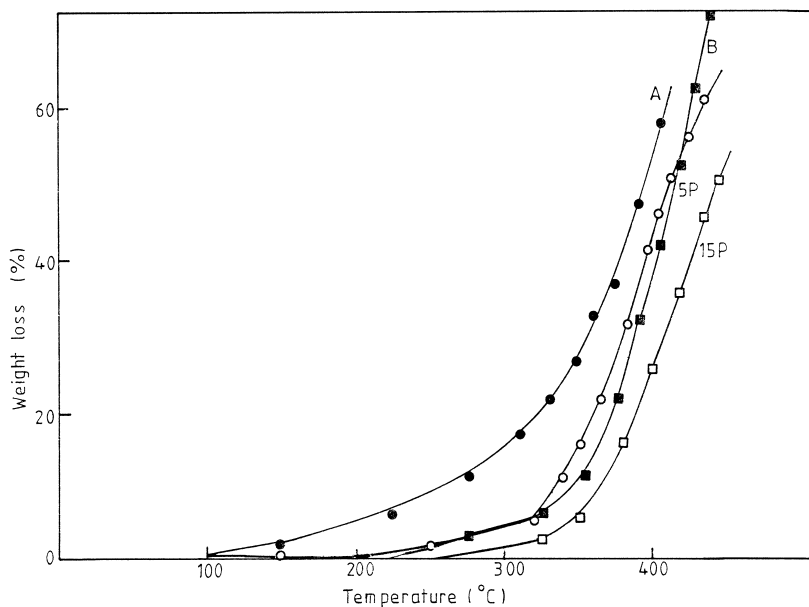

Fig. 3. TG curves of polymer supports and catalysts A and B.

the $+2$ oxidation state of Pd. It has been further confirmed by ESCA studies of the polymer bound palladium catalyst which gave the peaks due to Pd(3p 3/2), Pd(3d 5/2), N(1s), Cl(2p) and C(1s) for palladium-DAP (Fig. 2). The mode of anchoring of metal ion on the polymer matrix was confirmed by FTIR spectral studies. The various IR frequencies are assigned as (Pd–Cl) = 310 cm^{-1}, (Pd–N) = 504 cm^{-1}, (C–N) = 1107 cm^{-1}, (N–H) = 3406 and 1502 cm^{-1} and (–CH$_2$Cl) = 1266 cm^{-1} for catalyst A and (Pd–Cl) = 312 cm^{-1} (Pd–N) = 497 cm^{-1}, (C–N) = 1073 cm^{-1}, (N–H) = 3424 and 1549 cm^{-1} and (–CH$_2$Cl) = 1168 cm^{-1} for catalyst B. This confirms the formation of metal complex on the surface of the polymer. The thermal stability of polymer supports was observed to increase on increasing the cross linking of the polymer as was seen by TGA studies. The initial weight loss may be due to moisture content. The catalysts can be used safely below 100°C (Fig. 3).

Based on the spectroscopic evidence a probable structure of the catalyst is shown in Scheme 1.

3.2. Hydrogenation of cyclohexene

The kinetics of hydrogenation of cyclohexene was investigated for polymer supported catalyst A and B. The influence of various parameters on the rate of hydrogenation is discussed on the basis of experimental observation. The results are summarised in Tables 4 and 5.
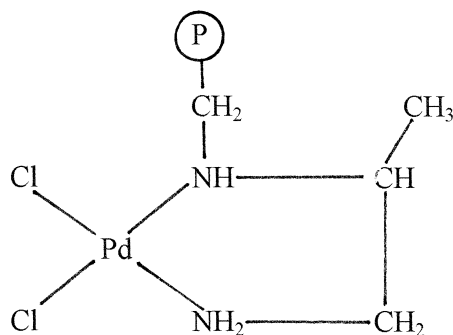
Scheme 1.

Table 4
Summary of kinetics of cyclohexene hydrogenation by catalyst A in methanol at atmospheric pressure

[Pd] (mol l^{-1} ×10^5)	[Cyclohexene] (mol l^{-1} ×10^3)	Temp (°C)	Methanol (ml)	Rate of reaction (ml min^{-1})
4.08	4.71	35	20	0.022
	9.42			0.037
	14.13			0.041
	18.84			0.046
2.04	9.42	35	20	0.029
4.08				0.037
6.13				0.038
8.17				0.055
4.08	9.42	30	20	0.030
		35		0.037
		40		0.046
		45		0.051
4.08	9.42	35	10	0.025
			20	0.037
			25	0.041
			30	0.048
			40	0.063

3.2.1. Effect of cyclohexene concentration

The influence of cyclohexene concentration on the rate of hydrogenation reaction was studied at 35°C under a pressure of 1 atm at constant catalyst concentration of 4.08×10^{-5} and 3.66×10^{-5} mol l^{-1} of Pd for catalysts A and B respectively (Tables 4 and 5). On increasing the substrate concentration from 4.71×10^{-3} to 18.84×10^{-3} mol l^{-1} for both catalysts the rate was found to increase from 0.022 to 0.046 and from 0.010 to 0.068 ml min^{-1} for catalyst A and B respectively (Tables 4 and 5). The order of reaction calculated from the linear plots of log (initial rate) vs. log [cyclohexene] was found to be 0.68 for catalyst A and unity for catalyst B. Linear plots of 1/rate vs. 1/[Cyclohexene] for both catalysts (Fig. 4) show that the rate of hydrogenation of cyclohexene, R is related to the concentration of cyclohexene $[S]$ by the relationship

$$\frac{1}{R} = a\frac{1}{[S]} + b$$

Where a and b are the slope and intercept of the linear plot. This is indicative of the forma-

Table 5
Summary of kinetics of cyclohexene hydrogenation by catalyst B in methanol at atmospheric pressure

[Pd] (mol $1^{-1} \times 10^5$)	[Cyclohexene] (mol $1^{-1} \times 10^3$)	Temp (°C)	Methanol (ml)	Rate of reaction (ml min^{-1})
3.66	4.71	35	20	0.010
	9.42			0.053
	14.13			0.054
	18.84			0.068
1.83	9.42	35	20	0.043
3.66				0.053
4.58				0.085
5.50				0.100
7.33				0.120
3.66	9.42	30	20	0.030
		35		0.053
		40		0.088
		45		0.090
3.66	9.42	35	10	0.052
			20	0.053
			25	0.059
			30	0.061
			40	0.068

Fig. 4. Plot of 1/rate vs. 1/[cyclohexene] for catalyst A and B.

tion of an intermediate complex through which the reaction proceeds.

3.2.2. Effect of catalyst concentration

The effect of catalyst concentration on the hydrogenation of cyclohexene was investigated over a range of 2.04×10^{-5} to 8.17×10^{-5} mol 1^{-1} of Pd for catalyst A and 1.83×10^{-5} to 7.33×10^{-5} mol 1^{-1} of Pd for catalyst B at a pressure of 1 atm and 35°C with a substrate concentration of 9.42×10^{-3} mol 1^{-1} and an increase in the rate was also observed under the range studied (Tables 4 and 5). The order of reaction calculated from the linear plots of log (initial rate) vs. log [Catalyst] was found to be unity for catalyst B whereas a fractional order was observed for catalyst A (0.72). The fractional order might be due to the non availability of catalytic sites, lack of swelling as well as steric hinderance [9].

3.2.3. Effect of temperature

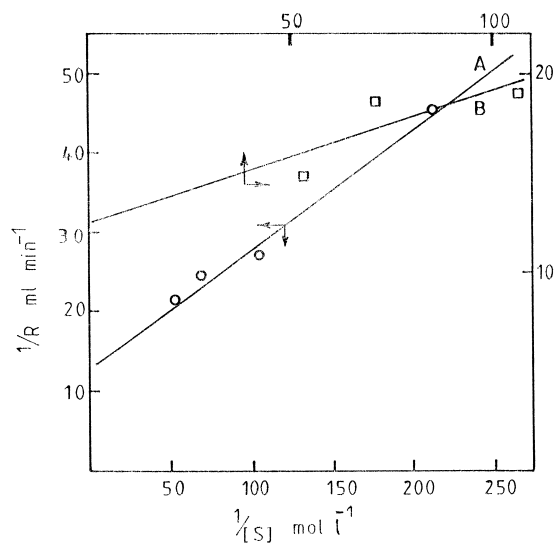The study for the rate of hydrogenation was carried out over a temperature range of 30–45°C

at a catalyst concentration of 4.08×10^{-5} and 3.66×10^{-5} mol 1^{-1} of Pd for catalyst A and B respectively (Tables 4 and 5) and an increase in the rate was observed. The values for the energy of activation calculated from the slope of the plot of log (initial rate) vs. $1/T$ (Fig. 5) were found to be 35.06 and 83.89 kJ mol^{-1} for
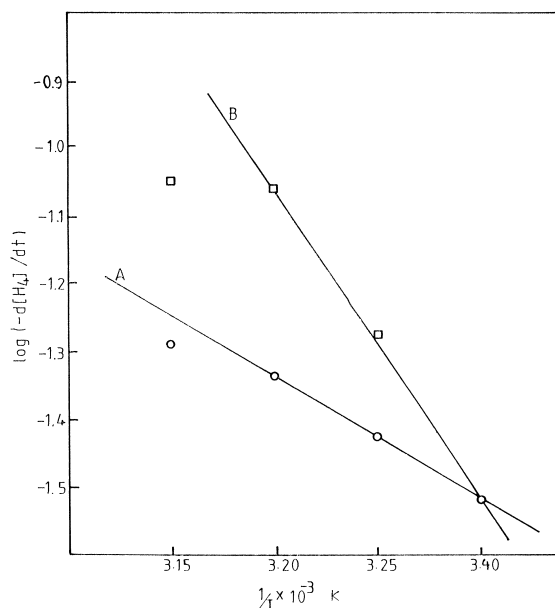

Fig. 5. Arrhenius plots for catalysts A and B.

Table 6

Summary of Kinetics of Cyclohexene hydrogenation by catalyst A and catalyst B in various solvents at atmospheric pressure

[Cyclohexene] (mol $l^{-1} \times 10^3$)	Temp (°C)	Solvent (20 ml)	Rate of reaction (ml min^{-1})	
			A	B
9.42	35	Methanol	0.037	0.053
		Ethanol	0.036	0.052
		Dioxane	0.028	0.043
		THF	0.015	0.031
		Benzene	0.008	0.009

[Pd] (mol $l^{-1} \times 10^5$) for catalyst A: 4.08 catalyst B: 3.66.

catalyst A and B respectively. The corresponding values for entropy of activation calculated from the kinetic data were found to be −48.07 and −6.22 eu. The decrease in enetropy corresponds to a considerable loss of freedom due to fixation of the catalyst molecules on the polymer matrix [1].

3.2.4. Effect of hydrogen concentration in solution

Tables 4 and 5 illustrate the influence of hydrogen concentration in methanol for both catalysts at fixed concentration of catalysts as well as substrate at 35°C and 1 atm pressure. It can be seen that the rate increases with increasing volume of methanol and hence hydrogen concentration.

3.2.5. Effect of solvent

The effect of five different solvents on the rate of hydrogenation was measured (Table 6). The rate was found to decrease as the nature of the solvent varies from polar to non polar. The enhancement in the reaction rate in the polar solvents might be due to the swelling of the polymer support and hence the availability of catalytic sites [17].

Hydrogenation by $[Pd(II)DAP\ Cl_2]$ was carried out in homogeneous medium and was found to be less catalytically active [9].

Table 7

Life cycle study for the catalysts at 35° 1 atm using 20 ml methanol

Fresh catalysts		Used catalysts	
Time (min)	Rate of reaction (ml min$^{-1} \times 10^2$)	Time (min)	Rate of reaction (ml min$^{-1} \times 10^2$)
Catalyst A[x]			
140	5.48	140	5.46
340	5.46	340	5.40
530	5.46	550	5.29
720	5.40	720	5.20
940	5.36	840	5.13
Catalyst B[y]			
140	12.10	140	12.10
340	12.10	340	12.08
530	12.00	550	12.06
720	11.82	720	11.62
940	11.68	840	11.02

[x]Amount of catalyst 0.4 g (8.17×10^{-5} mol l^{-1} of Pd) Total time on stream 15.6 h (14.00 h)∗.
[y]Amount of catalyst 0.4 g (7.33×10^{-5} mol l^{-1} of Pd) Total time on stream 15.6 h (14.00 h)∗.
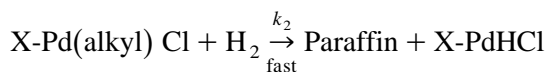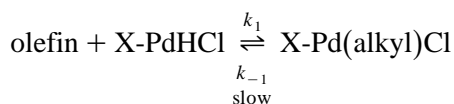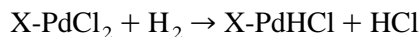∗Values given in parentheses indicate data for used catalyst.

3.3. Life cycle of catalysts

The main objective of supporting metal ions on to a polymer support is for its reuse. The polymer bound catalysts can lose its activity by the loss of metal ions, which is brought about by the leaching of metal complex or reduction to free metal [8]. In order to study the activity of the catalyst for reuse, recycling efficiency of the catalysts was tested for both used and fresh catalysts. The experiment was carried out at 35°C for 16 h by injecting a known amount of substrate (i.e., 10 μl) at 60 min intervals. The rate of hydrogenation was measured as a function of time for both used and fresh catalysts. It was observed that the maximum rates of reaction was maintained for about 10 h for both catalysts after which the rate decreases slowly (Table 7). The estimation of metal content at the end of the reaction showed a loss of about 50% of the metal from the support. The loss in catalytic activity may be due to low mechanical strength of the polymer support as also due to polymer bound complexes and polymer bound non coordinated ligand molecules leaching out in solution and forming stable complexes in solution which are less effective in catalysing the reaction [8].

4. Rate equation

The mechanism of olefin hydrogenation over a polymer bound palladium catalysts has been extensively studied [1]. On the basis of experimental results and evidence from the literature, the following mechanism and rate equation are proposed.

$$X\text{-PdCl}_2 + H_2 \rightarrow X\text{-PdHCl} + HCl$$

$$\text{olefin} + X\text{-PdHCl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X\text{-Pd(alkyl)Cl}$$
<div align="center">slow</div>

$$X\text{-Pd(alkyl) Cl} + H_2 \overset{k_2}{\rightarrow} \text{Paraffin} + X\text{-PdHCl}$$
<div align="center">fast</div>

where X is the polymer modified with the ligand DAP and k_1, k_{-1} and k_2 are the rate constants

$$\text{Rate}(R) = \frac{k_1 k_2 \,[S]\,[H_2]\,[C]}{k_{-1} + k_1\,[S] + k_2\,[H_2]}$$

where A is substrate and C is the catalyst.

5. Conclusion

Palladium-1,2-diaminopropane complex was successfully heterogenized by using copolymer of PS-DVB. The attachment and formation of the metal complex on the surface of the polymer was confirmed at various stages by carrying out studies of elemental microanalysis, IR, UV–vis, EPR and ESCA. A probable structure is proposed. Both the catalysts were found active for hydrogenation of cyclohexene under mild conditions. On the basis of energy of activation values, 5% crosslinked polymer supported catalyst was found to be more active than 15% cross-linked supported catalyst. Polymer supported catalysts were found to be more effective towards hydrogenation of cyclohexene than homogeneous complex. The recycling efficiency of the catalysts was seen and it was found to be active at least for five cycles after that a decrease in rate was observed. This may be due to leaching of the metal ions.

References

[1] K. Kaneda, T. Imanaka, Trends Org. Chem. 2 (1991) 109.
[2] P. Ciardelli, A. Altomare, G. Conti, G. Arribas, B. Mendez, A. Ismayel, Macromol. Symp. 80 (1994) 29.
[3] Y. Iwasawa, Tailored Metal Catalysts, Reidel, Dordrecht, 1986.

[4] F.R. Hartely, Supported Metal Complexes, Reidel, Dordrecht, 1985.

[5] Y.I. Yermakov, B.N. Kuznetsov, V.A. Zakharev, Catalysis by Supported Complexes, Elsevier, Amsterdam, 1981.

[6] C.U. Pitman, Jr., in: P. Hodge, D.C. Sherrington (Eds.), Polymer Supported Reactions in Organic Synthesis, Wiley, New York, 1980.

[7] S. Bhaduri, K. Sharma, J. Chem. Soc., Chem. Commun., 1988, 173.

[8] J.N. Shah, D.T. Gokak, R.N. Ram, J. Mol. Catal. 60 (1990) 141.

[9] J. John, R.N. Ram, Polym. Int. 34 (1994) 369.

[10] J.N. Shah, R.N. Ram, J. Mol. Catal. 83 (1993) 67.

[11] D.T. Gokak, R.N. Ram, J. Mol. Catal. 49 (1989) 285.

[12] D.T. Gokak, B.V. Kamath, R.N. Ram, React. Polym. 10 (1989) 37.

[13] D.T. Gokak, B.V. Kamath, R.N. Ram, J. Appl. Polym. Sci. 35 (1985) 1528.

[14] B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell (Eds.), Vogel's Textbook of Practical Organic Chemistry, Elbs. Longmann, London, 1978.

[15] J.D. Spivack, S. Vauey, U.S. Pat. 328 1505 (1966).

[16] P. Sarkar, P.K. Paria, J.K. Majumdar, J. Indian Chem. Soc. 65 (1988) 117.

[17] D.R. Patel, M.K. Dalal, R.N. Ram, J. Mol. Catal. A: Chem. 109 (2) (1996) 141.