LIST OF PUBLICATIONS

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1) Hydrogenation of 1-hexene using polymer supported Pd(II) complex as catalyst.
Mahesh K. Dalal and R.N.Ram
European Polymer Journal, 33 (9), (1997) 1495.

2) Preparation, properties and catalytic application of polymer-bound Ru(III) complexes.
Jacob John, **Mahesh K. Dalal**, Dilip R. Patel and R.N.Ram,
Journal of Macromolecular Science - Pure and Applied Chemistry, A 34(3), (1997) 489.

3) Oxidation of cyclohexane using polymer bound Ru(III) complexes as catalysts,
Jacob John, **Mahesh K. Dalal** & R.N.Ram
3rd World Congress on Oxidation Catalysis
Studies in surface science and catalysis,.
R.K.Grasseli , S.T.Oyama, A.M.Gaffeney and J.E.Lyons (Eds.) Elsevier, Amsterdam, **110** (1997) 1165

4) Preparation, characterization and catalytic activity of polymer supported Ru(III) complexes.
Dilip R. Patel, **Mahesh K. Dalal** and R.N.Ram.
Journal of Molecular Catalysis A :Chemical, 109, (1996), 141.

5) Synthesis, characterization and catalytic behaviour of polymer supported Ru(III) complex.
M.K.Dalal, D.R.Patel & R.N.Ram
Catalysis: Modern Trends
N.M.Gupta & D.K.Chakrabarty (Eds.), Narosa, New Delhi (1995) 503.

6) Oxidation of toluene using polymer supported Pd(II) complex as catalyst.
Dilip R. Patel, **Mahesh K. Dalal** & R.N.Ram.
Recent Advances in Basic and Applied Aspects of Industrial Catalysis,
Studies in Surface Science and Catalysis,
T.S.R. Prasada Rao and G. Murali Dhar (Eds.), **113**, (1998) 293.

7) Polymer anchored palladium(II) - diaminopropane complexes: Synthesis and catalytic behaviour.
Jacob John, **Mahesh K. Dalal** and R. N. Ram.
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HYDROGENATION OF 1-HEXENE USING POLYMER SUPPORTED Pd(II) COMPLEX CATALYST

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Abstract—Polymer supported Pd(II) complex catalyst was synthesised by chloromethylation of styrene–divinylbenzene copolymer (XAD-2), with sequential attachment of ethylenediamine and salicylaldehyde, followed by treatment with an ethanolic solution of palladium chloride. The synthesised catalyst, named 2PS, was characterised by various techniques, such as UV-vis reflectance spectroscopy, IR, SEM, TGA and ESR. Other physico-chemical properties, such as surface area (by the BET method), moisture content, bulk density and swelling by different solvents, have been studied. The catalytic activity of the catalyst was investigated for hydrogenation of 1-hexene by varying different parameters, such as temperature, amount of the catalyst and concentration of 1-hexene. © 1997 Elsevier Science Ltd

INTRODUCTION

Heterogenising a homogeneous metal complex by supporting it on a polymer has received wide attention in recent years [1]. It is a suitable method for solving practical problems, such as corrosion, catalyst recovery and plating out on the reactor wall [2]. We have carried out studies of catalytic activity of various metal complexes anchored to different functionalised polymer supports and mainly chelating amines were used as ligands [3–7]. It was therefore planned to synthesise a Pd(II) complex catalyst on to the surface of styrene–divinylbenzene copolymer using a Schiff base as the ligand and to investigate the catalytic activity for the hydrogenation of 1-hexene. The influence on the activity of various parameters have also been observed.

EXPERIMENTAL

Materials

Styrene–divinylbenzene copolymer (XAD-2), procurred from Fluka AG, was purified by soxhlet extraction using ethanol–benzene (1:1) mixture and dried at 70°C. THF, dioxane, methanol and 1-hexene were purified as reported in Ref [8]. 1,2-Dichloroethane, ethylenediamine and salicylaldehyde were distilled before use. Aluminium chloride was purified by sublimation. $PdCl_2$ (Lobachemie, Bombay) was used as received.

Equipment

Elemental analyses were carried out in our laboratory using a coleman analyser unit. UV-visible reflectance spectra of solid samples were recorded using a Shimadzu UV-240. IR spectra of the catalyst were recorded on a Beckman IR-4220. The surface area was determined using a Carlo-erba strumenzione and TGA on a Shimadzu DT-30. The EPR spectrum was scanned using a Breaker ESP-300 K band spectrometer using a 100 kHz field modulation. The EPR measurement was conducted on a powdered sample at 298 K in an atmosphere of nitrogen. A SEM was recorded on a Jeol SJM T-300 Swelling studies of the catalyst were carried out using polar and non-polar solvents at a constant temperature. The detailed procedure has been described earlier [3].

Synthesis of the catalyst

XAD-2 beads dried at ~70°C was chloromethylated using dry HCl gas, paraformaldehyde, acetic anhydride and 1,2-dichloroethane as a solvent, using anhydrous $AlCl_3$ as a catalyst. The chlorine content was found to be 5.3%

In order to functionalise the polymer support with the Schiff base, chloromethylated XAD-2 was treated with an appropriate quantity of ethylenediamine, using THF as a solvent at room temperature for 48 hr [3]. The beads were washed with deionized water, methanol and dry dioxane and dried at 60°C. It was then refluxed in a solution of salicylaldehyde prepared in benzene for 24 hr [9]. The liganded polymer was then purified with methanol using the soxhlet extraction method and dried at 80°C.

The percentage of C, H and N after ligand introduction were found to be 80.39, 6.52 and 2.52, respectively.

The functionalised polymer was kept in contact with ethanol for 30 min and an ethanolic solution of $PdCl_2$ (0.5% w/v) was added to it and kept at room temperature for seven days. The colour of the beads became yellow. The catalyst was washed with ethanol and dried in vacuum at 70°C. The quantity of Pd present on the surface of the polymer was estimated by a spectrophotometric method using nitroso-R-salt as a complexation material [10]

The unbound complex [Pd(II) Sal_2en]Cl_2 was obtained by mixing a 1.1 mixture of $PdCl_2$ and Sal_2en in ethanol.

Kinetics of hydrogenation of 1-hexene

The procedure adopted to investigate the kinetics of hydrogenation has already been described [3]. The quantity of hydrogen uptake was measured at different intervals of time. The initial rate was calculated from the slope of the plot of hydrogen uptake against time.

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Table 1 Physical properties of the catalyst 2PS

(a) Physical properties	
Particle size	0 5 mm
Surface area (NTP)	222 06 m^2 g^{-1}
Pore volume	0 46 cm^3 g^{-1}
Apparent bulk density	0 38 g cm^{-3}
Moisture content	0 35 wt%
Elemental analysis (wt%)	C 82 21, H 6 63, N 1 31 Pd 9 57 × 10^{-2}

(b) Swelling studies of the catalyst 2PS	
Solvent	*Swelling (mol%)*
Methanol	2 37
Ethanol	1 98
Dioxane	1 53
DMF	1 23
Cyclohexane	1 21
THF	1 11
Acetone	1 07
Dichloromethane	1 05
Benzene	1 03
n-hexane	0 62

RESULTS AND DISCUSSION

Physical properties

Physical properties of the catalyst 2PS are given in Table 1(a). A decrease in surface area observed after loading the metal ion on to the polymer support (surface area of the support 360 m^2 g^{-1} and that of the catalyst 2PS 222 06 m^2 g^{-1}) might be due to blocking of the pores of the polymer support after ligand and metal ion introduction. This is in accordance with earlier results [3, 5]. A decrease in swelling is observed as the nature of the solvent changes from polar to non-polar. Methanol was found to be a suitable swelling agent and was therefore employed as a solvent for hydrogenation of 1-hexene.

Thermal stability of the catalyst

The thermal stability of 2PS and the support was studied using TG analysis and both were found to be stable up to 120°C (Fig. 1). Initial weight loss might be due to moisture content, whereas degradation of the polymer results in weight loss at high temperature. It was concluded that the catalyst could be used safely up to 110°C.

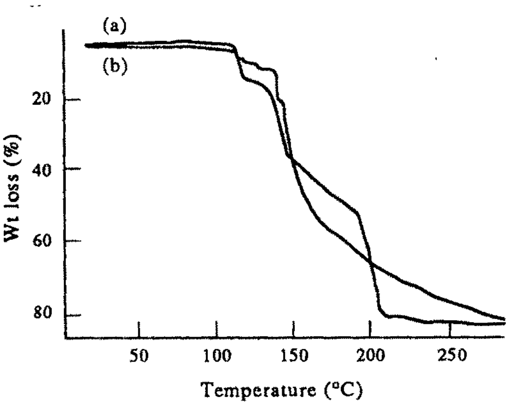


Fig. 1. TG curves of (a) the polymer support and (b) the catalyst 2PS

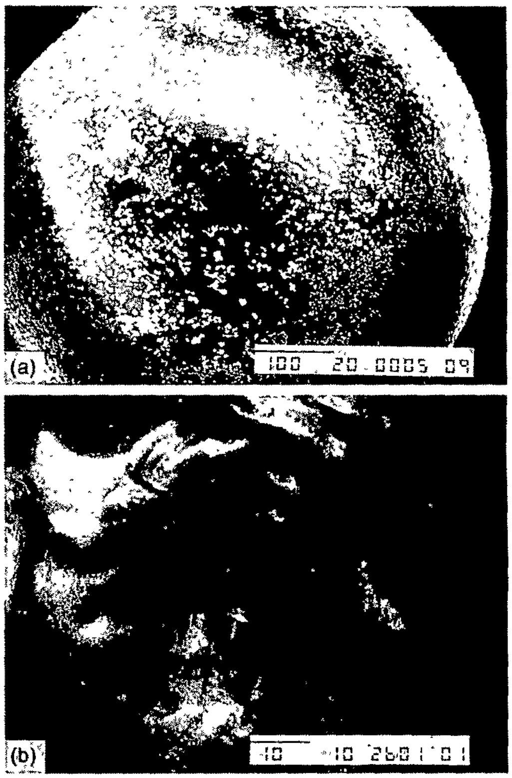


Fig 2. Scanning electron micrographs of (a) the polymer support and (b) the catalyst 2PS.

Morphology of the catalyst

The morphology of 2PS, as well as the polymer support, was studied using a scanning electron microscope [Fig. 2(a) and (b)] A clear change in morphology is observed after anchoring the metal complex on the polymer support

Spectroscopic studies

The UV-visible reflectance spectra of 2PS gave a broad peak at 400 nm, which might be due to the d–d transitions of Pd(II). Its homogeneous counterpart also shows a peak at 400 nm, which indicates that palladium is present in the +2 oxidation state in both cases. The inactive EPR spectrum

Table 2. Summary of the kinetics of hydrogenation of 1-hexene using polymer supported Pd(II) complex*

[Pd] (mol L^{-1})10^6	*n*-hexene (mol L^{-1})10^3	Temp (°C)	Rate (mL min^{-1})
5.74	8.00	35	0.050
7 66			0 080
9.57			0 083
11 49			0 093
9 57	2 00	35	0.050
	4 00		0 073
	6 00		0 080
	8 00		0 083
9 57	8 00	25	0.053
		30	0 067
		35	0.083
		40	0 099

*Volume of methanol 20 mL, pressure 1 atm

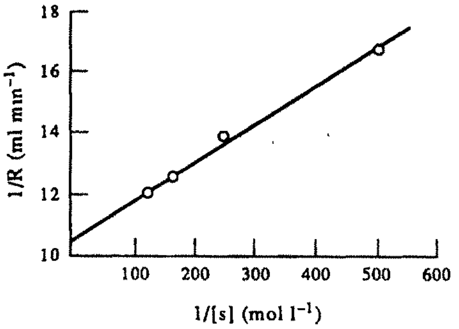
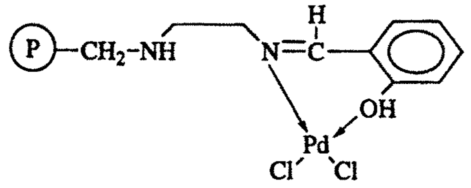


Fig 3. Plot of 1/rate vs 1/[1-hexene] for the catalyst 2PS.

of the unbound palladium-Schiff base complex further confirms the presence of palladium in the +2 oxidation state. Various IR frequencies were assigned as ν(N—H) = 3380 cm^{-1}, ν(C═N) = 1604 cm^{-1}, ν(Pd—N) = 440 cm^{-1}, ν(Pd—O) = 320 cm^{-1} and ν(Pd—Cl) = 262 cm^{-1}, which confirms the formation of the metal complex on the surface of the polymer.

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



Hydrogenation of 1-hexene

The influence of various parameters on the rate of hydrogenation of 1-hexene was studied (Table 2). While using the same amount of the unbound metal complex for hydrogenation of 1-hexene, a very small change was found in the hydrogen uptake, indicating lower catalytic activity in the homogeneous system than that of supported on the polymer.

Effect of 1-hexene concentration

The influence of 1-hexene concentration on the rate of hydrogenation was determined in the range of 2.00×10^{-3} mol L^{-1} to 8.00×10^{-3} mol L^{-1}, at a constant catalyst concentration of 9.57×10^{-6} mol L^{-1} of Pd at 35°C and 1 atm. pressure (Table 2). It was observed that the rate of hydrogenation varies linearly with substrate concentration. The order of reaction calculated from the linear plot of log (initial rate) vs log [1-hexene] was found to be fractional (plot not given). A linear plot of 1/rate vs 1/[1-hexene] for the supported catalyst (Fig. 3) indicates that the rate of hydrogenation of 1-hexene, R, is related to the concentration of 1-hexene [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.

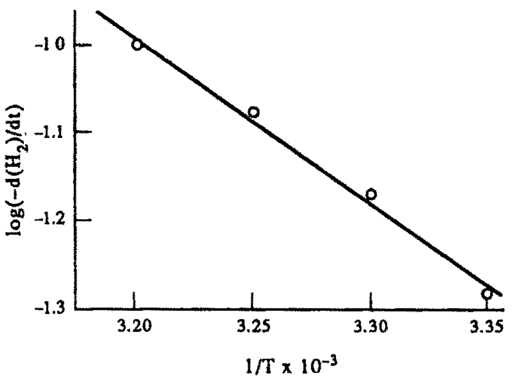


Fig. 4. Arrhenius plot for the catalyst 2PS.

Effect of catalyst concentration

The influence of concentration of the catalyst on the rate of hydrogenation of 1-hexene was investigated over a range of 5.74–11.49×10^{-6} mol L^{-1} of Pd(II) at 35°C, 1 atm. pressure and a substrate concentration 8.00×10^{-3} mol L^{-1} (Table 2). The order of the reaction obtained from the plot of log (initial rate) vs log [catalyst] was found to be fractional with respect to catalyst concentration. The reason might be due to the non-availability of catalytic sites, or due to the lack of swelling of the catalyst and steric hinderance.

Effect of temperature

The kinetics of hydrogenation of 1-hexene were also studied at various temperatures in the range of 25–40°C, keeping all other parameters constant, and the rate was found to be dependent on temperature. The energy of activation calculated from the Arrhenius plot (Fig. 4) was found to be 36.06 kJ mol^{-1}.

CONCLUSION

The study shows that the synthesised polymer bound complex has a higher catalytic activity than its homogeneous counterpart for the hydrogenation of 1-hexene. The mechanism is under investigation.

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