RESEARCH PUBLICATIONS

LIST OF PUBLICATIONS

1. "A study of synthesis, characterization and catalytic hydrogenation by polymer anchored Pd(II)-amino acid complexes"
V.B. Valodkar, G.L. Tembe, M. Ravindranathan, R.N. Ram and H.S. Rama
Journal of Molecular Catalysis: A Chemical (Accepted, In press). 2003, 202, 47-64.

2. "Catalytic epoxidation of olefins by polymer anchored amino acid ruthenium complexes"
V.B. Valodkar, G.L. Tembe, M. Ravindranathan and H.S. Rama
Reactive & Functional Polymers (Accepted, In press). 2003, 56, 1-15.

3. "Catalytic hydrogenation by recyclable supported Pd(II)-amino acid complex"
V.B. Valodkar, G.L. Tembe, M. Ravindranathan, R.N. Ram and H.S. Rama
Reaction Kinetics & Catalytic Letters (Accepted, In press).

4. "Asymmetric epoxidation of unfuctionalized aliphatic olefins by polymer supported Mn(II) & Ru(III) catalysts"
V.B. Valodkar, G.L. Tembe, R.N. Ram and H.S. Rama
***New Journal of Chemistry*, RSC** **(Communicated).**

5. "Polymer supported copper(II)-L-valine complexes, synthesis, characterization and catalytic oxidation"
V.B. Valodkar, G.L. Tembe, M. Ravindranathan, R.N. Ram and H.S. Rama
Journal of Molecular Catalysis: A Chemical **(Accepted).**

6. "Catalytic oxidation by polymer anchored amino acid-ruthenium complexes"
V.B. Valodkar, G.L. Tembe, M. Ravindranathan and H.S. Rama
Journal of Molecular Catalysis: A Chemical **(Accepted).**

7. "Catalytic asymmetric epoxidation of unfunctionalized olefins by supported Cu(II)-amino acid complexes"
V.B. Valodkar, G.L. Tembe, R.N. Ram and H.S. Rama
Catalysis Letters **(Accepted).**

8. "Synthesis, Characterization and Catalytic activity of polymer anchored amino acid Mn(II) Complexes"
V.B. Valodkar, G.L. Tembe, M. Ravindranathan, R.N. Ram and H.S. Rama
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A study of synthesis, characterization and catalytic hydrogenation by polymer anchored Pd(II)-amino acid complexes

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Abstract

L-Valine was anchored to 6% and 8% cross-linked poly(styrene-divinyl benzene) resin and its complex with palladium chloride was prepared. The newly synthesized catalysts were characterized by various techniques such as elemental analysis, FT-IR, DRS, SEM and TGA. Physico-chemical properties like surface area, swelling behavior in different solvents, bulk density, etc have been determined. The polymer supported Pd complexes behave as versatile and recyclable catalysts for the hydrogenation of 1-octene, cyclohexene, acetophenone and nitrobenzene. Kinetics of hydrogenation of 1-octene has been investigated in detail. The influence of different reaction parameters on conversion and selectivity to products are reported.
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Keywords Amino acid supported Pd catalysts, Hydrogenation, Catalytic activity, Reusable catalysts, High pressure kinetics

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1. Introduction

Interest in the preparation of active transition metal complexes immobilized on polymeric matrix originated with efforts to develop industrially competitive homogeneous catalysts. The potential advantages to be gained from the heterogenization or anchoring process stem from overcoming separation and recycling problems thereby facilitating convenient operation in flow reactors for continuous production [1].

Cross-linked poly(styrene-divinylbenzene) resin is one of the most widely used macromolecular support for functionalization and attachment to various metal ions. Polymer supported catalysts for hydrogenation of organic substrates, notably involve complexes of Rh(I) [2–4] and Ru(II) [5,6]. These have been studied as mimics of their homogeneous counterparts which include, amongst others Wilkinson's hydrogenation catalyst. On the other hand complexes of Pd though extensively employed in catalytic carbon–carbon bond formation reactions [7] their application in hydrogenation has been limited. The earliest work on Pd supported catalysts involved the use of a cationic $[Pd(NH_3)_4]^{2+}$ complex anchored on sulphonated polystyrene [8] The catalyst was effective in olefin hydrogenation reaction only after reducing Pd(II) by

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hydrazine to a finely dispersed metallic Pd(Pd^0) on the support. Later examples of supported Pd(II) catalysts utilized polystyrene functionalized with phosphine [9–12], 2,2′-bipyridyl [13,14] and anthranilic acid [15–17] as ligands. The catalytic activity of these systems is greatly influenced by the nature of ligand bound to the polymeric backbone, type of olefinic substrate, percentage cross-linking, polarity of solvent, etc.

The chemical modification of polystyrene-divinylbenzene incorporating bifunctional ligand, such as an amino acid (N,O donor set) has not been well studied. Because of the presence of reactive amino and carboxylic end groups application of conventional immobilization methods for optically active amino acids often lead to formation of complex mixtures posing product separation as a major challenge.

Literature search revealed one of the first instance of an amino acid complex of Cu(II) bound to cross-linked poly(styrene-divinylbenzene) resin [18]. This study indicated that about 15% of the benzene rings in the styrene-divinylbenzene co-polymer were substituted by α-amino acids, such as proline, threonine, phenylalanine, etc. No catalytic activity was however, reported.

In continuation of our work on the catalytic application of bidentate Schiff base (N,O donor) polymer-metal complexes [19,20] we have in the present work, evolved a simple synthetic route for anchoring an amino acid L-valine on moderately cross-linked chloromethylated poly(styrene-divinylbenzene) matrix followed by complexation with divalent Pd(II) metal ion. These newly synthesized heterogenized catalysts were evaluated for their performance in hydrogenation of 1-octene and other substrates. The effect of various reaction parameters on hydrogenation as well as the kinetics of this reaction with 1-octene as model substrate has been studied both at ambient and higher pressures.

2. Experimental

2.1. Materials

Chloromethylated poly(styrene-co-divinylbenzene) as spherical beads with 6% and 8% cross-link (18–44 mesh, chlorine content 16% and 17.5%, respectively) were received from Ion-Exchange India Ltd. The commercial resin was pretreated with aqueous dioxane (50:50 (v/v)) and finally washed with methanol and dried under vaccum at 90 °C for 8 h before chemical functionalization. $PdCl_2$ (Loba chemie, Bombay), L-valine (Merck), 1-octene (Merck), acetophenone (Merck), nitrobenzene (Merck) and cyclohexene (Fluka) were used as received. A.R grade 1,4-dioxane, methanol, acetonitrile and ethanol were freshly distilled using standard methods prior to use [21].

2.2. Measurements

Elemental analyses of polymer metal complexes were carried out using a Carlo-Erba Strumentazione microanalyser. The total Pd content on the polymeric support after loading was estimated using an Optima 4300DV Inductively Coupled Plasma Emission Spectrometer (Perkin-Elmer). Chlorine content was estimated gravimetrically by precipitation of chloride as AgCl. Surface area of supports and the Pd-anchored polymer was determined on a Carlo-Erba surface analyzer employing BET relationship. UV-visible reflectance spectra of catalysts were recorded on a Perkin-Elmer UV-Vis-NIR Lambda 19 instrument using spectroscopic grade $BaSO_4$ as a reference. UV-Vis spectra in solution (200–900 nm) were recorded on Shimadzu UV 2201 spectrophotometer. IR and Far-IR spectra of polymer supported Pd-complexes at various stages of synthesis were recorded on a Nicolet Magna 550 spectrophotometer. Thermo gravimetric analyses of compounds were carried out on Shimadzu DT-30 instrument at a heating rate of 10 °C min^{-1} under an atmosphere of nitrogen. Scanning electron micrographs of catalysts and supports were taken on a CAMICA SU30 instrument with SE electrode at 20 kV. The analyses of various liquid products obtained in the catalytic hydrogenation reactions were carried out on Shimadzu 15A gas chromatograph using a 15% Carbowax column (1/8 in. × 2 M) and Data lab GC 9000 using capillary column DB-5 (0.547 mm × 30 M) attached to a flame ionization detector and N_2 as carrier gas. Product identification was also carried on a Finnigan MAT 9001 GCQ-GC/MS system operated in the full scan mode and a quadrupole ion trap mass analyzer. The swelling behavior of supported catalysts in representative polar and non-polar solvents was carried out at 27 ± 1 °C by a procedure described previously [22].

2.3. Synthesis of polymer anchored amino acid

Pre-washed chloromethylated styrene-divinyl benzene copolymer beads (12 g) were allowed to swell in 35 ml methanol for 1 h. An aqueous solution of L-valine (9 g) in 250 ml distilled water was separately prepared. The swollen polymer in methanol and the amino acid solution were refluxed for 16 h in presence of pyridine. The overall molar ratio of different reagents based on percent replaceable chlorine on resin approximately corresponds to 1:1.25:1.25 for Cl:amino acid:base. The contents were cooled and kept aside for one week with occasional shaking. At the end of this period, pH of the reaction mixture came down from the initial value of 7.1–5.1. The colour of the beads changed from off-white to pale yellow indicating the attachment of the amino acid. Finally the L-valine linked polymer beads were filtered, washed with hot water followed by ethanol and finally dried under vacuum at 90 °C for 8 h to yield 13.8 g of product.

In order to confirm the presence of free –COOH group after functionalization of L-valine through amino group on the polymer support, a known weight of the dry resin (8% poly(S-DVB)L-val, 0.5 g) in 30 ml of distilled water was refluxed for 10–12 h in presence of excess NaOH (10 ml, 0.1 N) containing a few drops of phenolphthalein indicator. Upon cooling, the solution was filtered, washed carefully with 2 ml × 5 ml portions of water and the filtrate back titrated with 0.1 N HCl. A simple calculation based on titer values showed that about 2.46% N equivalent to 1.76 mmol L-valine to be anchored per gram of polymer. In the case of 6% poly(S-DVB)L-val, this value was 2.43% N (1.74 mmol L-val/g). Independently estimated nitrogen from microanalysis of the same samples (Table 2) gave values of 2.56% N (1.83 mmol L-val/g) and 2.47% N (1.76 mmol L-val/g), respectively. The close agreement of these results thus allowed to quantify unambiguously the extent of amino acid loading on the cross-linked polymeric support.

2.4. Palladium loading

The loading of palladium on the polymer was carried out as follows: P(S-DVB)L-val (12.5 g) was kept in contact with ethanol (50 ml) for 45 min. To this was added an ethanolic solution (100 ml) of palladium(II) chloride (1.5 g, 8.4 mmol); the contents gently agitated on a shaker at constant speed for 8 days at 25 °C (pH = 2.5). The colour of the beads changed from pale yellow to brown during this period indicating the formation of metal complex on the polymer matrix (pH of the solution remained around 2.7 after 8 days.) At the end of this period the brown colored polymer was filtered, washed thoroughly with ethanol, dioxane and methanol to ensure the removal of any unreacted metal chloride and dried in vacuum for 6 h at 90 °C.

2.5. Catalytic hydrogenation

Hydrogenation reactions were carried out in a 160 ml Parr stainless steel autoclave and a motor driven stirrer. The reactor was connected to a Parr 4842 process controller having a digital readout for measuring temperature, pressure and stirrer speed. At the end of specified time, the contents were analyzed by GC. Control experiments in the absence of catalyst showed practically no (<0.1%) reduction of substrate. Peak positions of various reaction products were compared and matched with the retention times of authentic samples. Identity of the products was also confirmed by GC–MS.

In a typical experiment 100 mg of Pd A and 30 ml of methanol were taken in the reactor and allowed to swell for 30 min. Then 10 mmol (1.55 ml) of 1-octene were added and pressurized with hydrogen to 200 psi at 50 °C and agitator set at 300 rpm. After 6 h the reaction was stopped, reactor cooled to room temperature and excess pressure was carefully vented. Reactions in which 1-octene concentration was varied, the total volume of substrate and methanol were maintained constant to ~31.6 ml by adjusting the volume of methanol.

3. Results and discussion

3.1. Grafting of L-valine

The earlier methods for anchoring amino acid to chloromethylated (PS-DVB) employed one of the following procedures:

(a) Iodomethylation of the resin followed by reaction with amino acid [23].
(b) Reaction of amino acid with the polymer in presence of NaI and a tertiary amine [24].
(c) Reaction of sodium salt of amino acid with chlorosulfonated polymer [18,25].

The reported yields in these procedures varied widely depending on the nature of α-amino acid. Moderately good attachment was claimed in the case of reaction with chlorosulfonated polystyrene. Poor yields were noted with other methods.

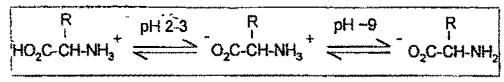
In the present work initial experiments to react L-valine with chloromethylated poly (S-DVB) in aqueous as well as in methanolic solution including reflux conditions for several days were unsuccessful. After several screening experiments, the reaction of amino acid and Merrifield's resin in presence of pyridine as a base showed encouraging result. Using slightly more than molar excess of L-valine and pyridine satisfactory grafting on the resin could be achieved (Table 2). Analysis for nitrogen after ligand attachment gave values of 2.56 and 2.46%, respectively, for 8 and 6% cross-linked supports. This corresponds to 1.83 and 1.76 mmol of L-valine anchored per gram of support. In a control experiment pyridine was reacted with Merrifield's resin in absence of amino acid under identical conditions. After the usual work up analysis of the resin treated with pyridine did not show any nitrogen. This indicates that there is no side reaction taking place in presence of pyridine and the observed nitrogen percent in liganded resin entirely comes from the anchored amino acid fragment. This was further confirmed by estimation of the free carboxylic groups on the resin which would be equivalent to the amino acid loaded, the details of which are given in the Section 2.

In a related experiment effort for *N*-functionalization of L-valine using K_2CO_3 in aqueous methanolic solution as described in a previous report was not effective in our case [26]. Further, indirect verification of mode of linkage was arrived at by reacting benzyl chloride with valine giving *N*-benzyl valine (mp = 255 °C) [26,27] which supports that ligand attachment on polymer occurs from the amine end. The probability of C-alkylation [28] of L-valine under these conditions is thus overruled. The synthetic protocol is depicted in Scheme 1.

3.2. Complex formation

The reaction of palladium chloride with polymer anchored L-valine was conducted in the pH range of 2.5–2.6 at a metal:ligand molar ratio of 1:2 (based on mmol L-valine anchored). A maximum Pd loading of up to 3.06% was obtained (Table 2). Estimation of chlorine content on complex formation showed an increase of 2.10% for 8% cross linked polymer and 2.23% for 6% cross linked polymer.

It is known from literature that amino acids undergo two reversible proton ionization steps, viz.



$$HO_2C\text{-}\overset{R}{C}H\text{-}NH_3^+ \xrightleftharpoons{pH\ 2\text{-}3} {}^-O_2C\text{-}\overset{R}{C}H\text{-}NH_3^+ \xrightleftharpoons{pH\ \sim 9} {}^-O_2C\text{-}\overset{R}{C}H\text{-}NH_2$$

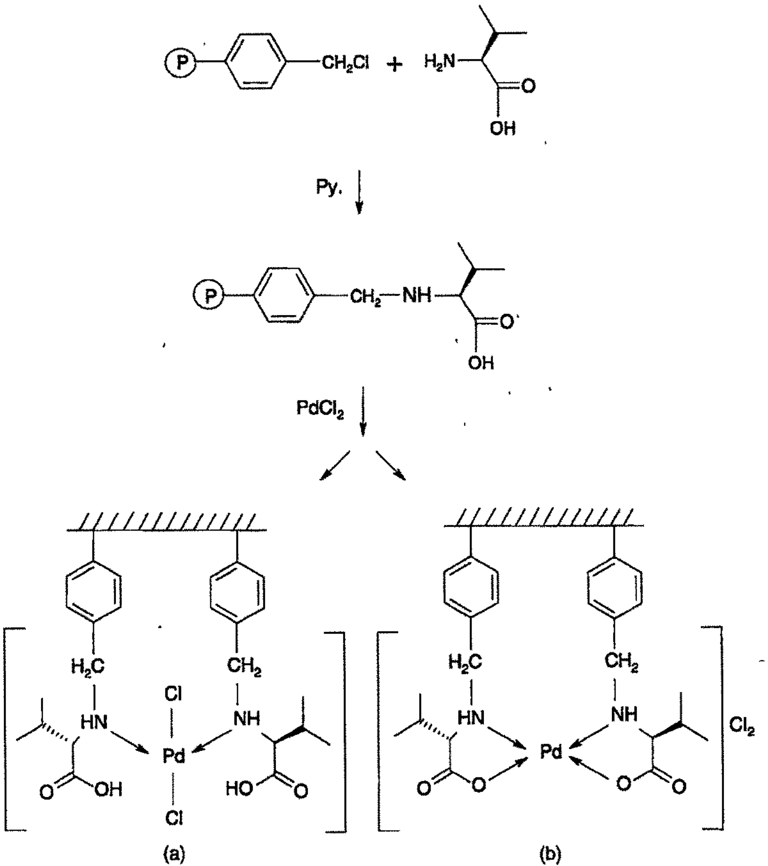
Consequently depending on the solution pH, L-valine can coordinate to metal ion through either or both of amino (NH_2) or carboxyl (CO_2^-) groups. Moreover, the order of stability constants for transition metal ions follows the Irving-Williams series [29]. For the bivalent Pd^{+2} ion, it is expected that the formation of Pd(L-val)$_2$Cl$_2$ type of complex may be favored with essentially square planar configuration around the central metal ion [30]. Based on pK_a values Gillard et al. reported (N, O) chelation for different amino acid complexes at lower pH range [31]. The two polymer anchored Pd complexes used in the present work for catalytic reduction of olefins, ketones and nitro compounds are designated as under

Pd **A** : 8% poly(S-DVB)l-val Pd(II) complex

Pd **B** : 6% poly(S-DVB)l-val Pd(II) complex.

3.3. Catalyst characterization

Some of the important physical properties of these catalysts have been measured and the data compiled in Table 1. Pd **B** has a slightly higher surface area and larger pore volume than Pd **A**. The metal loading on Pd **A** with 8% cross-link (Pd 2.93%) was lower than Pd **B** with 6% cross-link (Pd 3.06%) (Table 2). There is a noticeable decrease in surface area of the supports by 5–10% after loading of Pd salt indicating some pore blocking of polymer support after introduction of metal ions. Similar results have been reported for other surface modified polymeric catalysts [32,33].



Scheme 1. Synthesis of poly(S-DVB) supported amino acid Pd(II) complex

The results of swelling behavior indicate that swellability increased in polar solvents than in non-polar aliphatic and aromatic hydrocarbon solvents. Both Pd **A** and Pd **B** show lower swelling in polar as well as non-polar solvents compared to unfunctionalized (starting) resin (Table 3).

In order to ascertain the attachment of amino acid and the metal on the polymer support IR spectra were

Table 1
Physical properties of Pd-supported poly(S-DVB) catalysts

Sample	Surface area ($m^2\,g^{-1}$)	Bulk density ($g\,cm^{-3}$)	Pore volume ($cm^3\,g^{-1}$)
8% poly(S-DVB)CH_2Cl	32.7	0.44	0.20
6% poly(S-DVB)CH_2Cl	38.3	0.38	0.29
Pd **A**	22.6	0.52	0.14
Pd **B**	32.2	0.46	0.21

Table 2
Analytical data of polymer support, ligand and Pd-anchored catalysts

Compound	C%	H%	Cl%	N%	Pd%
8% poly(S-DVB)CH_2Cl	70.38	5 77	17.56	–	–
6% poly(S-DVB)CH_2Cl	76 26	6 36	16 14	–	–
8% poly(S-DVB)-L-val	60 15	5 00	9 47	2 56	–
6% poly(S-DVB)-L-val	63 28	5 44	9.48	2 47	–
Pd **A**	56 20	5 10	11 57	2 59	2.93
Pd **B**	57 41	5 19	11 71	2 55	3.06

recorded separately in mid (4000–400 cm^{-1}) and far IR (600–30 cm^{-1}) regions at different stages of synthesis. The sharp C–Cl peak (due to $-CH_2Cl$ group) at 1261 cm^{-1} in the starting polymer was practically absent or seen as a weak band after introduction of valine on the support. A strong band at 3423 cm^{-1} in poly (S-DVB)-L-valine is assigned to –NH (secondary amine) vibration. Medium intensity band due to C–N stretching appears at 1082 cm^{-1} both in the supported ligand and the catalysts. A slight shift in the –NH structural band (~7–10 cm^{-1}) in Pd **A** and Pd **B** indicates the coordination of 'N' of amino acid to the metal [34]. Representative IR spectra of polymer supports and catalysts are shown in Fig. 1. Two characteristic strong absorptions due to ν_{asym} COO^- structure and ν_{sym} COO^- structure of carboxylic group are seen at 1633 and 1485 cm^{-1}, respectively, in the ligands. There is a slight positive shift in the ν_{asym} COO^- structure in Pd **A** and Pd **B** and appears at 1639–40 cm^{-1}. This indicates possible metal-oxygen interaction on complexation. Weak bands in the far IR region at ~300–310 cm^{-1} and 440–460 cm^{-1} have been assigned to ν Pd-Cl and ν Pd-N vibrations. The intensities of these bands are considerably affected due to lower metal loadings on the support. Bidentate N,O coordination has been confirmed for simple amino acid complexes of palladium by CD and IR spectra by other workers [36–38]. From the elemental analysis (Pd, N, and Cl) and spectral data two possible structures [(a) and (b)] can be proposed for the above complexes which are shown in Scheme 1.

The diffuse reflectance spectra (200–800 nm) of Pd **A** and Pd **B** display nearly identical features with two strong absorption bands in the UV region at 303 and 340 nm and weak and broad bands in the visible region at ~435 and 560 nm with reference to the $BaSO_4$ standard (Fig. 2). Absorption spectrum of neutral Pd(II) complexes are generally characterized by ligand–metal charge transfer d–p transition. The observed spectral features are consistent with Pd(II) [d^8] diamagnetic species [39–41].

Scanning electron micrographs (SEM) at various stages of preparation of the polymer supported L-valine and the palladium complexes were recorded to understand morphological changes occurring on the surface of the polymer. Scanning was done at 50–100 μm range across the length of the polymer beads. Comparison of images taken at a magnification of ~ 5 × 10^3 showed that the smooth and flat surface of the starting poly (S-DVB) (Fig. 3a) is distinctly altered, exhibiting considerable roughening of the top layer upon anchoring of the amino acid (Fig. 3b). After metal incorporation, randomly oriented depositions on the external surface of the resin were seen (Fig. 3c and d). Porosity of chloromethylated (S-DVB) copolymer beads being relatively low, the complex formation reaction with L-valine occurs at the surface only.

Table 3
Swelling study (mol%)

Solvent	8% poly (S-DVB)CH_2Cl	8% poly (S-DVB)CH_2Cl	Pd **A**	Pd **B**
Acetonitrile	1.99	2 02	1 70	1 78
Benzene	1 07	1 11	0 95	0 98
Dichloromethane	1 48	1 77	1 07	1 37
Ethanol	1 70	1.90	1 30	1 85
n-Heptane	0 58	0 59	0.39	0 49
Methanol	2.73	2 82	2 08	2 60
Tetrahydrofuran	1 44	1.53	0.95	1 11
Toluene	1.08	1 13	0 66	0 86

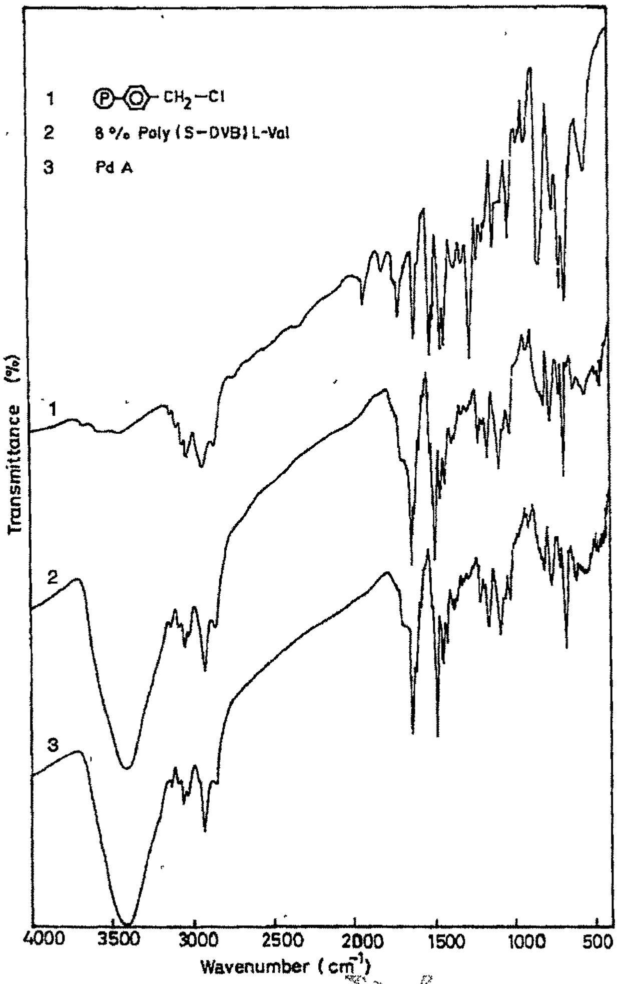


Fig. 1. FT-IR spectra of: **1** 8% poly(S-DVB)CH$_2$Cl; **2** poly(S-DVB)L-Val; and **3** Pd **A**.

A single step degradation peak in the TG was observed for the unsupported polymer in the 410–440 °C temperature range. On the other hand both palladium supported catalysts degrade at considerably lower temperatures as shown in Table 4. The variation in cross-linking in Pd **A** and Pd **B** does not however, show much deviation in their thermal stabilities as seen from the wt. loss which was between 20 and 22% at 360–370 °C. From the decomposition profile it appears that either the dissociation of covalently bound amino acid ligand moieties or a partial scission of polymeric chain might be occurring at this temperature. Some weight loss (~2%) was also observed at ~110 °C due to loosely bound surface moisture or volatiles on the surface of catalysts. These features are depicted in Fig. 4.

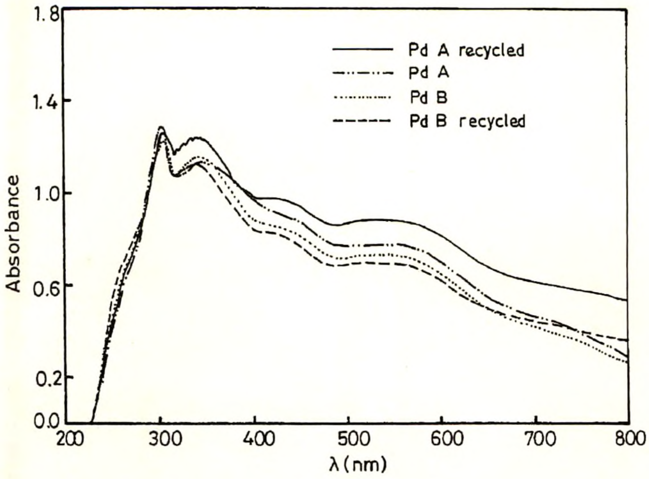
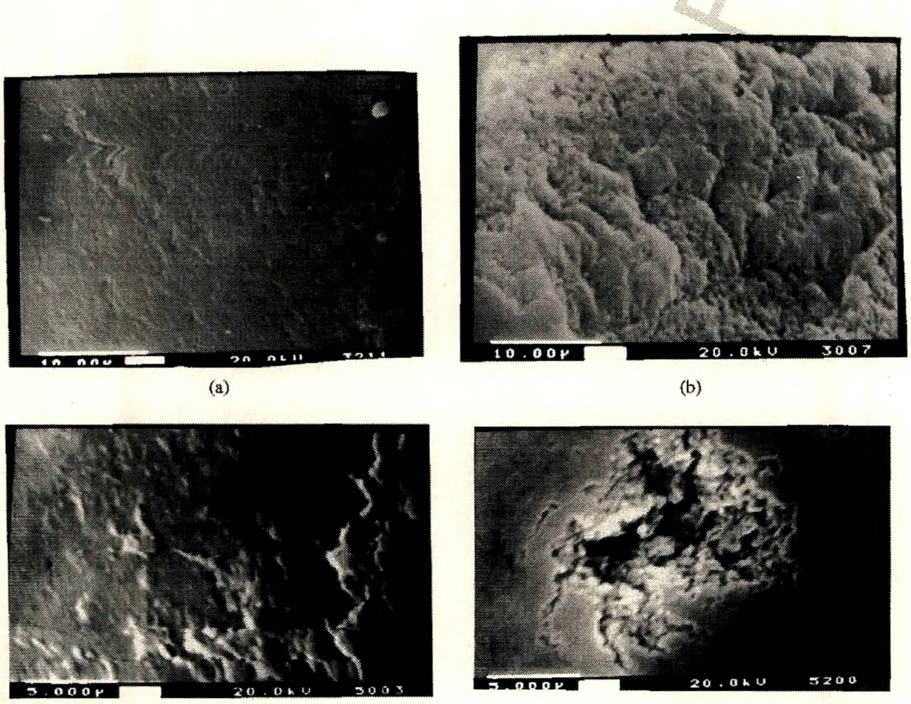


Fig. 2. Diffuse reflectance spectra of catalysts.



(a) (b) (c) (d)

Fig. 3. Scanning electron micrographs of (a) P(S-DVB)CH$_2$Cl, (b) 8% P(S-DVB) L-Val, (c) Pd **A**, and (d) Pd **B**.

Table 4
TG data of polymeric supports and anchored Pd(II) catalysts

Compound	Temperature (°C)	Loss (wt %)
8% poly(S-DVB)CH_2Cl	440	21 0
6% poly(S-DVB)CH_2Cl	410	21 0
Pd **A**	110	2.5
	360	20 0
Pd **B**	110	2 2
	372	22.0

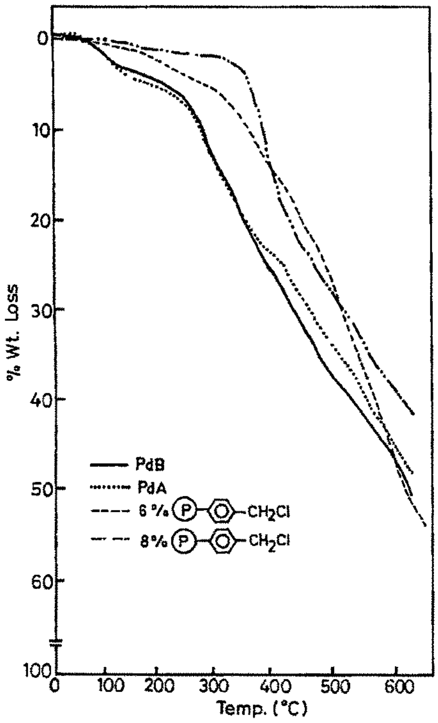


Fig 4 TG of chloromethylated 8 and 6% poly(styrene-divinylbenzene), Pd **A** and Pd **B**

Table 5
Catalytic reduction with Pd **A** and Pd **B**

Catalyst[a]	Substrate[b]	Yield (%)[c]	Products/ selectivity (wt %)	TON[d]
Pd **A**	1-octene	51 8	n-octane (100)	189
Pd **B**		50.1	n-octane (100)	175
Pd **A**	Cyclohexene	19 0	Cyclohexane (100)	69
Pd **B**		23.7	Cyclohexane (100)	83
Pd **A**	Nitrobenzene	22 1	Aniline (100)	81
Pd **B**		06.8	Aniline (100)	25
Pd **A**	Acetophenone[e]	24 0	1-phenyl ethanol (100)	89
Pd **B**		13 9	1-phenyl ethanol (100)	49

[a] 0 10 g (Pd = 2 7 × 10^{-5} M Pd)
[b] 10 0 mmol
[c] Yield based on starting material
[d] Turnover number mmol products/mmol Pd; time 6 h; solvent methanol (30 ml), temperature 50 °C, pressure 200 psi
[e] Reaction conducted in presence of ^{t}BuOK

3.4. Catalytic reduction

The performance of the supported palladium catalysts was evaluated in the hydrogenation of various substrates at constant temperature (50 °C) and pressure of hydrogen (200 psi). These results are summarized in Table 5. Both Pd **A** and Pd **B** catalyze the hydrogenation of 1-octene, cyclohexene, nitrobenzene and acetophenone with high selectivity to the corresponding reduced products. The reduction of acetophenone to 1-phenylethanol was carried out using potassium *tert*-butoxide as the base [42]. Yields obtained with Pd **A** were generally higher compared to Pd **B** and a maximum catalytic activity (~52%) was observed for 1-octene. After a brief induction period, the 1-octene conversions increase steadily with time under a fixed catalyst concentration and hydrogen pressure. This trend is depicted in Fig. 5. The reaction becomes slower after 3 h and reaches a plateau after ~5 h (conversion 51%). For a proper understanding of the efficacy of the present polymer supported catalysts vis-à-vis its homogeneous counterpart, for e.g. Pd(L-valine)$_2$ complex, direct comparison of catalytic activities under optimized reaction conditions is essential. In the absence of relevant data on hydrogenation of olefin using homogeneous amino acid-Pd catalysts, an attempt was made to generate in situ (without isolation) a simple L-valine complex of Pd(II) by mixing the ligand and $PdCl_2$ in 1:2 molar ratio in an aqueous solution at a pH of ~1.2. After a reaction period of 6 h (reaction temperature 50 °C) an aliquot of the solution containing equivalent amount of Pd as in 100 mg of the Pd **A** was taken up for subsequent hydrogenation of 1-octene. The overall yield was only slightly higher

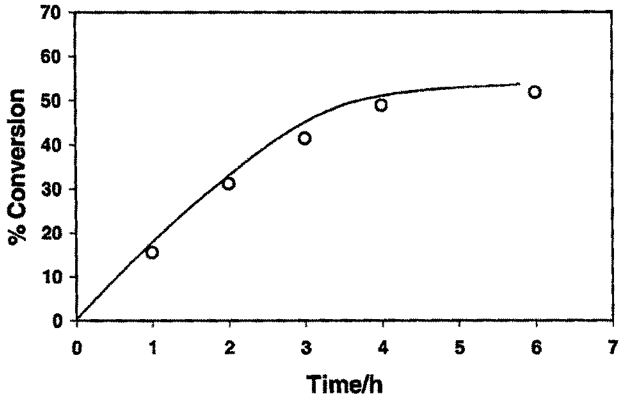


Fig 5. Plot of conversion as a function of time at 50 °C and 200 psi pH_2 using Pd A

than the supported catalyst. Additionally, comparative evaluation was also made with commercially available hydrogenation catalyst, 5% Pd on activated carbon. These results are shown in Table 6. Expectedly Pd/C gave higher yields than either Pd A or Pd(L-valine)$_2$.

The effect of operating conditions on the catalytic hydrogenation of 1-octene as model substrate was examined in detail with Pd A. From the results presented in Table 7, it can be seen that of the five different reaction variables studied, the effect of hydrogen pressure (H_2 concentration) is much more pronounced than other parameters. For instance no hydrogenation occurs in the absence of catalyst at 200 psi and 50 °C. However, in the presence of catalyst but at 15 psi (~1 atm) and 50 °C only 4.5% of *n*-octane was obtained (entry 4). Increasing the pressure to 400 psi (27.2 atm) while maintaining other conditions same a dramatic increase in the yield of *n*-octane (62%) was observed (entry 8). The variation in catalyst concentration from 10 mg (0.27×10^{-5} M Pd) to 100 mg (2.7×10^{-5} M Pd) at 50 °C and 200 psi H_2 shows an increase of 16% in the yields (entries 9–12). Only moderate increase in yields (~10%) is noticed by varying the temperature from ambient to 60 °C (entry 1–3). Similar trend is observed by varying the substrate concentration from 5 to 15 mmol. The nature of solvent also affects the reaction to a great extent. Whereas very high activities are realized using methanol as solvent, nearly complete inhibition of activity was observed in case of acetonitrile and dichloromethane as solvents. The swelling behavior for these solvents follows the sequence $CH_3OH < CH_3CN < CH_2Cl_2$ (Table 3) which partially explains the increased reactivity in methanol. Another possible reason for higher activity may be due to higher solubility of hydrogen in methanol under the experimental conditions [43].

Table 6
Hydrogenation of 1-octene with different catalysts

Entries	Catalyst	Yield (%)
1	Pd A	51.8
2	Pd(L-Val)$_2$ homogeneous	57.2
3	5% Pd on activated carbon	76.4

Reaction conditions same as given in Table 5

3.5. Kinetics of hydrogenation

Most of the previous works on kinetics of hydrogenation of olefins using polymer supported Palladium catalysts have been based on data generated at atmospheric pressure of hydrogen [13–15,44–47]. From a practical view point of process development it is necessary to understand the effects of hydrogen pressure on the reaction along with other operating parameters. Keeping this in mind we have made an attempt to investigate in detail the kinetics of high pressure hydrogenation of 1-octene to *n*-octane.

The hydrogenation reaction was followed by recording the hydrogen pressure drop with time at different

Table 7
Reduction of 1-octene using Pd A under different reaction conditions

Entry	Parameters	1-octene (mmol)	Catalyst weight (g)	Temperature (°C)	Pressure (psi)	Solvent	Yield (%)[a]
1	Temperature	10.0	0.100	25	200	CH_3OH	43.3
2		10.0	0.100	40	200	CH_3OH	49.6
3		10.0	0.100	50	200	CH_3OH	51.8
4		10.0	0.100	60	200	CH_3OH	54.0
5	Pressure	10.0	0.100	50	15	CH_3OH	4.5
6		10.0	0.100	50	100	CH_3OH	46.2
7		10.0	0.100	50	200	CH_3OH	51.8
8		10.0	0.100	50	300	CH_3OH	57.7
9		10.0	0.100	50	400	CH_3OH	61.7
10	Catalyst conc	10.0	0.010	50	200	CH_3OH	36.0
11		10.0	0.015	50	200	CH_3OH	43.1
12		10.0	0.050	50	200	CH_3OH	47.4
13		10.0	0.100	50	200	CH_3OH	51.8
14	Substrate concentration	5.0	0.010	50	200	CH_3OH	37.5
15		10.0	0.010	50	200	CH_3OH	36.0
16		15.0	0.010	50	200	CH_3OH	27.3
17	Solvent	10.0	0.100	50	200	CH_3CN	1.6
18		10.0	0.100	50	200	CH_2Cl_2	0.5
19		10.0	0.100	50	200	CH_3OH	51.8

[a] Yield based on starting material, reaction time: 6 h; solvent: 30 ml.

catalyst and substrate concentration and at different temperatures and H_2 pressures. As the total volume of solvent and substrate in the reactor was always maintained constant in all the experiments, it is assumed that the concentration of hydrogen in the solution is proportional to the H_2 pressure at a constant stirring rate. Thus the $\Delta p\,H_2$ values, which are proportional to the amount of *n*-octane produced, were calculated and these values were plotted as a function of time. This was also verified by analyzing the actual conversions of 1-octene to *n*-octane periodically during the reaction time of 6 h. Isomerization occurred to some extent even in the absence of hydrogen at room temperature but was not taken into account for quantification as the selectivity to *n*-octane after hydrogenation was in excess of 98%. Generally 15–20 min was allowed for dissolution of H_2 and the dip tube inside the reactor was isolated prior to charging of the gas. Since the conversion of 1-octene was low enough in the studied period of time, we have applied the initial rate method for estimating the initial rate from the plot of $\Delta p(H_2)$ values (which is proportional to *n*-octane produced) as a function of time [48]. Making allowance for the initial induction period initial rate r_i was determined from the slope of linear plot of $\Delta p\,H_2$ (atm) versus time between 1 and 3 h. Values for r_i under different sets of conditions for Pd A are collected in Table 8. Conventional linear regression software was employed for all straight line fits.

3.6. Effect of 1-octene concentration

The influence of 1-octene concentration on the rate of hydrogenation was studied at 50 °C and 200 psi (13.61 atm) H_2 pressure. The substrate concentration was varied between 0.5×10^{-2} and 6.5×10^{-2} M at a constant catalyst concentration of 0.27×10^{-5} M Pd (entries 7–9, Table 8). The initial rates show a direct dependence on 1-octene concentration Fig. 6(a). The order of reaction calculated from the plot of log (initial rate) versus log (1-octene) was found to be less than unity and equals 0.74 (Fig. 6b). This behavior suggests the possible formation of an intermediate complex with 1-octene through which the reaction might proceed. The order of reaction found from the linear fit was 0.69 and matches well with that determined experimentally [$-\log r_i = -\log(\text{1-octene})\,0.694 - 3.173$, $R^2 = 0.948$]. As would be expected the $1/r_i$ versus

Table 8
Kinetic data for the hydrogenation of 1-octene with Pd **A**

Entry	Pd × 10^{-5} (M)	1-octene × 10^{-2} (M)	$p(H_2)$ (psi)	Temperature (°C)	Initial rate, r_i × 10^{-5} (atm s^{-1})
1	0.27	1.0	200	50	4.38
2	0.41	1.0	200	50	4.79
3	1.37	1.0	200	50	4.95
4	2.74	1.0	200	50	5.20
5	0.27	0.5	200	50	1.57
6	0.27	1.0	200	50	2.75
7	0.27	1.5	200	50	4.38
8	0.27	3.2	200	50	5.48
9	0.27	6.5	200	50	4.36
10	2.74	1.0	15	50	ND
11	2.74	1.0	100	50	5.08
12	2.74	1.0	200	50	5.22
13	2.74	1.0	300	50	5.30
14	2.74	1.0	400	50	5.40
15	2.74	1.0	200	25	5.20
16	2.74	1.0	200	40	5.37
17	2.74	1.0	200	50	5.44
18	2.74	1.0	200	60	5.55

ND: not determined.

1/1-octene plot shows an intercept on the rate axis as shown in Fig. 6b.

3.7. Catalyst concentration

The concentration of Pd in Pd **A** was varied from 0.27 × 10^{-5} to 2.7 × 10^{-5} M (entries 1–4) while 1-octene concentration (10 mmol), temperature (50°) and pH_2 (200 psi) were kept constant. The initial rates show a direct dependence with respect to the catalyst concentration as indicated by the straight line plot of −log(initial rate) versus −log(Pd) (Fig. 7a). However, the order of reaction is several times lower than unity suggesting that the catalyst behaves truly in a heterogeneous manner [$-\log r_i = -\log(\mathrm{Pd}) \times 0.0789-3.918$; $R^2 = 0.994$].

The rate dependence is also indicated by the plot of [r_i] versus [Pd] which again shows an intercept on the rate axis (Fig. 7b). It is evident that the transport of substrate to the active catalytic sites on the surface of the polymer plays a major role in the kinetics of this reaction [49,50].

3.8. Effect of hydrogen pressure

As discussed earlier, the conversion of 1-octene at 1 atmosphere of hydrogen is very low. In Fig. 8(a) is shown the dependence of initial rate on hydrogen pressure which was varied between 100 and 400 psi (entries 12–15) at 50 °C and 10 mmol 1-octene concentration. In this case too, the rates are much lower than unity [$\log r_i = \log H_2 \times 0.0484-4.33$; $R^2 = 0.959$]. Similarly the plot of r_i versus H_2 does not pass through the origin and intercepts on the rate axis (Fig. 8b).

The results obtained suggest that the hydrogenation of 1-octene by supported Pd-catalyst proceeds according to the rate equation

$$\mathrm{rate} = K_{\mathrm{cat}}[\mathrm{Pd}]^{n_0}[\text{1-octene}]^{n_1}\,p[H_2]^{n_2}$$

where the hydrogenation reaction is of fractional order in Pd, 1-octene and dihydrogen concentration (i.e. $n_0 < 1$; $n_1, n_2 \ll 1$). The values of specific rate constant were calculated using the above equation under different condition as follows:

$$K_{\mathrm{cat}} = \frac{r_i}{[\mathrm{Pd\,A} \times 10^{-5}\,\mathrm{mol/l}][\text{1-octene} \times 10^{-2}\,\mathrm{mol}] \times [pH_2(\mathrm{atm})]}$$

3.9. Effect of reaction temperature

To study the effect of temperature on the rate constant the hydrogenation of 1-octene was performed at different temperatures.

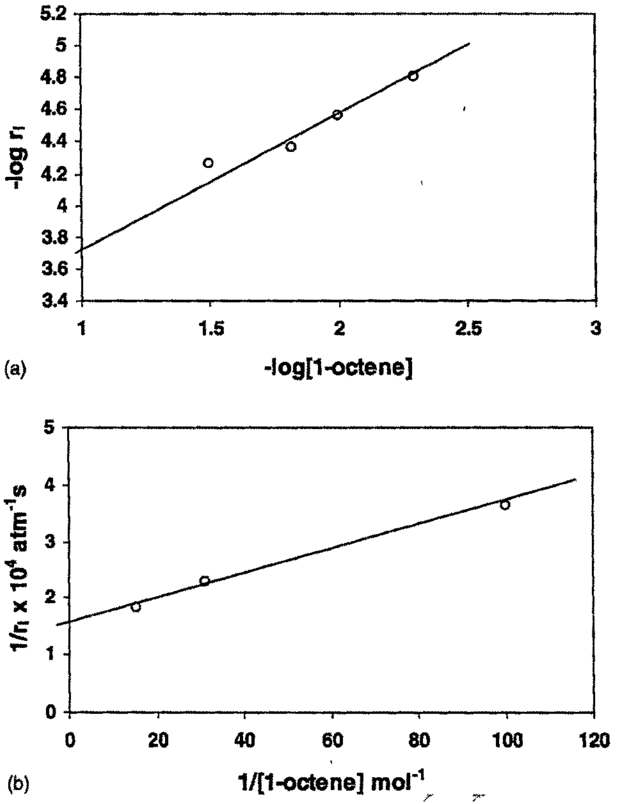


Fig 6 (a) Double logarithmic plot of initial rate vs substrate, (b) reciprocal of initial rate vs. reciprocal of 1-octene concentration

The hydrogenations were conducted by varying the temperature from 25 to 60 °C at a fixed 1-octene concentration of 1×10^{-2} mol and Pd concentration of 2.7×10^{-5} mol and $p\mathrm{H_2}$ of 200 psi (13.6 atm) (entries 15–18). It is assumed that the solubility of hydrogen in methanol will not affect the rates appreciably. The plot of $\log K_{\mathrm{cat}}$ versus $1/T$ yields a straight line (Fig. 9) as would be expected from the Arrhenius relationship.

$$K_{\mathrm{cat}} = \mathrm{A}\,\mathrm{e}^{-E_{\mathrm{a}}/RT} \quad \text{or} \quad \log K_{\mathrm{cat}} = \log \mathrm{A} - \frac{E_{\mathrm{a}}}{2.303\,RT}$$

The activation energy E_{a} can be evaluated from the slope of the graph shown in Fig. 8, which is equal to $-E_{\mathrm{a}}/2.303 \times R$ ($\log K = -82.63/T + 1.416$, $R^2 = 0.975$). The calculated value of E_{a} 1.6 kJ mol^{-1} (299 K) is very low compared to the values obtained for homogeneous Pd catalysts. Similarly the calculated value of entropy of activation ($\Delta S^{\ddagger} = -225$ eu) was low and is indicative of considerable loss of freedom on fixing of the catalyst on the polymer matrix [50]. The kinetic characteristics of catalysis with this heterogenized Pd-complex evidently occur in a liquid–solid heterogeneous system [51–53].

The sensitivity of hydrogen pressure on the rates of hydrogenations at atmospheric and at elevated pressures as discussed earlier leads us to conclude that accurate rate comparisons can be made between different types of supported catalyst only after taking into account amongst others, factors like mass-transfer, type of reactor (CSTR, fixed or pulse), substrate transport, etc. For most homogeneous Pd catalysts in hydrogenation reactions first order rates have been observed with

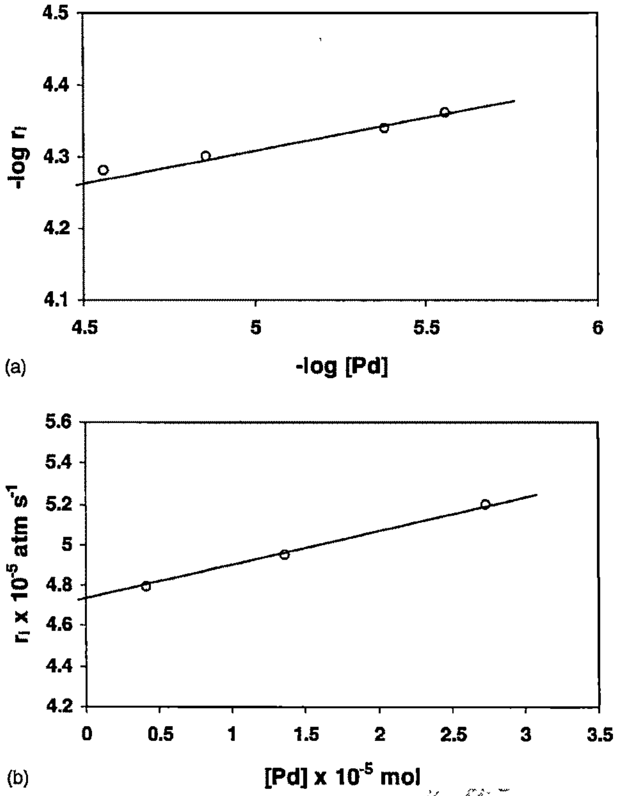


Fig. 7. (a) Double logarithmic plot of initial rate vs. Pd concentration, (b) plot of initial rate vs. Pd concentration.

respect to Pd, olefin and hydrogen concentration in the solvent (at atmospheric pressure). Mass transfer limitations are negligible and do not affect the kinetics of reactions [48].

3.10. Catalyst recycling

The main purpose of supporting a homogeneous catalyst onto a polymer support is to evaluate the potential of catalyst for practical application. A preliminary study of the recycling efficiency of Pd A was undertaken in the hydrogenation of 1-octene. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with solvent and dried to constant weight before reusing in the next cycle. As shown in Table 9, Pd A was recycled five times with a substantial retention of activity as evidenced by the conversions which was around ~35% (this corresponds to very high TON of ~1300) even up to five cycles. Comparison of diffuse reflectance spectrum of

Table 9
Recycling of Pd A in 1-octene hydrogenation

Cycle number	Yield (%)[a]
1	36.7
2	35.2
3	34.8
4	35.2
5	35.0

[a] Yield based on starting material (substrate) taken, catalyst 0.010 g, substrate: 10.0 mmol, time 6 h, temperature 50 °C, pressure 200 psi, solvent methanol.

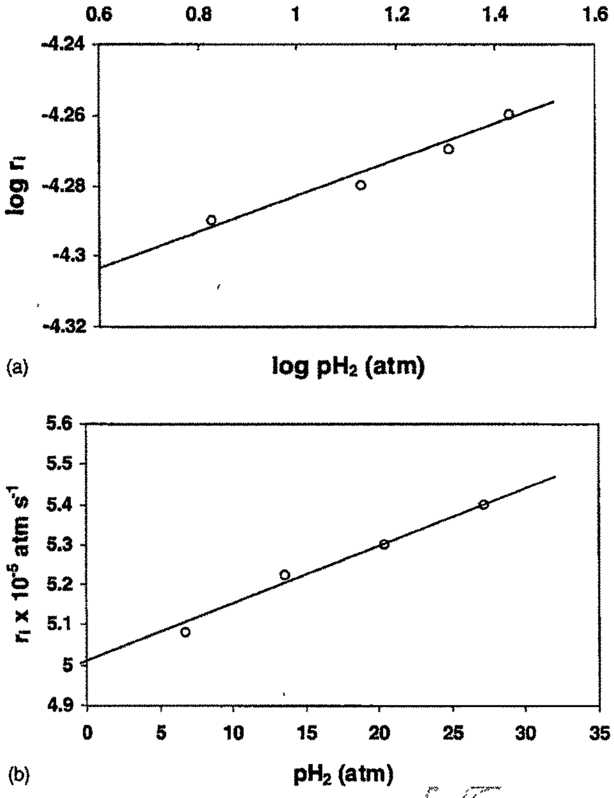


Fig 8. (a) Double logarithmic plot of initial rate vs dihydrogen pressure, (b) plot of initial rate vs dihydrogen pressure

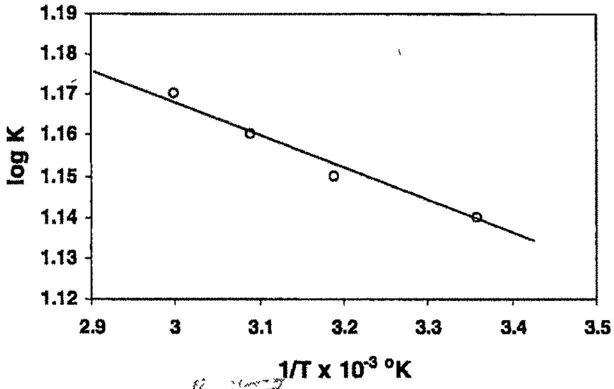
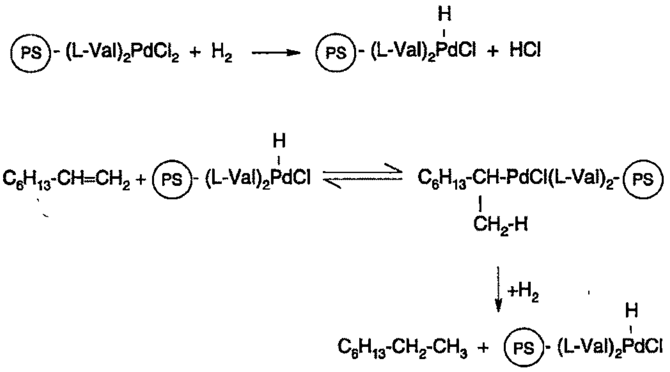


Fig 9 Plot of specific rate constant vs reaction temperature.



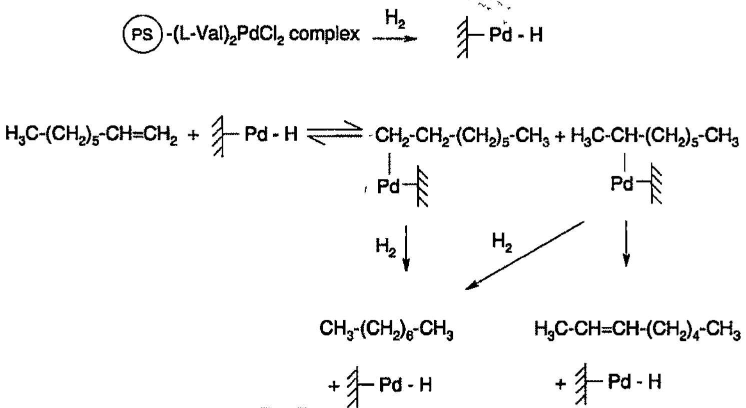
Scheme 2 Mechanism of oxidative addition of hydrogen

recycled catalyst with the starting Pd A revealed no marked change in the spectrum. Only a minor shift (~10 nm) in peak maxima was noticed (Fig. 2). It means that the active catalyst might involve a Pd^{2+} species in our case unlike that found in phosphine supported systems where the reaction occurs through a Pd^0 intermediate. Estimation of Pd present in the recycled catalyst after five cycles gave a value of 2.42% Pd which corresponds to about 15% Pd loss. Since the yields after repeated cycles did not change much the active metal content in Pd A could be assumed to be substantially unchanged with time, though some loss due to leaching is observed.

3.11. *Mechanism of hydrogenation*

Metal catalyzed hydrogenations are known to follow one of the four mechanistic pathways [54,55] namely (a) an oxidative addition of hydrogen, (b) formation of an alkyl intermediate, (c) olefin insertion (co-ordination) and (d) hydride species.

Considering the high stability of Pd-amino acid complexes the pathways (b) and (c) can be ruled out as the active intermediates may be unstable under the experimental conditions. Though the exact nature of active species remains unresolved at present, the possibility of oxidative addition of hydrogen to the



Scheme 3. Hydride mechanism

Pd-catalyst can occur through a heterolytic scission of H_2, according to pathway in (a) viz. (Scheme 2).

Alternatively, on the basis of many other studies of homogeneously catalyzed hydrogenations the actual catalysts have often been indicated to involve Pd-hydride species (pathway d). Though the origin of such species has not been established they may be assumed to be formed by interaction with gas phase H_2, solvent or substrate molecules. A simplified mechanistic pathway for the reaction of 1-octene is shown in Scheme 3, which involves 1,2-addition of Pd–H species across the double bond. Re-elimination in the direction opposite to addition leads to isomerization and hydrogenolysis of Pd–C bond yields the desired hydrogenated product.

4. Conclusion

The polymer supported palladium catalysts are able to hydrogenate various substrates under mild conditions and high selectivity. High pressure kinetics of 1-octene hydrogenation in a CSTR type reactor revealed that the reaction is sensitive to this parameter. The immobilized Pd catalysts behave in a truly heterogeneous manner as evident from the reaction orders obtained under different sets of experimental conditions. The kinetics of olefin hydrogenation prompt us to emphasize the need to include mass-transfer and substrate transport effects in deriving rate expressions while studying polymer supported catalyst system. Recycle experiments suggest that activity of the catalyst is retained over extended use which can be of importance for practical applications.

Uncited reference

[35].

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