CHAPTER – 4

RESULTS & DISCUSSION

PART – II (HYDROGENATION)

In this chapter the results of characterization and catalytic activity of Pd complexes supported on poly(styrene-divinylbenzene) is described. These polymer supported Pd complexes have been examined as catalysts in the hydrogenation of olefins, ketone & nitro compounds. The chapter is subdivided into following sections :

4.1. Polymer supported Pd(II) amino acid complexes
4.2. Kinetics & mechanism of hydrogenation
4.3. Asymmetric reduction of acetophenone
4.4. References

4.1. Poly(styrene-divinylbenzene) supported Pd(II) amino acid complexes

The palladium catalysts studied in this section 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

Pd C = 8% Poly(S-DVB)L-ph ala Pd(II) complex

Complex formation

The reaction of palladium chloride with polymer anchored amino acid was conducted in the pH range of 2.5 – 2.6 at a metal : ligand molar ratio of 1:2 (based on mmole L-valine anchored). A maximum Pd loading of up to 3.06% / gm resin was obtained (**Table 4.1.1.**). 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.

Catalyst characterization

The data on physical properties of Pd catalysts have been measured and compiled in **Table 4.1.2. Pd B** has a slightly higher surface area and larger pore volume than **Pd A** & **Pd C**. The metal loading on **Pd A** & **Pd C** with 8% cross-link (Pd 2.93% & 2.96% / gm resin) was lower than **Pd B** with 6% cross-link (Pd 3.06% / gm resin) (**Table 4.1.1.**). 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. The Pd supported catalysts show lower swelling in polar as well as non polar solvents compared to starting resin (**Table 4.1.3.**).

Representative IR spectra of catalysts are shown in **Fig. 4.1.1**. Bidentate N,O coordination has been confirmed for simple amino acid complexes of palladium by CD and IR spectra by other workers [1-3]. Weak bands in the far IR region at ~300-310cm^{-1} and 440-460 cm^{-1} have been assigned to ν Pd-Cl and ν Pd-N vibrations. From the elemental analysis (Pd, N, and Cl) and spectral data two possible structures [(a) & (b)] can be proposed for the above complexes which are shown in **Scheme 4.1.1.**

The diffuse reflectance spectra (200-800 nm) of **Pd A** and **Pd B** display two strong absorption bands in the UV region at 303 nm and 340 nm in addition to weak & broad bands in the visible region at ~435nm and 560 nm (**Fig. 4.1.2**). 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 [4-6].

Scanning electron micrographs (SEM) at various stages of preparation of the polymer supported amino acid and the palladium complexes were recorded to understand morphological changes occurring on the surface of the polymer. Comparison of SEM's showed that the smooth surface of the starting poly (S-DVB) (**Fig. 4.1.3a & 4.1.4a**) is distinctly altered, exhibiting considerable roughening of the top layer upon anchoring of the amino acid (**Fig. 4.1.3b & 4.1.4b**). After loading of Pd randomly oriented depositions on the external surface of the resin were seen (**Fig. 4.1.3c, 4.1.3d & 4.1.4c**).

The T.G data allow us to conclude that palladium supported catalysts degrade at considerably lower temperatures than the unsupported polymer as shown in **Table 4.1.4.** Representative thermograms are depicted in **Fig. 4.1.5.**

Catalytic reduction

The activity of the supported palladium catalysts was investigated in the hydrogenation of various substrates at constant temperature (50°C) and pressure of hydrogen (200 psi). These results are summarized in **Table 4.1.5.** Both **Pd A** and **Pd B** catalyze the hydrogenation of 1-octene, cyclohexene, nitrobenzene and acetophenone with high selectivity to the corresponding reduced products (catalytic evaluation of **Pd C** is discussed in section 4.3). The reduction of acetophenone to 1-phenyl ethanol was carried out using potassium *tert*-butoxide as the base [7]. 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. 4.1.6.** The reaction becomes slower after 3 h and reaches a plateau after ~5 h (conv. 51 %). Hydrogenation of 1-octene using *in situ* generated homogeneous amino acid-Pd catalyst (1:2, pH ~1.2) gave slightly higher yields than the supported catalyst. Comparative evaluation was also made with a commercially available hydrogenation catalyst, 5% Pd on activated carbon. These results are shown in **Table 4.1.6.** Expectedly Pd/C gave higher yields than either **Pd A** or Pd(L-valine)$_2$.

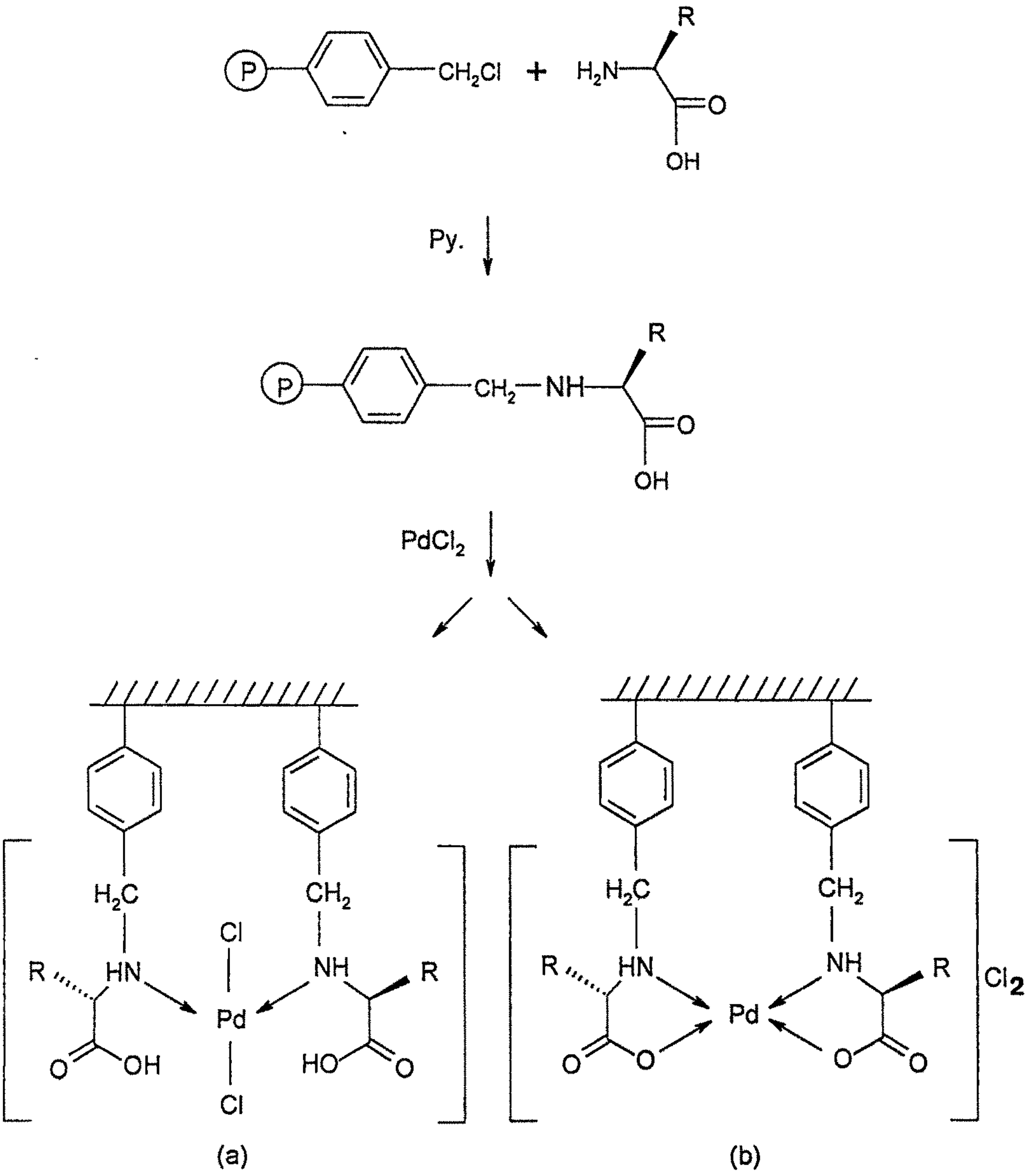
The effect of reaction conditions on catalytic hydrogenation of 1-octene as model substrate was examined in detail with **Pd A.** From the results presented in **Table 4.1.7.** it can be seen that of the five different reaction variables studied, the effect of hydrogen pressure (H_2 concentration) is 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 (~1atm.) 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 to 12). Only moderate increase in yields (~10%) is noticed by varying the temperature from ambient to 60 °C (entry 1 to 3). Similar trend is observed by varying the substrate concentration from 5 mmol 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 4.1.3.**) 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 [8].

Performance of **Pd C** was also examined in the hydrogenation of 1-octene (50°C, pH_2 200 psi). From the results presented in **Table 4.1.8.** it can be seen that the effect of hydrogen pressure (H_2 concentration) is much more pronounced than other parameters. 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. Only moderate increase in yields (~9%) is noticed by varying the temperature from ambient to 60 °C.

Confirmatory evidence for the *heterogeneity* of the catalyst was arrived at by applying the probe of Sheldon *et. al* [9]. The catalyst **Pd A** was filtered at the reaction temperature of 50°C after 2 h (*prior* to completion of the reaction) and the filtrate tested for activity after the reaction time of 6 h (conv. 19.1%). There was practically no change in the yields than that observed at 2 h period (conv. 18.3%). The actual conversion in presence of **Pd A** is ~52% after 6h (**Table 4.1.5.**).

Catalyst recycling

The recycling efficiency of a representative catalyst **Pd A** was evaluated. As shown in **Table 4.1.9.** the catalyst was recycled five times with substantial retention of activity as evidenced by the conversion which was around ~35%. **This corresponds to very high TON of ~1300** even up to the fifth cycle. Comparison of diffuse reflectance spectrum of recycled catalyst with the starting **Pd A** revealed no marked change in the spectrum. Only minor shift (~10 nm) in peak maxima at 340 nm & 435 nm were noticed (**Fig. 4.1.2**). 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 is known to occur *via* 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.



R = -CH(CH$_3$)$_2$ for L-val.; R = -CH$_2$Ph for L-ph ala

Scheme 4.1.1 Synthesis of poly(S-DVB) supported amino acid Pd(II) complex.

Table 4.1.1. Analytical data of Polymer Support, Ligand and Pd-anchored catalysts

Table 4.1.1. 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	--
8%Poly(S-DVB)-L-ph ala	62.19	5.59	9.82	2.34	--
Pd A	56.20	5.10	11.57	2.59	2.93
Pd B	57.41	5.19	11.71	2.55	3.06
Pd C	59.21	5.23	11.88	2.29	2.96

Table 4.1.2. 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
Pd C	26.2	0.54	0.16

Table 4.1.3. Swelling study (mol %)

Solvent	8% Poly (S-DVB)CH_2Cl	8% Poly (S-DVB)CH_2Cl	**Pd A**	**Pd B**	**Pd C**
Acetonitrile	2.0	2.0	1.7	1.8	1.5
Benzene	1.1	1.1	0.9	1.0	0.9
Dichloromethane	1.5	1.8	1.1	1.4	1.2
Ethanol	1.7	1.9	1.3	1.8	1.4
n-Heptane	0.6	0.6	0.4	0.5	0.4
Methanol	2.7	2.8	2.1	2.6	2.4
Tetrahydrofuran	1.4	1.5	1.0	1.1	0.8
Toluene	1.1	1.1	0.7	0.8	0.7

Table 4.1.4. TG data of supports and Pd(II) catalysts

Compound	Degr. Temp.(°C)	Wt. loss (%)
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
Pd C	108	2.0
	366	21.3

Table 4.1.5. Catalytic reduction with Pd A and Pd B

Catalyst[a]	Substrate[b]	Yield (%)[c]	Product	TON[d]
Pd A	1-Octene	51.8	n-Octane	189
Pd B		50.1	n-Octane	175
Pd A	Cyclohexene	19.0	Cyclohexane	69
Pd B		23.7	Cyclohexane	83
Pd A	Nitrobenzene	22.1	Aniline	81
Pd B		06.8	Aniline	25
Pd A	Acetophenone[e]	24.0	1-Phenyl ethanol	89
Pd B		13.9	1-Phenyl ethanol	49

[a] = 0.10 g (Pd = 2.7 x 10^{-5} M) ; [b] = 10.0 mmol ; [c] = Yield based on starting material ; [d] = Turnover Number = mmol products/mmol Pd; Time = 6 h; Solvent = methanol (30 ml) ; Temp = 50°C ; Pressure = 200 psi.; [e] = Reaction conducted in presence of ^{t}BuOK

Table 4.1.6. Comparison of activities with different catalysts

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

Reaction conditions same as given in **Table 4.1.5.**

Table 4.1.7. Reduction of 1-octene using Pd A under different reaction conditions

Entry	Parameters	1-octene (mmol)	Catalyst wt. (g)	Temp. (°C)	pH_2 (psi)	Solvent	Yield[a] (%)
1		10.0	0.100	25	200	CH_3OH	43.3
2	Temperature	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		10.0	0.100	50	15	CH_3OH	4.5
6		10.0	0.100	50	100	CH_3OH	46.2
7	Pressure	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		10.0	0.010	50	200	CH_3OH	36.0
11	Catalyst conc.	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		5.0	0.010	50	200	CH_3OH	37.5
15	Substrate conc.	10.0	0.010	50	200	CH_3OH	36.0
16		15.0	0.010	50	200	CH_3OH	27.3
17		10.0	0.100	50	200	CH_3CN	1.6
18	Solvent	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.

Table 4.1.8. Catalytic hydrogenation of 1-octene with Pd C[a]

Temp. (^oC)	Pressure (psi)	Selectivity	% yield
28	200	98.7	44.2
40	200	98.7	50.1
50	200	98.3	51.5
60	200	98.0	53.2
50	300	98.4	57.2
50	400	98.4	62.1

[a] reaction condition: solvent = 30 ml MeOH, reaction time = 8 h, catalyst = 100 mg, substrate = 10.0 mmol, yield based on starting material.

Table 4.1.9. Recycling of Pd A in 1-octene hydrogenation

Cycle no.	Yield (%)[a]
1	36.7
2	35.2
3	34.8
4	35.2
5	35.0

[a] Yield based on 1-octene taken; **Pd A** = 0.010 g; 1-octene = 10.0 mmol; Time = 6 h; Temp. = 50°C; $p\mathrm{H}_2$ = 200 psi ; Solvent = methanol.

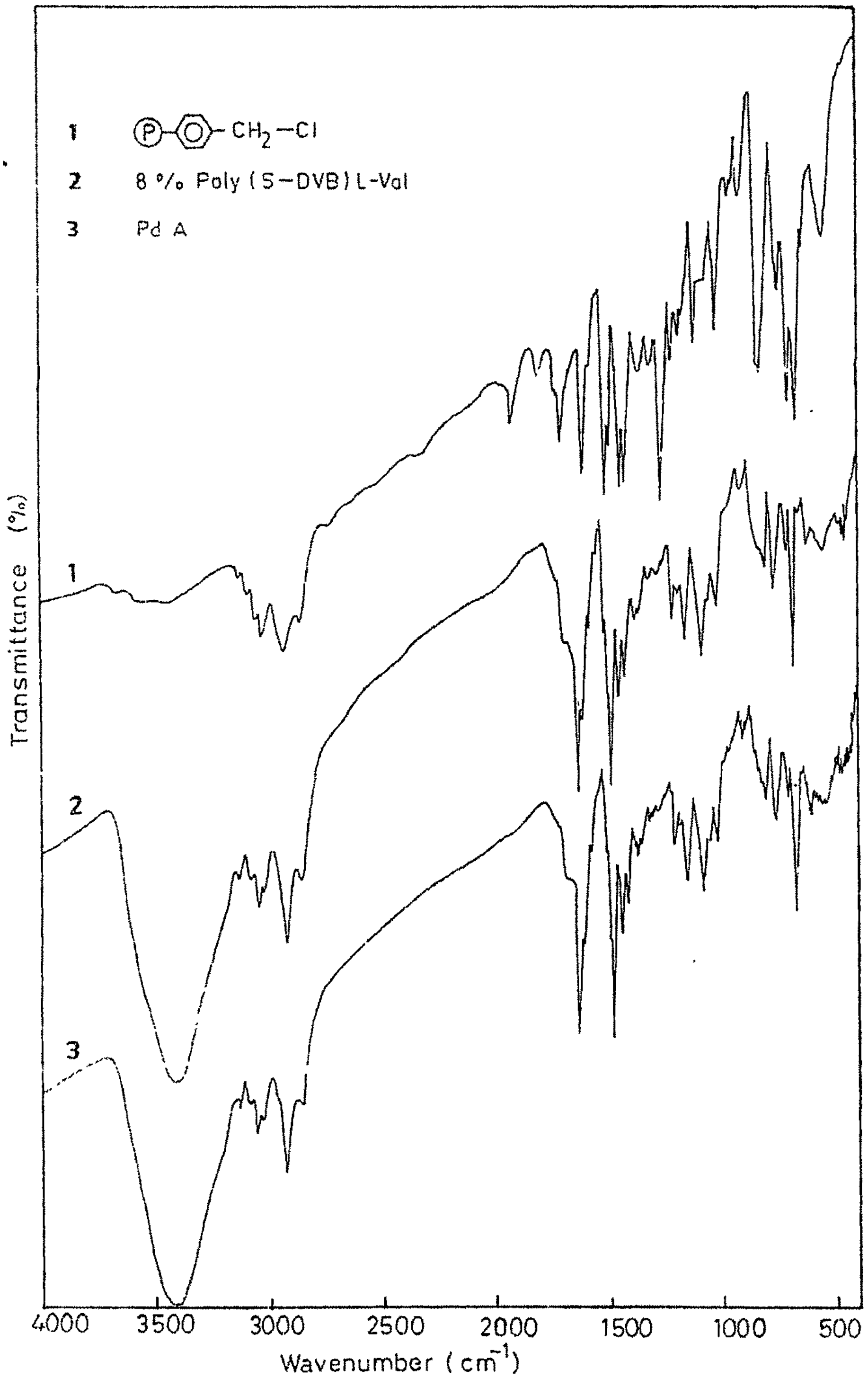


Fig. 4.1.1 FT-IR spectra of support, liganded polymer and Pd catalyst

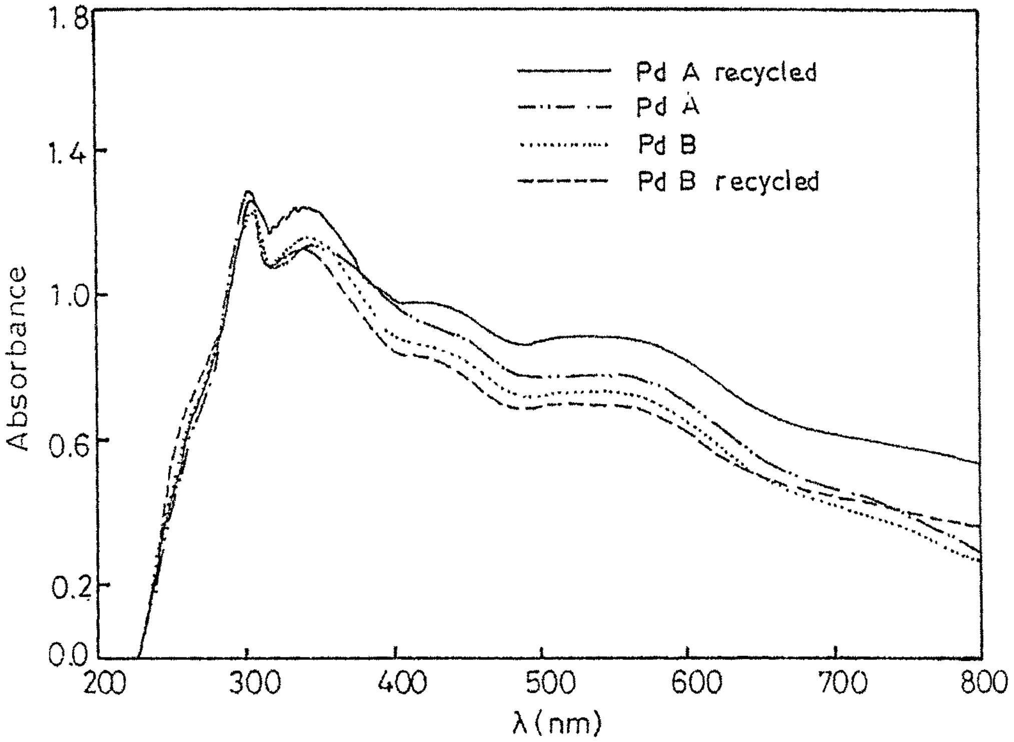
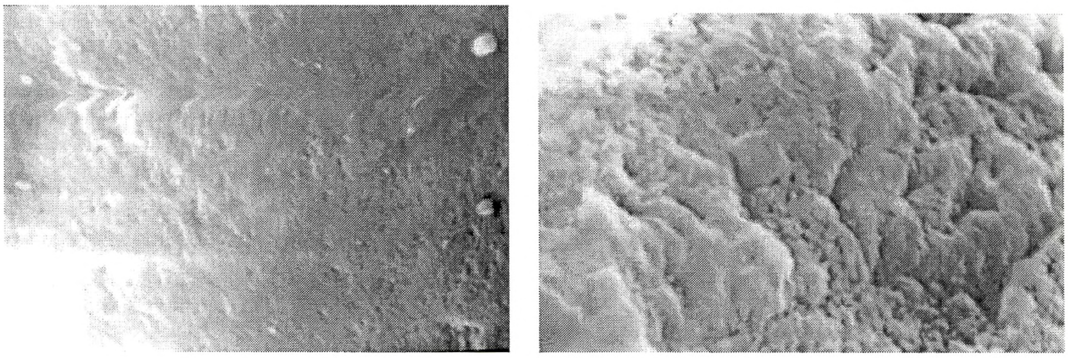
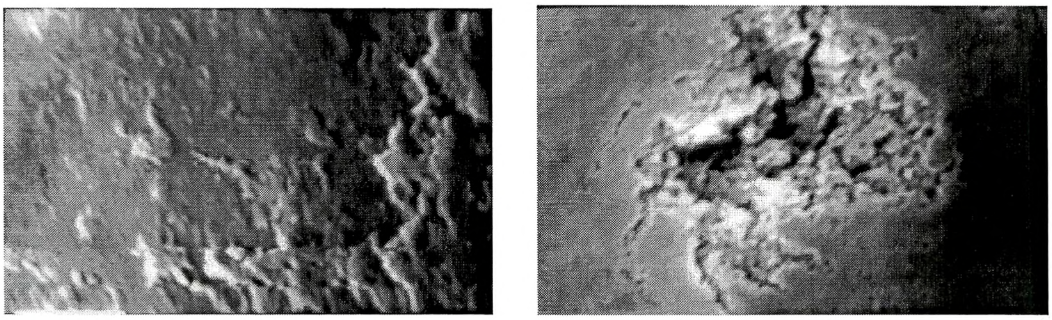


Fig. 4.1.2 Diffuse reflectance spectra of Pd catalysts.



(a) P(S-DVB)CH_2Cl **(b)** P(S-DVB) L Val



(c) Pd A **(d) Pd B**

Fig. 4.1.3 Scanning Electron Micrographs

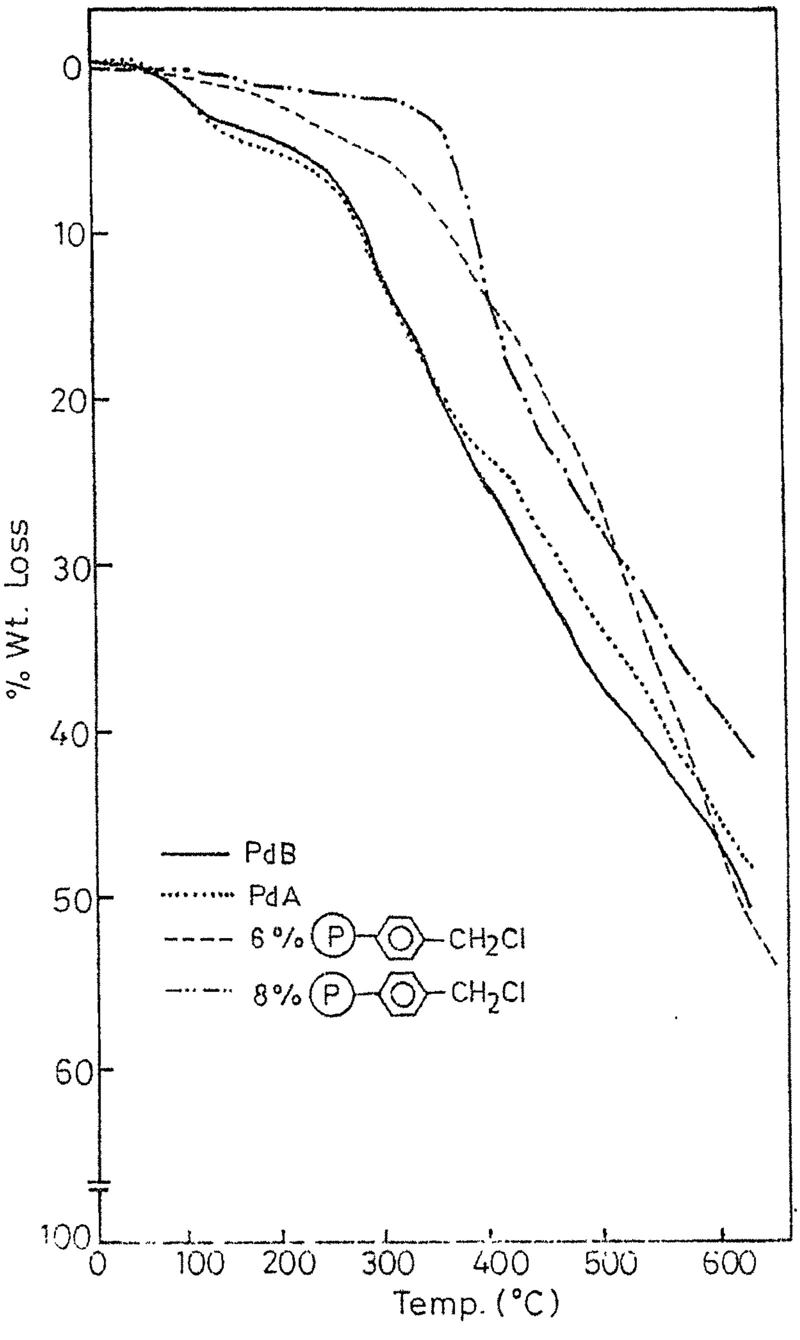


Fig. 4.1.5 TG of support & catalysts.

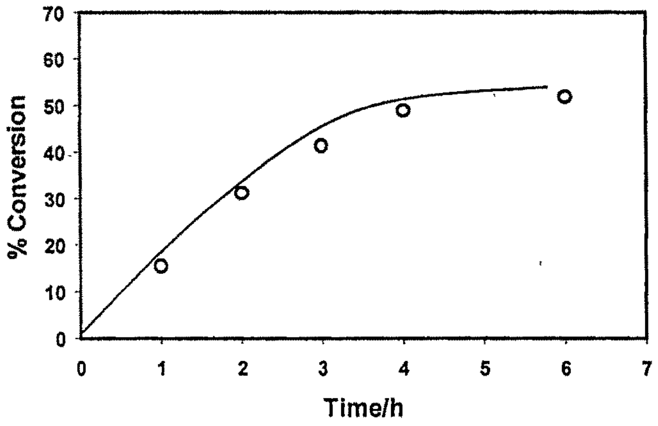


Fig. 4.1.6 Plot of variation of conversion as a function of time at 50°C and 200 psi H_2 using **Pd A**

4.2. Kinetics & mechanism of hydrogenation reaction catalyzed by polymer supported Pd(II) amino acid complexes

Kinetics of hydrogenation

Previous works on kinetics of hydrogenation of olefins using polymer supported palladium catalysts have been based on data generated at atmospheric pressure of hydrogen [10-16]. 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 catalyst and substrate concentrations 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 ΔpH_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 6h. 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 [17]. Making allowance for the initial induction period, initial rate r_i was determined from the slope of linear plot of ΔpH_2 (atm.) *vs.* time between 1-3 h. Values for r_i under different sets of conditions for **Pd A** are collected in **Table 4.2.1.** Conventional linear regression software was employed for all straight line fits.

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} M – 6.5×10^{-2} M at a constant catalyst concentration of 0.27×10^{-5} M Pd (entries 7-9, **Table 4.2.1.**). The initial rates show a direct dependence on 1-octene concentration **Fig. 4.2.1(a)**. The order of reaction calculated from the plot of log (initial rate) *vs.* log (1-octene) was found to be less than unity and equals 0.74 (**Fig. 4.2.1b**). 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 [$-\log r_i = -\log$ (1-octene) $0.694 - 3.173$, $R^2 = 0.948$]. As would be expected the $1/r_i$ *vs.* 1/1-octene plot shows an intercept on the rate axis as shown in **Fig. 4.2.1(b)**.

Catalyst concentration

The concentration of Pd in **Pd A** was varied from 0.27×10^{-5} M to 2.7×10^{-5} M (entries 1-4, **Table 4.2.1.**) while 1-octene concentration (10 mmol), temperature (50°C) 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) *vs.* –log(Pd) (**Fig. 4.2.2a**). 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] *vs.* [Pd] which again shows an intercept on the rate axis (**Fig. 4.2.2b**). 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 [18,19].

Effect of hydrogen pressure

As discussed earlier, the conversion of 1- octene at 1 atmosphere of hydrogen is very low. In **Fig. 4.2.3(a)** is shown the dependence of initial rate on hydrogen pressure which was varied between 100 psi – 400 psi (entries 12-15, **Table 4.2.1.**) 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 *vs.* H_2 does not pass through the origin and intercepts on the rate axis **(Fig. 4.2.3b)**.

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

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

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 conditions as follows:

$$K_{cat} = \frac{r_i}{[\mathbf{Pd\ A} \times 10^{-5}\ \text{moles/liter}]\ [\text{1-octene} \times 10^{-2}\ \text{moles}]\ [pH_2\ (\text{atm})]}$$

Effect of reaction temperature

The hydrogenations were conducted by varying the temperature from 25°C to 60°C at a fixed 1-octene concentration of 1 x 10^{-2} mol and Pd concentration of 2.7 x 10^{-5} mol and pH_2 of 200 psi (13.6 atm) (entries 15-18, **Table 4.2.1.**). It is assumed that the solubility of hydrogen in methanol will not affect the rates appreciably. The plot of $\log K_{cat}$ *vs.* 1/T yields a straight line (**Fig. 4.2.4**) as would be expected from the Arrhenius relationship.

$$K_{cat} = A\ e^{-Ea/RT} \qquad \text{or} \qquad \log K_{cat} = \log A - \frac{Ea}{2.303\ RT}$$

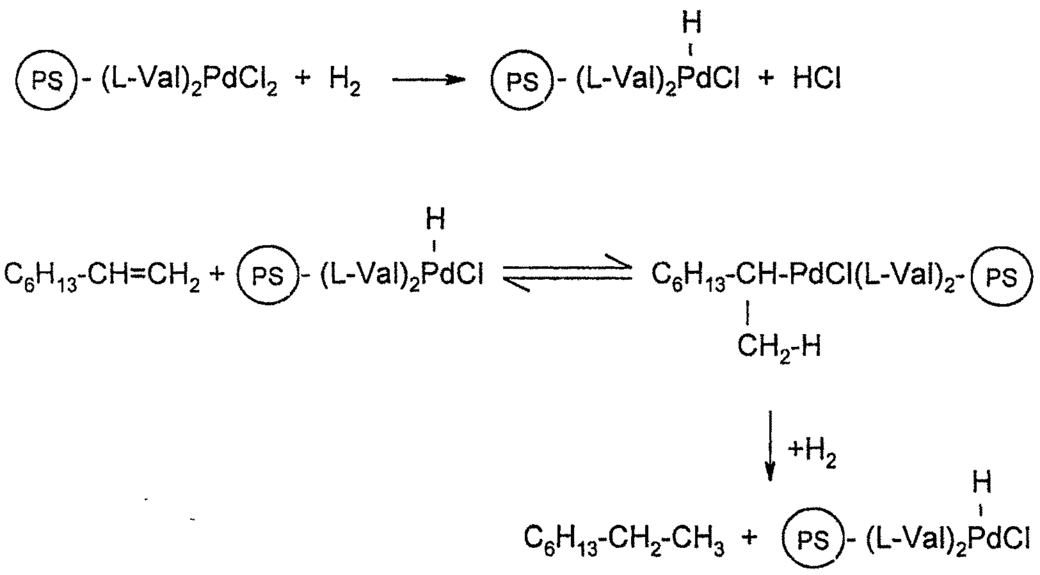
The activation energy E_a can be evaluated from the slope of the graph shown in Fig. 4.2.3, which is equal to –Ea/2.303 x R ($\log K = -82.63/T + 1.416$, $R^2 = 0.975$). The calculated value of E_a 1.6 kJ mol^{-1} (299°K) is very low compared to the values obtained for homogeneous Pd catalysts. Similarly 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 [19]. The kinetic characteristics of catalysis with this heterogenized Pd-complex evidently occur in a liquid-solid heterogeneous system [20-22].

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 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 [17].

Mechanism of hydrogenation

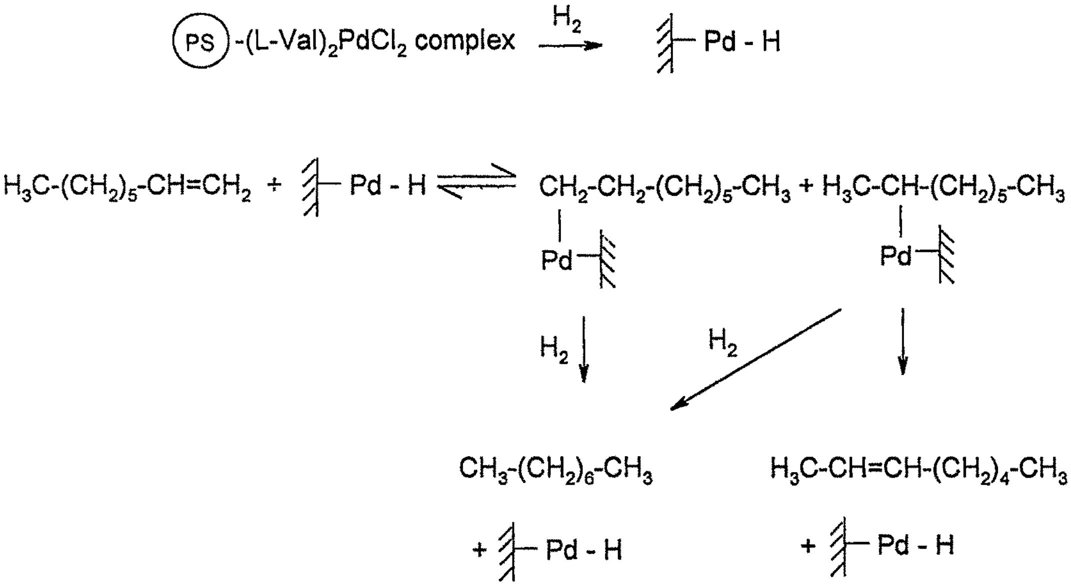
Metal catalyzed hydrogenations are known to follow one of the four mechanistic pathways [23,24] namely (a) an oxidative addition of hydrogen (b) formation of an alkyl intermediate (c) olefin insertion (co-ordination) and (d) hydride species.

Considering the high stability of Pd-amino acid complexes the pathways (b) & (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 Pd – catalyst can occur through a heterolytic scission of H_2, according to pathway in (a) *viz.* **(Scheme 4.2.1)**



Scheme 4.2.1 Mechanism of oxidative addition of hydrogen

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 4.2.2**, 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.

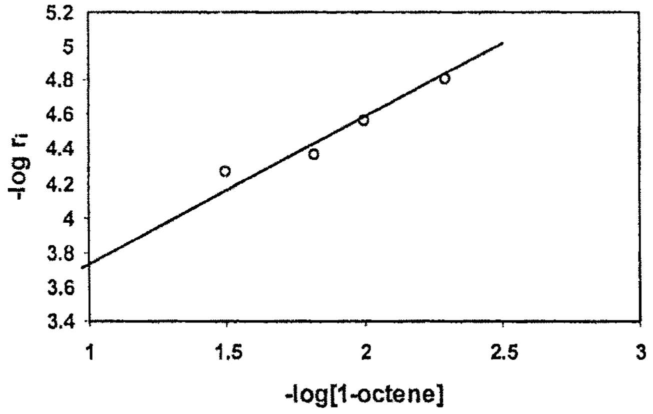


Scheme 4.2.2 Hydride mechanism

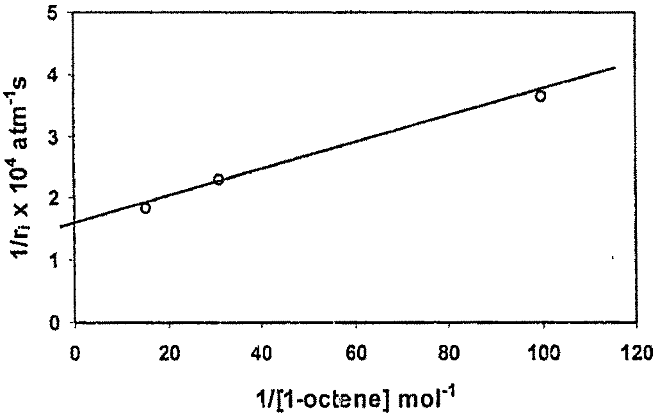
Table 4.2.1. Kinetic data for the hydrogenation of 1-octene with Pd A

Entry	Pd x 10^{-5} (M)	1-octene x10^{-2}(M)	$p(H_2)$ (psi)	Temp. (°C)	Initial rate, r_i x 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	n.d.
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

n.d. = not determined.

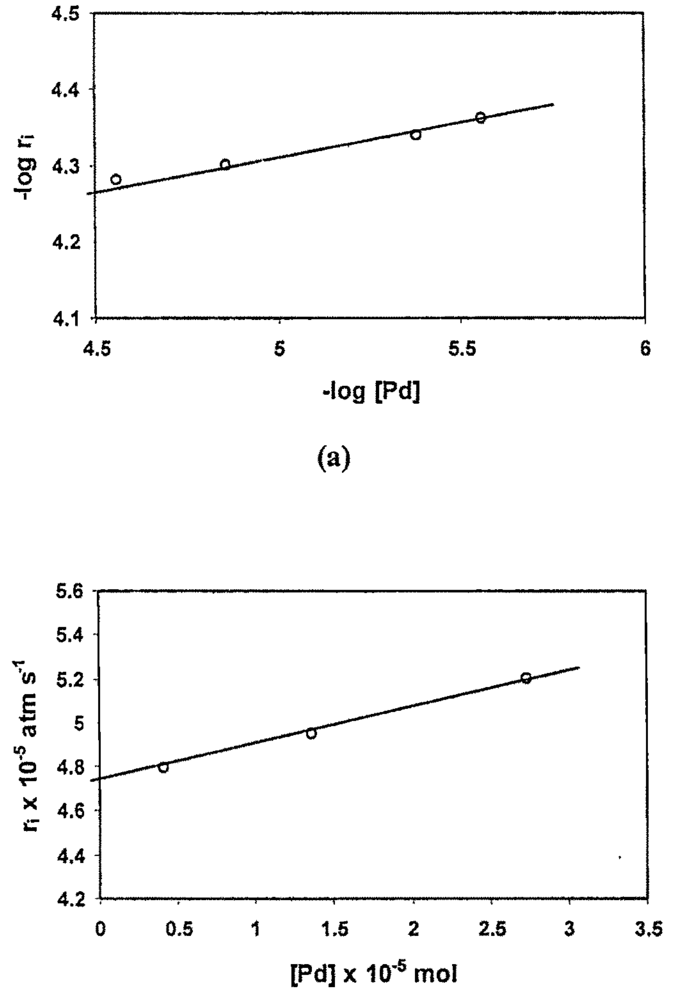


(a)



(b)

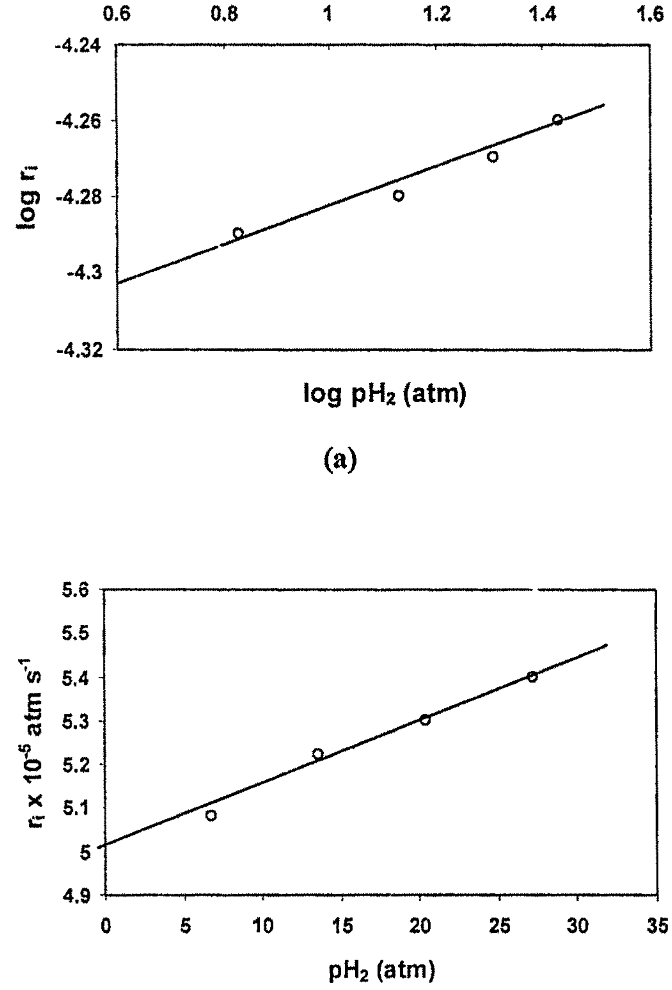
Fig. 4.2.1 (a) Double logarithmic plot of initial rate *vs.* substrate conc.
(b) Reciprocal of initial rate *vs.* reciprocal of 1-octene conc.



(a)

(b)

Fig. 4.2.2 (a) Double logarithmic plot of initial rate *vs*. Pd conc.
(b) Plot of initial rate *vs*. Pd conc.



(a)

(b)

Fig. 4.2.3 (a) Double logarithmic plot of initial rate *vs.* dihydrogen pressure
(b) Plot of initial rate *vs.* dihydrogen pressure.

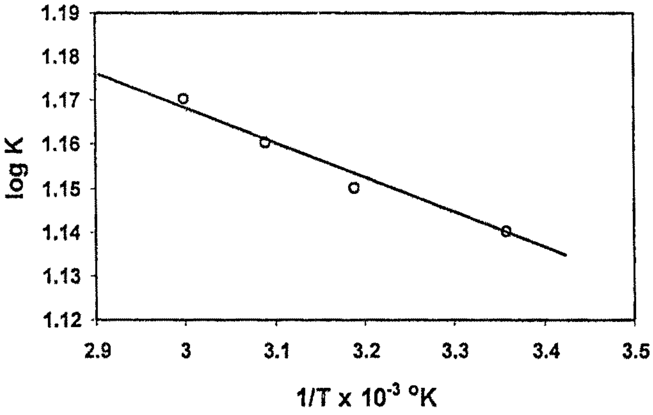


Fig. 4.2.4 Plot of specific rate constant *vs.* reaction temperature.

4.3. Asymmetric reduction of acetophenone using polymer supported Pd(II) amino acid complexes

Asymmetric catalytic reduction

The performance of **Pd C** was examined in the asymmetric hydrogenation of acetophenone (40°C, pH_2 300psi). The reaction was carried out using potassium *tert*-butoxide as a base [7]. Maximum observed yields were ~74% with greater than 98.5% selectivity to 1-phenyl ethanol.

From the results presented in **Table 4.3.1.** it is evident that the optical yields are sensitive to changes in temperature rather than the effect of hydrogen pressure. The %ee remain constant between 28^0C- 40^0C but is lowered with further increase in temperature. The reduction of acetophenone in presence of **Pd C** at 40°C gave moderate optical yields of ~14% though the overall conversions were high .Varying the H_2 pressure from 200 psi (13.7 kg/cm^2) to 400 psi (27.4 kg/cm^2) does not affect the % ee to any great extent. Such a behaviour may be the result of induced rigidity around the chiral center on anchoring to the polymeric support.

Catalyst recycling

A preliminary study of the recycling efficiency of **Pd C** was undertaken in the asymmetric hydrogenation of acetophenone. As shown in **Table 4.3.2.**, **Pd C** was recycled three times with substantial retention of activity as evidenced by the conversions which was around ~66%. Interestingly optical yields were also unaffected and the % ee was around ~14%.

Table 4.3.1. Catalytic hydrogenation of acetophenone with Pd C[a]

Temp. (°C)	pH_2 (psi)	Selectivity (%)	yield (%)	% ee
28	300	98.8	68.2	14.8
40	300	99.0	70.3	14.4
50	300	98.2	72.2	11.7
40	200	98.7	67.4	14.3
40	400	98.7	74.2	14.5

[a], reaction condition: solvent = 30 ml MeOH, time = 24 h, substrate = 1.0 mmol, catalyst = 100mg (2.7 x 10^{-5} M Pd), *t*-BuOK = 0.2 g. (yield based on starting material)

Table 4.3.2. Recycling of Pd C in asymmetric reduction of acetophenone

Cycle no.	1-phenyl ethanol[a]	
	% yield	% ee
1	70.4	14.4
2	67.3	14.2
3	66.1	14.4

[a] solvent = 30 ml MeOH, catalyst = 100 mg, substrate = 1.0 mmol, temp.= 40°C, pH_2 = 300 psi, time = 24 h, *t*-BuOK = 0.2 g. (yield based on starting material)

4.4. References

[1] J. S. Coe, J. R. Lyons, J. Chem. Soc. A. **1971**, 829.

[2] P. A. Boudrean, R. J. Hooper, J. Inorg. Nucl. Chem. 39, **1977**, 1247.

[3] L. D. Pettit, M. Bezer, Coord. Chem. Rev. 61, **1985**, 97.

[4] A. B. P. Lever, *Inorganic electronic spectroscopy, Elsevier,* New York **1984**.

[5] D. S. Martin, R. M. Rush, G. A. Robbin, Inorg. Chem. 19, **1980**, 1705.

[6] G. Wilkinson, F. A. Cotton, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley, New York. **1999**.

[7] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. Englad, T. Ikariya, R. Noyori, Angew. Chem., Int. Ed. 37, **1998**, 1703.

[8] L. Hines, K.F. O. Driscoll, G. L. Rempel, J. Catal. 38, **1975**, 435.

[9] R. A. Sheldon, M. Wallau, Isabel W. C. E. Arends and U. Schuchardt, Acc. Chem. Res., 31, **1998**, 485.

[10] R. S. Drago, E. D. Nyberg, A. G. El A'mma, Inorg. Chem. 20, **1981**, 2461.

[11] R. J. Card, C. E. Liesner, D. C. Neckers, J. Org. Chem. 44, **1979**, 729.

[12] N. L. Holy, J. Org. Chem. 43, **1978**, 4686.

[13] V. A. Semikolenov, V.A. Kikholobov, G. Vbalentim, G. Braca, F. Giardelli, React. Kinet. Catal. Lett. 15, **1980**, 383.

[14] R. P. Macdonald, J. M. Winterbottom, J. Catal. 57, **1979**, 195.

[15] P. C. Selvaraj, V. Mahadevan, J. Poly. Sci. A, Poly chem. 35, **1997**, 105.

[16] J. John, M.K. Dalal, R.N. Ram, J. Mol. Catal. A: Chemical 137, **1999**, 183.

[17] I. M. Angulo, E. Bouwman, J. Mol. Catal. A: Chemical. 175, **2001**, 65.

[18] W. T. Ford, Polymeric reagents and catalysts ACS Symposium series. 308, **1986**, 69.

[19] (a) K. Kaneda, T. Imanaka, Trends Org. Chem. 2, **1991**, 109 ; (b) R. H. Grubbs, L. C. Kroll, E. M. Sweet, J. Macromol. Sci. Chem. A7, **1973**, 1047 ; (c) M. H. J. M. De Croon, J. W. E. Coenen, J. Mol. Catal. 11, **1981**, 301.

[20] H. Olive, Angew. Chem, Eng. Ed. **1974**, 549.

[21] B. R. James, *Homogeneous hydrogenation,* John Wiley: New York. **1973.**

[22] G. C. Bond, *Catalysis by metals,* Academic Press London. **1962.**

[23] E. W. Stern, P. K. Maples, J. Catal. 27, **1972**, 120.

[24] D. Foster, J. F. Roth, (Ed.) *Homogeneous Catalysis, Part II, Adv. Chem. Series.* **1974**, 132.