CHAPTER 4
KINETICS OF HYDROGENATION

KINETICS OF HYDROGENATION

4.1 **Kinetics of hydrogenation of cyclohexene using polymer supported Pd(II) and Ru(III) complexes.**

4.1.1 Introduction

The ability to influence the rate of a chemical reaction is the prime factor which decides the usefulness of a catalytic substance. In the present investigation the catalytic activity of the prepared catalysts have been investigated for the industrially important reaction i.e., the hydrogenation of cyclohexene. Catalytic hydrogenation is one of the most useful broad-scoped reactions for the synthesis of organic compounds as well as to the industries. The high purity of the cyclohexane synthesised by the hydrogenation reaction is used as a raw material in the manufacturing of nylon 6 and nylon 6,6.

The success of homogeneous catalysts(1-4) has lead to a great interest in supporting them on an insoluble material. The majority of the industrial hydrogenation reactions have now been performed using heterogeneous catalysts(5-6). But for lab-scale reactions, homogeneous catalysts were found to be suitable, viz the synthesis of thermally unstable or otherwise sensitive product, application of prochiral catalysts for the production of optically active products and mechanistic studies (7-10).

Transition metals of group VIII or their complexes have been used as hydrogenation catalyst (11-12). Effective combinations have resulted from d^8 spin paired (low-spin) configuration arising from strong ligand fields or electron delocalizing (π -acceptor) ligands. The mechanism by which these homogeneous catalysts activate molecular hydrogen and substrate molecules and transfer of activated hydrogen to the substrate often with considerable stereospecificity is well understood (7,13-14).

The platinum group complexes have been widely used as catalysts in homogeneous hydrogenation of olefins (7,15-21). $RuCl_2$ catalyzed the hydrogenation of α, β unsaturated acids but failed to catalyse the olefin hydrogenation (22). However, an enhanced activity was observed in the hydrogenation of unsaturated acids in the presence of triphenyl phosphine probably due to the formation of hydride complex during the reaction. Thus the formation of hydrido complex from $RuCl_2(PPh_3)_3$ and hydrogen in the presence of triethylamine was observed to be the most active hydrogenation catlayst. (23). Investigations have also been carried out for the homogeneous hydrogenation of cyclohexene using various metal ions/complexes of Rh(I), Ru(III) and Ir(I) (24-32), Pd(33-34) and Ru(I) & Ru (III) (35-42) as catalysts. Other metal ions /complexes such as Mn(43), Co(44) Ti(45) and Pt(46) have also been found to be useful for the same reaction.

The main disadvantages of these expensive catalysts are the difficulty of seperation from the reaction mixture, handling of these sensitive organometallic compounds with metals in low oxidation states and the choice of the solvent which invariably depends on the solubility of the catalyst. These catalysts are usually co-ordinatively unsaturated and have a tendency to aggregate thereby blocking the co-ordination sites necessary for catalysis. The catalytic activity of these metal ions/ complexes, active in their monomeric form may be enhanced by attaching them to a rigid inorganic oxide. Thus, the titanocene monomers supported on silica following reduction with BuLi have shown a higher activity in the hydrogenation of olefins (6).

A number of hydrogenation reactions have been carried out for olefins catalysed by metal/metal complexes supported on inorganic oxides (47-52). Thus the hydrogenation of 1-hexene using Pd/Zeolite (53) and aniline by Rh/Al_2O_3 (54) has been carried out and the activity was found to be higher than the homogeneous counter parts. Gattania has used ruthenium clusters supported on alumina and silica for CO hydrogenation reaction (55). Taqui Khan et. al have reported the reduction of natural oil using Ru(IV) dihydrido species formed with the interaction of hydrogen and the ruthenium complex on the surface of montmorillonite (56). Other studies include the hydrogenation of toluene and xylenes by Pd and Pd on SiO_2, Al_2O_3, MgO and TiO_3 (57-58) and methyl ester by Pd, Pt, Rh, Ru on activated charcoal (59). The hydrogenation of cyclohexene has been studied widely using various noble metal ions supported on Al_2O_3/SiO_2(60-68). Recently bimetallic catalysts such as Ir-Ru as well as Ir-Rh supported on silica have been introduced to investigate the hydrogenation of cyclohexene (69). Silica supported poly vinylpyridine composite of Pd(II) complex has been used by Mathew et al for the reduction of cyclohexene (70). Molga et al have studied the hydrogenation of 2,4-dinitrotoluene over a palladium on alumina catalyst (71). The kinetics of hydrogenation of butynediol to 1,4-butanediol has been investigated by Xuan et al using palladium catalyst in slurry reactor (72).

The main difficulty with the anchored catalysts on inorganic oxides is the leaching of the metal ions from the surface which could deactivate the catalysts as also the susceptibility of poisoning the catalysts by adsorbed substances. This problem could be solved by heterogenizing the homogeneous catalyst on polymeric support (73,74). Hydrogenation reactions using polymer bound non-chelated metal complexes have been studied extensively (75-79). But these transition metal complexes are occasionally so labile and they fail to act as a supported catalyst (80-81) or sometimes it results a significant metal leaching into the solution (82).

Metal ions attached to polymer bound chelating ligands were found to be more stable and showed high catalytic activity (83-85). Neckers and card (86) have reported the attachment of 2,2'-bipyridine to an insoluble polystyrene support and demonstrated its versatility as a polymer bound chelate by preparing a wide variety of transition metal complexes. Recently Ram et. al have also studied the hydrogenation of 1-octene and cyclohexene using Rh(I), Rh(II), Co(II) and Ru(III) anchored on polymer bound chelated ligands and catalytic activity was observed to be higher than the homogeneous counter part(87-91).

In the present investigation polymer bound chelated metal complexes of palladium and ruthenium have been used for the kinetics of hydrogenation of cyclohexene under mild operating conditions. The influence of various parameters such as catalyst and substrate concentrations, temperature of the system, amount of solvent used and also the effect of various solvents on the rate of the reaction has been investigated. From the analysis of the rate data, the order of the reaction with respect to the catalyst and substrate concentration have been determined. The life cycle of the catalyst has also been studied.

4.2 Experimental

4.2.1 Measurement of catalytic activity for hydrogenation reactions.

The hydrogenation reaction was carried out in a magnetically stirred glass reactor using methanol as the solvent for homogeneous as well as the polymer bound catalysts. Methanol was selected as the solvent, after carrying out swelling studies of the catalysts in different solvents. The progress of the reaction was followed by measuring the uptake of hydrogen as a function of reaction time at a constant temperature and pressure using a glass manometric apparatus. The experimental set-up and detailed procedure are described in Chapter-2.

4.2.2 Analysis of kinetic data

The kinetic data for the hydrogenation reaction were obtained in a kinetic regime of stirring speed of 650 rpm at $35^{o}C$. The stoichiometry of the reaction was checked by carrying out few experiments at constant temperature and at one atmospheric pressure with different concentrations of cyclohexene for a longer time interval (i.e., $\simeq$ 4 hours). In all these experiments the amount of hydrogen abosorbed was stoichiometrically proportional to the cyclohexene converted (Based on GC analysis of the products) which suggests that formation of any side product is negligible. The initial rate data (based on hydrogen uptake measurements) is used to evaluate the kinetic parameters.

In each case the uptake of hydrogen was measured as a function of time. Figure 4.3 shows the plot of the hydrogen uptake at various interval of time for the catalyst 5PPd(II)DAP. The values for the rate of hydrogenation were calculated from the slope of these plots.

4.3 Results and discussion

4.3.1 Effect of cyclohexene concentration

The influence of cyclohexene concentration on the rate of reaction for different catalysts has been studied and the

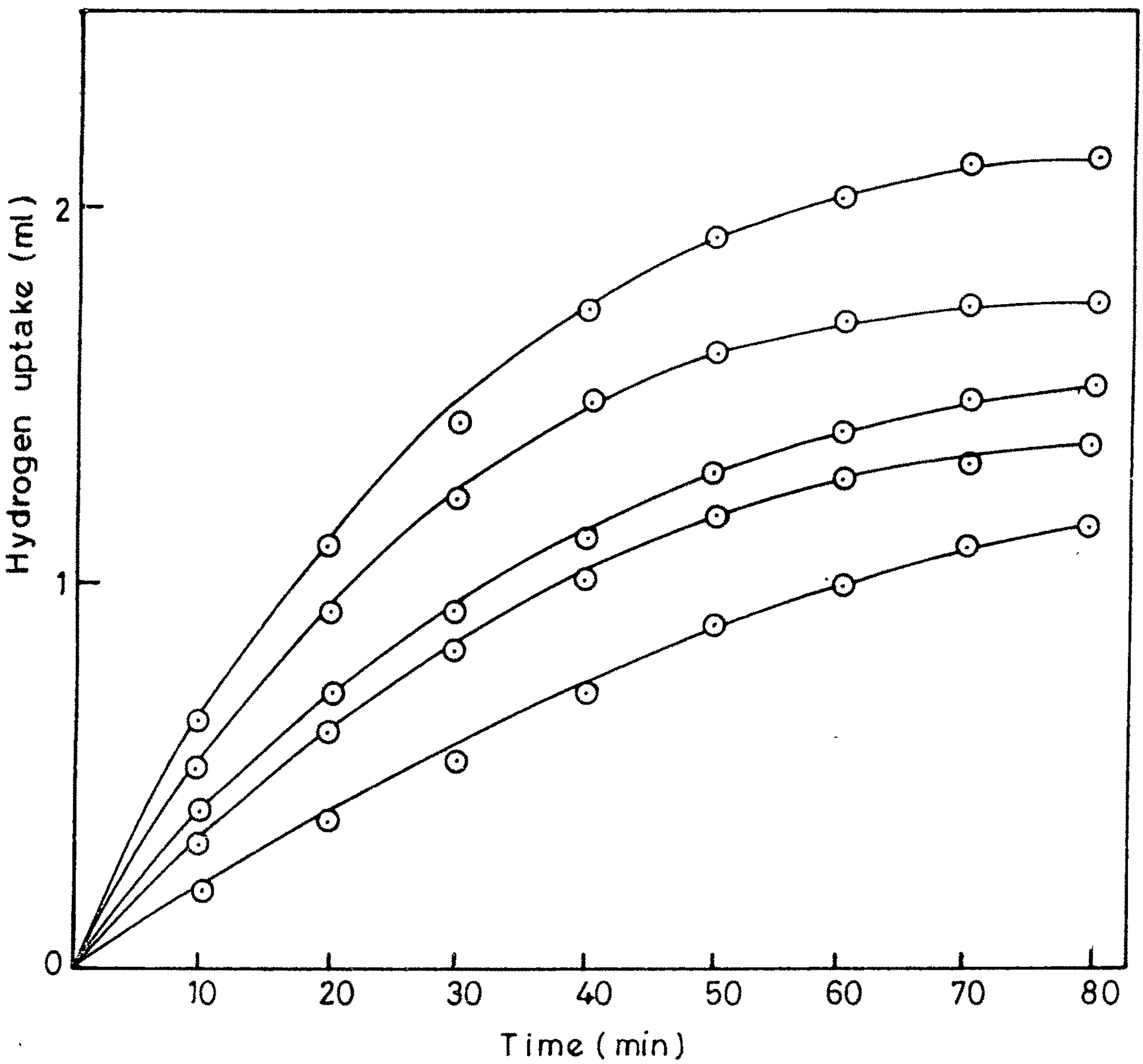

Fig. 4.3 Plot of hydrogen uptake against time for the catalyst 5PPd(II)DAP

results are summarized in Tables 4.3.1 to 4.3.3. It was found that the rate of the reaction increases with an increase in concentration of cyclohexene keeping the catalyst concentration constant. For example, in the case of 5PRu(III)DAP catalyst, the rate increases from $1.69x10^{-2}$ to $2.97x10^{-2}$ ml/min when the cyclohexene concentration varies from $4.71x10^{-3}$ to $18.84x10^{-3}$ mols/lit; in the case of 5PPd(II)DAP the rate increased from $2.20x10^{-2}$ to $4.64x10^{-2}$ ml/min at 35^{o}C and one atm pressure.

The plot of log (initial rate) against log (cyclohexene) at a fixed concentration of catalyst, hydrogen pressure and temperature is found to be linear. (Figs.4.3.1 & 4.3.2) The order of reaction calculated from the slopes of these plots are given in Table 4.3.7.

Thy hydrogenation reaction was carried out for homogeneous complexes of Ru(III) and Pd(II) under similar condition and the rate was found to be slow as compared to the heterogenised homogeneous catalysts containing the same amount of metal ions present on the surface. For a lower concentration of metal ions it is difficult to measure the rate and hence a higher concentration of metal ions has been chosen for actual experiments in homogeneous system. The results are summarized in Table 4.3.3. The values for the rate of reaction for homogeneous and heterogenised homogeneous systems are $2.75x10^{-2}$ ml/min and $1.69x10^{-2}$ ml/min

Table 4.3.1

Effect of concentration of cyclohexene on the rate of hydrogenation for supported catalysts in methanol at atmospheric pressure.

Reaction temperature = 35^{o}C
Quantity of methanol used = 20 ml.

Catalyst	Ru present (mol/lit)	[cyclohexene] (mol/litx10^3)	Rate of reaction (ml/minx10^2)
5PRu(III)DAP	$3.7x10^{-5}$	4.71	1.69
		9.42	2.04
		11.77	2.24
		14.13	2.37
		18.84	2.97
15PRu(III)DAP	$3.2x10^{-5}$	4.71	2.14
		9.42	3.55
		11.77	4.13
		14.13	5.06
		18.84	5.73
2XRu(III)DAP	$3.16x10^{-6}$	4.71	2.02
		9.42	2.48
		11.77	2.91
		14.13	3.37
		18.84	4.26
8XRu(III)DAP	$1.55x10^{-6}$	4.71	1.79
		9.42	2.20
		11.77	2.24
		14.13	2.97
		18.84	3.41

Table 4.3.2

Effect of Concentration of cyclohexene in the rate of hydrogenation for supported catalysts in methanol at atmospheric pressure.

Reaction temperature = 35°C
Quantity of methanol used = 20 ml

Catalyst	Ru present (mol/lit)	[cyclohexene] (mol/litx10^3)	Rate of reaction (ml/minx10^2)
5PPd(II)DAP	4.08×10^{-5}	4.71	2.20
		9.42	2.90
		11.77	3.41
		14.13	4.12
		18.84	4.64
15PPd(II)DAP	3.66×10^{-5}	4.71	1.04
		9.42	2.81
		11.77	5.36
		14.13	5.40
		18.84	6.80
2XPd(II)DAP	2.06×10^{-6}	4.71	1.60
		9.42	2.58
		11.77	2.89
		14.13	3.24
		18.84	3.61
8XPd(II)DAP	1.97×10^{-6}	4.71	6.00
		9.42	9.00
		11.77	10.00
		14.13	11.02
		18.84	12.40

Table 4.3.3

Effect of Concentration of cyclohexene on the rate of hydrogenation for homogeneous catalysts in methanol at atmospheric pressure.

Reaction temperature = $35^{o}C$
Quantity of methanol used = 20 ml

Catalyst	Ru present (mol/lit)	[cyclohexene] (mol/litx10^{3})	Rate of reaction (ml/minx10^{2})
$[RuDAPCl_2]Cl$	$1.60x10^{-3}$	4.71	2.75
		9.42	3.35
		11.77	3.84
		14.13	4.21
		18.84	4.67
$[PdDAP]Cl_2]$	$1.8x10^{-3}$	4.71	2.95
		9.42	4.07
		11.77	4.73
		14.13	5.10
		18.84	5.91

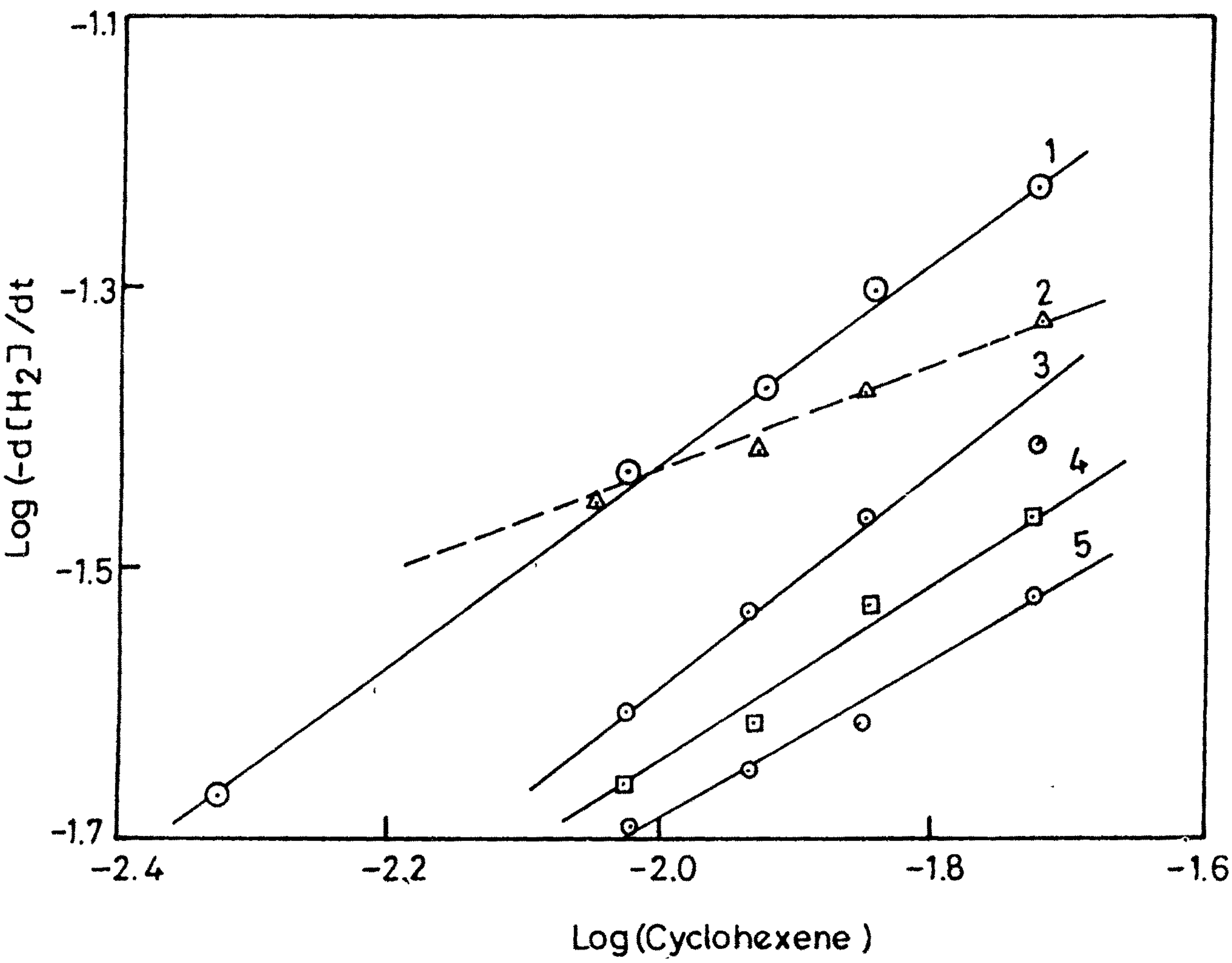

Fig. 4.3.1 Plot of log ($-d[H_2]/dt$) vs log [cyclohexene] for catalyst
1. 15PRu(III)DAP 2. [RuDAPCl_2]Cl 3. 2XRu(III)DAP
4. 8XRu(III)DAP 5. 5PRu(III)DAP

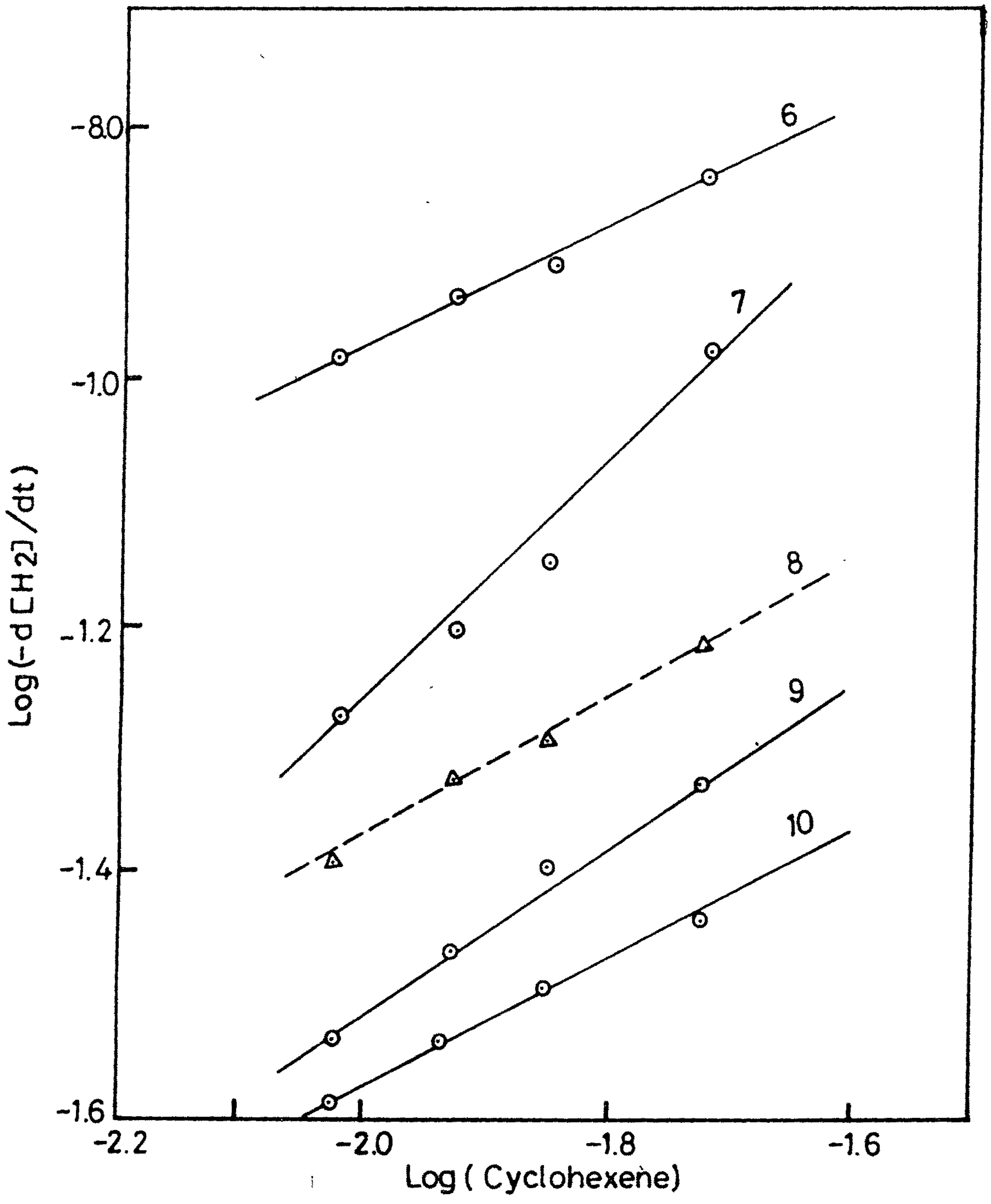

Fig. 4.3.2 Plot of log(-d[H_2]/dt) vs log[cyclohexene] for catalysts 6. 8X Pd(II)DAP 7. 15PPd(II)DAP 8. [PdDAP]Cl_2 9. 5PPd(II)DAP 10. 2XPd(II)DAP

as the Ru concentration present in the catalysts are 1.60×10^{-3} mol/lit and 3.70×10^{-5} mol/lit respectively. Similar results are obtained with Pd catalysts and the values obtained are 2.95×10^{-2} ml/min and 2.20×10^{-2} ml/min for unbound palladium complex and 5PPd(II)DAP catalyst respectively for a palladium metal concentration of 1.80×10^{-3} mol/lit and 4.08×10^{-5} mol/lit. From the results it is obvious that the catalytic activity increases when the metal ions are heterogenised on a polymeric support.

Effect of the nature of support

The hydrogenation reaction carried out with the above catalyst shows that the rate of hydrogenation is dependent on the nature of the polymeric support used (Tables 4.3.1 and 4.3.2). As the crosslinking increases from 5% to 15% the rate of reaction increased from 1.69×10^{-2} ml/min to 2.14×10^{-2} ml/min for a constant concentration of Ru(III). Similar results have also been observed using commercially available polymeric support (XAD-2 and XAD-8) used for preparing the anchored catalysts. Increase in the rate might be attributed due to the better dispersion of the active components with increase in degree of crosslinking of the polymeric support. Sokolskii et.al have also reported that the nature of the supports considerably affect the rate and mechanism of catalytic processes for hydrogenation of allylalcohol using poly-2-vinylpyridine-Pd(II) catalyst (92). Dietzmann et al observed an increase in the activity of Rh complexes bound to poly (Sty-DVB) of different crosslinking for the hydrosilylation reaction with increasing surface area and pore radius(93).

4.3.2 **Influence of catalyst concentration**

The influence of catalyst concentration on the rate of hydrogenation of cyclohexene has been studied for different catalyst systems. The results are given in Tables 4.3.4 to 4.3.6. It is found that when the concentration of Ru is changed from 1.85×10^{-5} to 7.42×10^{-5} mol/lit, the rate of reaction varies from 1.66×10^{-2} ml/min to 3.82×10^{-2} ml/min for 5PRu(III)DAP catalyst at 35^{o}C and one atmospheric pressure. In the case of all the catalyst system studied, the rate increases with an increase in catalyst concentration. Thus in the case of 5PPd(II)DAP the rate increased from 2.88×10^{-2} ml/min to 5.55×10^{-2} ml/min as the concentration of Pd changed from 2.04×10^{-5} mol/lit to 8.17×10^{-5} mol/lit.

The order of reaction with respect to the concentration of catalyst was calculated from the plots of log (initial rate) vs log (catalyst) at a fixed concentration of substrate at 35^{o}C. The order is found to be fractional in all cases. (Tables 4.3.7 and Figs 4.3.3 to 4.3.5). The fractional order of the reaction may be due to non accessibility of catalytic sites and steric hindrance due to the ligand molecule.

The experiments were repeated for homogeneous complexes of Pd(II) and Ru(III) ions and the results are given in Table

4.3.6. It was observed that when the concentration of Ru(III) ions varies from 0.643×10^{-3} to 1.60×10^{-3} mol/lit the rate of hydrogenation changes from 2.18×10^{-2} to 3.98×10^{-2} ml/min. for a cyclohexene concentration of 9.42×10^{-3} mol/lit at 35°C and at one atmosphere pressure. In the case of Pd(II) ion the rate varied from 2.69×10^{-2} to 5.49×10^{-2} ml/min with a catalyst concentration of 0.79×10^{-3} to 1.80×10^{-3} mol/lit of Pd under similar conditions.

4.3.3 **Effect of temperature**

Temperature has a profound effect on the rate of a chemical reaction. It was observed that the rate of molecules undergoing chemical transformation is proportional to the number of molecules that exist in an appropriately activated condition. This number which determines the order of magnitude of the reaction velocity is an exponential function of temperature(94). In case of homogeneous reaction for every ten degree rise in temperature the rate of reaction is doubled or trippled.

For heterogeneous reaction also the rate of the reaction generally increases with an increase in temperature.

The effect of temeprature on the rate of hydrogenation of cyclohexene has been studied in the range of 30-45°C and the results are summarized in Tables 4.3.8 to 4.3.10. The

Table 4.3.4

Influence of catalyst concentration on the rate of hydrogenation for the supported catalysts in methanol at atmospheric pressure.

Reaction temperature = 35^{o}C
Quantity of methanol used = 20 ml
[Cyclohexene] (mol/lit) = $9.42x10^{-3}$

Catalyst	Ru present (mol/lit)	Rate of reaction (ml/minx10^{2})
5PRu(III)DAP	$1.85x10^{-5}$	1.66
	$3.71x10^{-5}$	1.88
	$4.63x10^{-5}$	2.66
	$5.57x10^{-5}$	2.87
	$7.42x10^{-5}$	3.82
15PRu(III)DAP	$1.61x10^{-5}$	3.04
	$3.22x10^{-5}$	3.44
	$4.01x10^{-5}$	4.70
	$4.83x10^{-5}$	6.00
	$6.43x10^{-5}$	7.29
2XRu(III)DAP	$1.58x10^{-6}$	2.00
	$3.16x10^{-6}$	2.38
	$3.95x10^{-6}$	2.50
	$4.75x10^{-6}$	2.85
	$6.33x10^{-6}$	3.22
8XRu(III)DAP	$0.77x10^{-6}$	2.01
	$1.55x10^{-6}$	2.40
	$1.94x10^{-6}$	2.64
	$2.33x10^{-6}$	3.52
	$3.10x10^{-6}$	4.23

Table 4.3.5

Influence of Catalyst concentration on the rate of hydrogenation for the supported catalysts in methanol at atmospheric pressure.

Reaction temperature = 35^{o}C
Quantity of methanol used = 20 ml
[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Ru present (mol/lit)	Rate of reaction (ml/min$\times 10^{2}$)
5PPd(II)DAP	2.04×10^{-5}	2.88
	4.08×10^{-5}	3.40
	5.11×10^{-5}	3.70
	6.13×10^{-5}	3.80
	8.17×10^{-5}	5.55
15PPd(II)DAP	1.83×10^{-5}	4.28
	3.66×10^{-5}	5.28
	4.58×10^{-5}	8.46
	5.50×10^{-5}	10.29
	7.33×10^{-5}	12.11
2XPd(II)DAP	1.03×10^{-6}	2.20
	2.06×10^{-6}	2.50
	2.58×10^{-6}	2.95
	3.10×10^{-6}	3.12
	4.13×10^{-6}	5.30
8XPd(II)DAP	0.986×10^{-6}	5.90
	1.97×10^{-6}	10.20
	2.46×10^{-6}	11.40
	2.96×10^{-6}	14.40
	3.94×10^{-6}	17.30

Table 4.3.6

Influence of catalyst concentration on the rate of hydrogenation for the homogeneous catalysts in methanol at atmospheric pressure.

Reaction temperature = 35°C
Quantity of methanol used = 20 ml
[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Ru present (mol/lit)	Rate of reaction ($ml/min \times 10^2$)
$[RuDAPCl_2]Cl$	0.643×10^{-3}	2.18
	0.803×10^{-3}	2.54
	0.960×10^{-3}	2.81
	1.28×10^{-3}	3.30
	1.60×10^{-3}	3.98
$[PdDAP]Cl_2$	0.79×10^{-3}	2.69
	0.98×10^{-3}	3.38
	1.18×10^{-3}	3.98
	1.58×10^{-3}	5.01
	1.80×10^{-3}	5.49

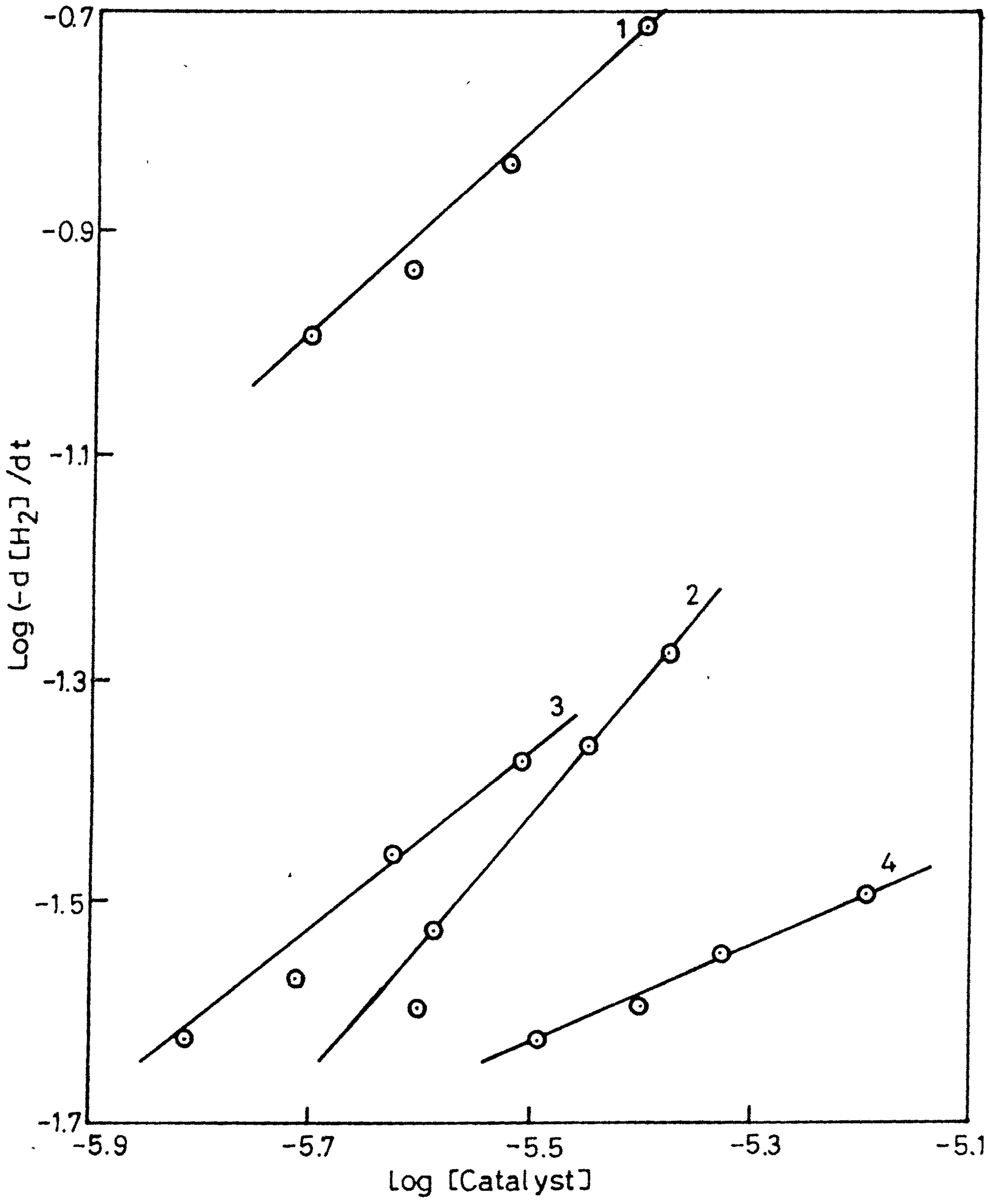

Fig. 4.3.3 Plot of log (-d[H_2]/dt vs log[catalyst] for catalysts

1. 8XPd(II)DAP 2. 2XPd(II)DAP
3. 8XRu(III)DAP 4. 2XRu(III)DAP

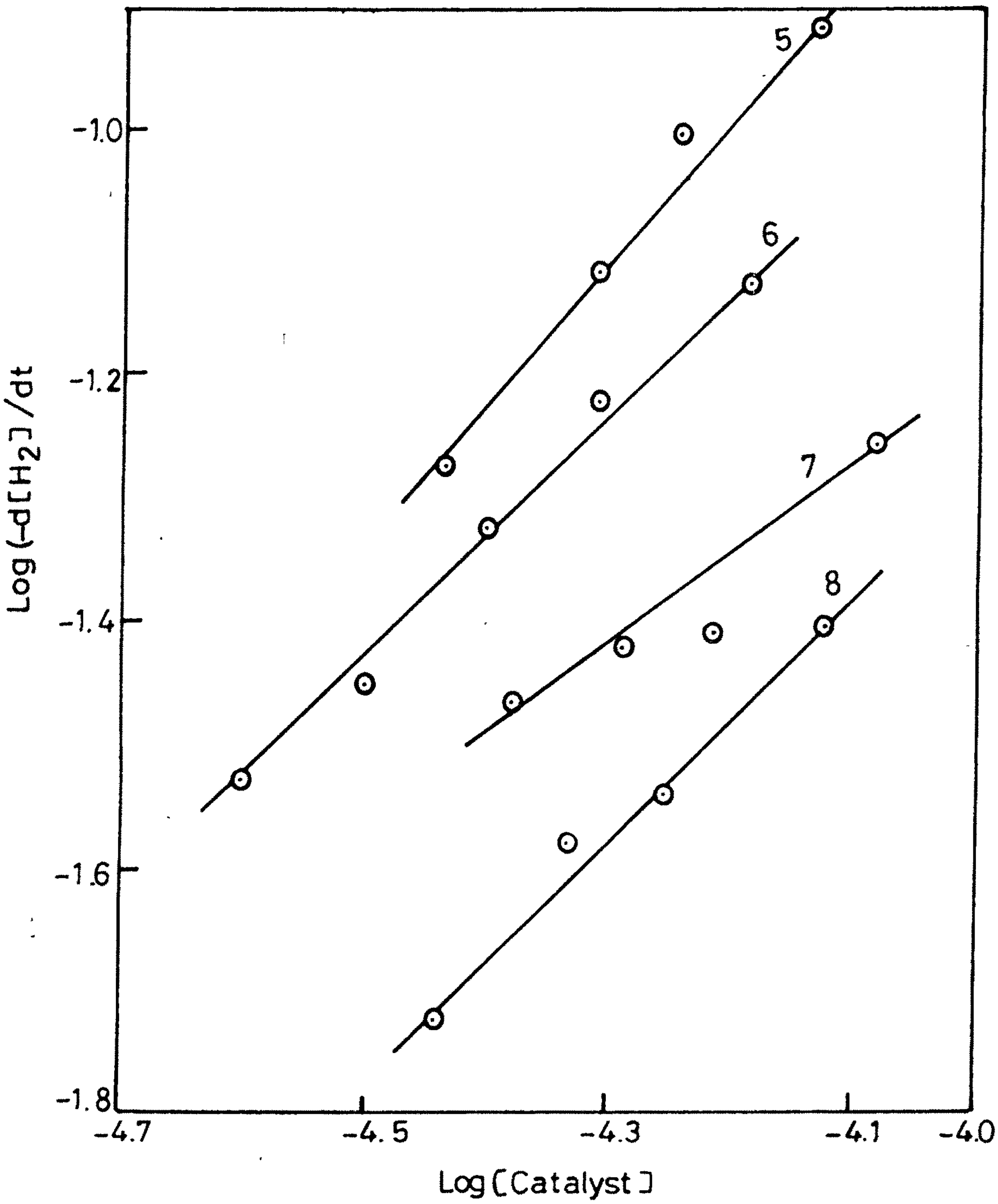

Fig. 4.3.4 Plot of log ($-d[H_2]/dt$) vs log [catalyst] for catalysts

5. 15PPd(II)DAP 6. 15PRu(III)DAP
7. 5PPd(II)DAP 8. 5PRu(III)DAP

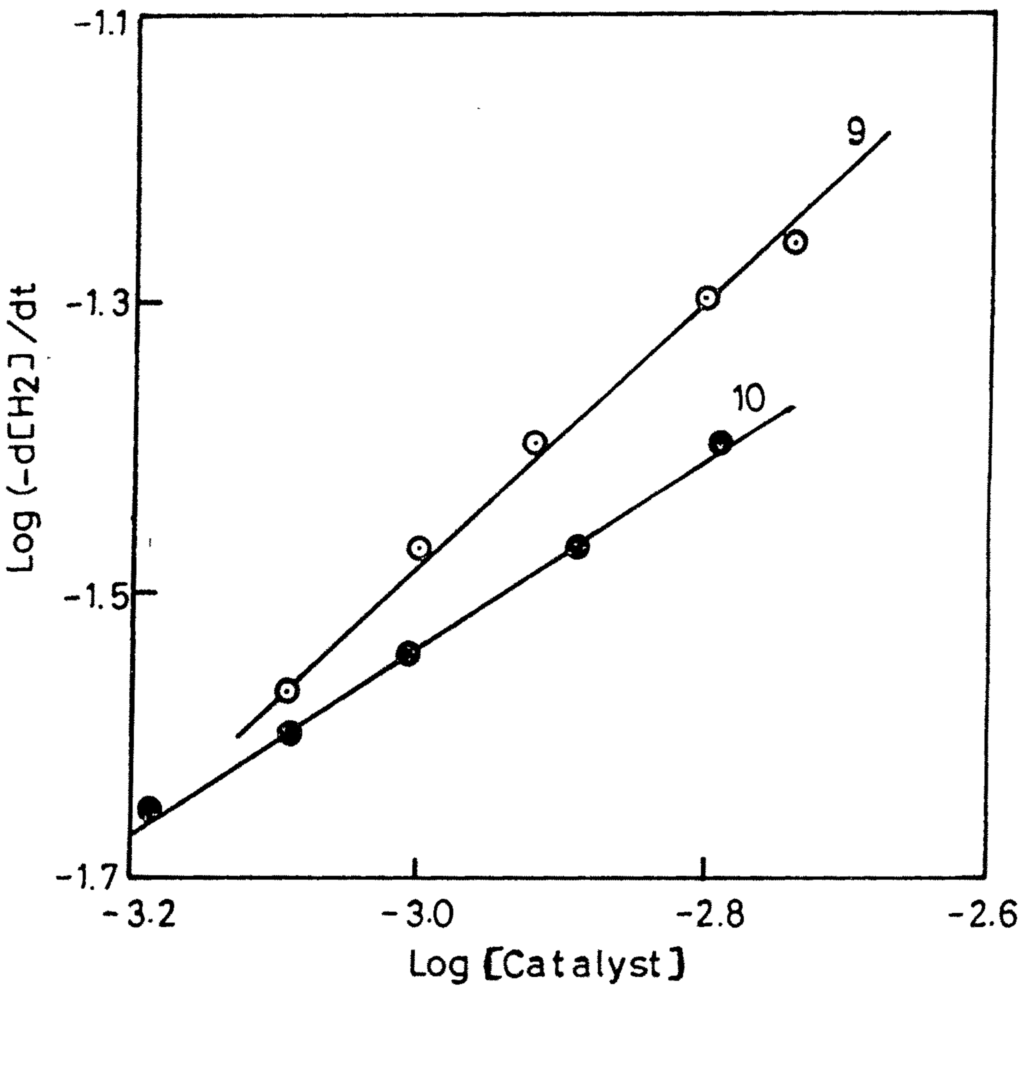

Fig. 4.3.5 Plot of log (-d[H]/dt) vs log [catalyst] for catalysts
9. $[PdDAP]Cl_2$ 10. $[RuDAPCl_2]Cl$

Table 4.3.7

The values of order of reaction for various catalysts

Catalyst	Order of reaction with respect to [Cyclohexene]	Order of reaction with respect to [Catalyst]
5PRu(III)DAP	0.57	0.98
15PRu(III)DAP	0.73	0.94
2XRu(III)DAP	0.77	0.442
8XRu(III)DAP	0.63	0.802
5PPd(II)DAP	0.68	0.72
15PPd(II)DAP	0.96	1.12
2XPd(II)DAP	0.53	1.10
8XPd(II)DAP	0.50	0.92
$[RuDAPCl_2]Cl$	0.36	0.64
$[PdDAP]Cl_2$	0.54	0.90

hydrogenation rate was found to increase with an increase in temperature for all the catalysts studied. Thus the rate of the reaction increases from 1.66×10^{-2} to 4.03×10^{-2} ml/min as the temperature is increased from 30 to 45°C using 5PRu(III)DAP catalyst containing 3.71×10^{-5} mol/lit of Ru. Similar results were obtained while using Pd catalysts. Hence the rate of reaction increases from 3.01×10^{-2} to 5.10×10^{-2} ml/min for an increase in temperature from 30 to 45°C with 4.08×10^{-5} mol/lit of Pd for 5PPd(II)DAP.

In the case of homogeneous system the activity was found to be very low in comparison to the heterogenised homogeneous catalysts. Thus the amount of the catalyst was chosen in such away that the rate of the reaction could be measured. It was observed that the rate increases from 4.46×10^{-2} to 6.38×10^{-2} ml/min as the temperature is increased from 30 to 45°C by the use of $[RuDAPCl_2]Cl$ catalyst (1.60×10^{-3} mol/lit of Ru); for $[PdDAP]Cl_2$ catalyst (1.8×10^{-3} mol/lit Pd), the rate varies from 4.89×10^{-2} to 8.91×10^{-2} ml/min (Table 4.3.10).

The values for the energy of activation calculated from the slope of the straight line plot of log (initial rate) against 1/T (Figures 4.3.6 to 4.3.8) are given in Table 4.3.11. In the case of polymer bound Ru(III) catlaysts the energy of activation was found to be in the range of 9.4 to 13.5 Kcal/mole while in the case of Pd(II) catalysts 5.7 to

8.6 Kcal/mol which indicates that Pd(II) has a moderately higher catalytic activity for hydrogenation reaction. The results could not be compared here with the homogeneous counterparts because a large amount of the catalyst has been taken for the reaction. However, in the case of Ru(III) and Pd(II) complex catalyst in homogeneous system the energy of activation was found to be 7.94 and 4.58 Kcal/mole respectively.

4.3.4 **Effect of Solvents**

The nature of the solvent can have a profound effect on the activity of a supported catalyst. Polymer swelling is a very useful parameter to control both specificity and selectivity in a batch reactor. The activity and selectivity of supported catalysts may be varied by the nature of the solvent (95). Thus coordinating solvents often take part in the intimate mechanism of the reaction being co-ordinated to and displaced from the active site during the catalytic cycle. The second way in which a solvent can influence a reaction is through its ability to swell the support. Thirdly the polarity of the solvent will lead to a polarity gradient between the bulk solvent and the local environment of the catalytic site. Hence, the suitable solvent would be one that combines the good swelling ability and high polarity.

Table 4.3.8

Effect of temperature on cyclohexene hydrogenation reaction for supported catalysts in methanol at atmospheric pressure.

[Cyclohexene] (mol/lit) = 9.42×10^{-3}
Qty. of methanol used = 20 ml

Catalyst	Ru present (mol/lit)	Temperature (^{o}C)	Rate of reaction (ml/min$\times 10^{2}$)
5PRu(III)DAP	3.71×10^{-5}	30	1.66
		35	2.30
		40	2.35
		45	4.03
15PRu(III)DAP	3.22×10^{-5}	30	4.00
		35	5.68
		40	8.20
		45	12.00
2XRu(III)DAP	3.16×10^{-6}	30	2.50
		35	2.56
		40	3.18
		45	5.03
8XRu(III)DAP	1.55×10^{-6}	30	2.35
		35	3.20
		40	3.84
		45	4.65

Table 4.3.9

Effect of temperature on cyclohexene hydrogenation for polymer supported catalysts in methanol at atmospheric pressure.

[Cyclohexene] (mol/lit) = 9.42×10^{-3}
Qty. of methanol used = 20 ml

Catalyst	Pd present (mol/lit)	Temperature (^{o}C)	Rate of reaction (ml/min$\times 10^{2}$)
5PPd(II)DAP	4.08×10^{-5}	30	3.01
		35	3.92
		40	4.60
		45	5.10
15PPd(II)DAP	3.66×10^{-5}	30	3.02
		35	8.80
		40	8.85
		45	9.00
2XPd(II)DAP	2.06×10^{-6}	30	2.37
		35	2.68
		40	3.10
		45	4.50
8XPd(II)DAP	1.97×10^{-6}	30	11.00
		35	13.15
		40	13.38
		45	14.27

Table 4.3.10

Effect of temperature on cyclohexene hydrogenation for homogeneous catalysts in methanol at atmospheric pressure.

[Cyclohexene] (mol/lit) = 9.42×10^{-3}
Qty. of methanol used = 20 ml

Catalyst	Ru/Pd present (mol/lit)	Temperature (^{o}C)	Rate of reaction (ml/min$\times 10^{2}$)
[Ru $DAPCl_2$]Cl	1.6×10^{-3}	30	4.46
		35	4.95
		40	5.88
		45	6.38
[Pd DAP]Cl_2	1.8×10^{-3}	30	4.89
		35	6.02
		40	7.24
		45	8.91

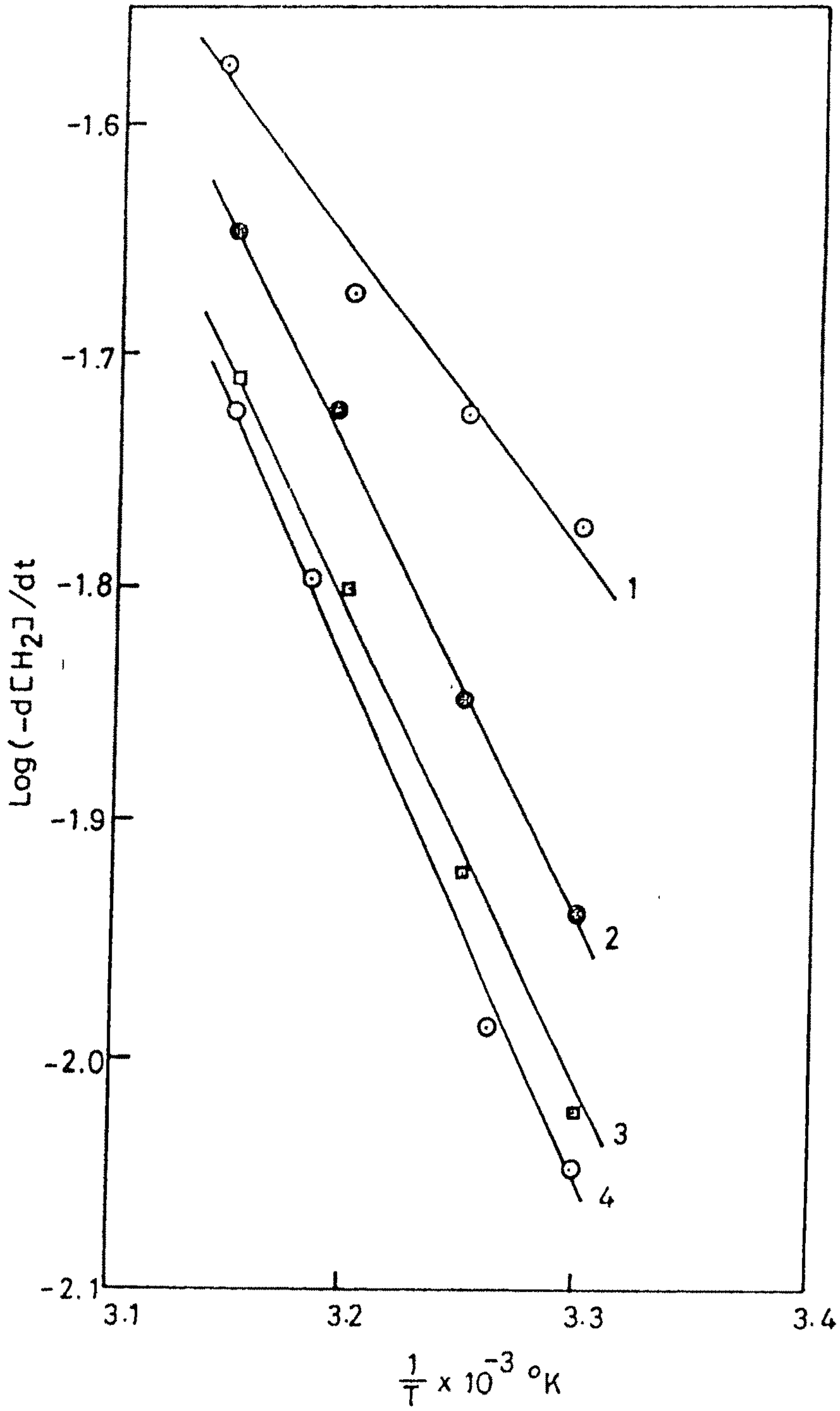

Fig. 4.3.6 Arrhenius plot for catalysts

1. 8XPd(II)DAP 2. 8XRu(III)DAP
3. 15PRu(III)DAP 4. 2XRu(III)DAP

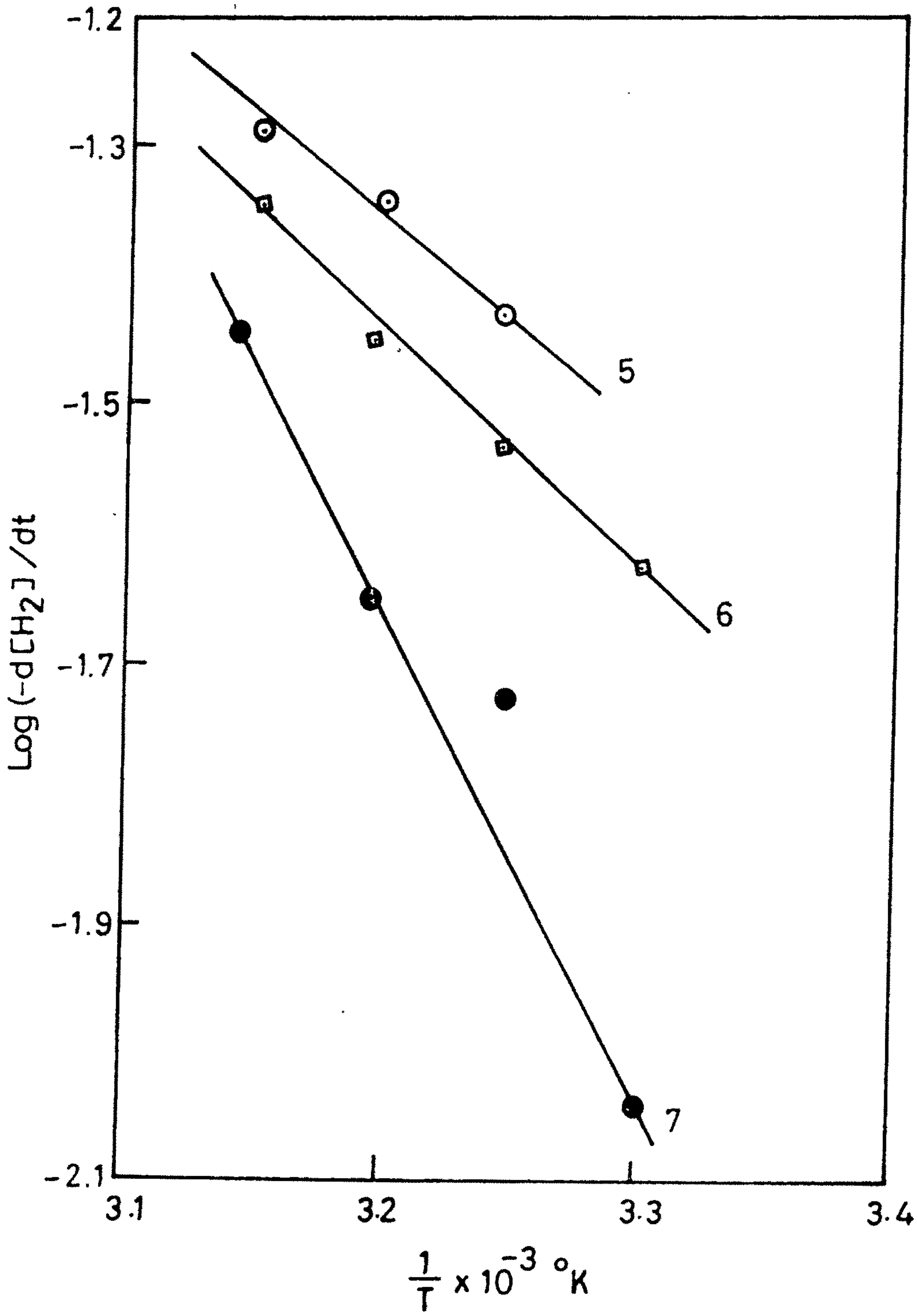

Fig. 4.3.7 Arrhenius plot for catalysts
5. 15PPd(II)DAP 6. 2XPd(II)DAP 7. 5PPd(II)DAP

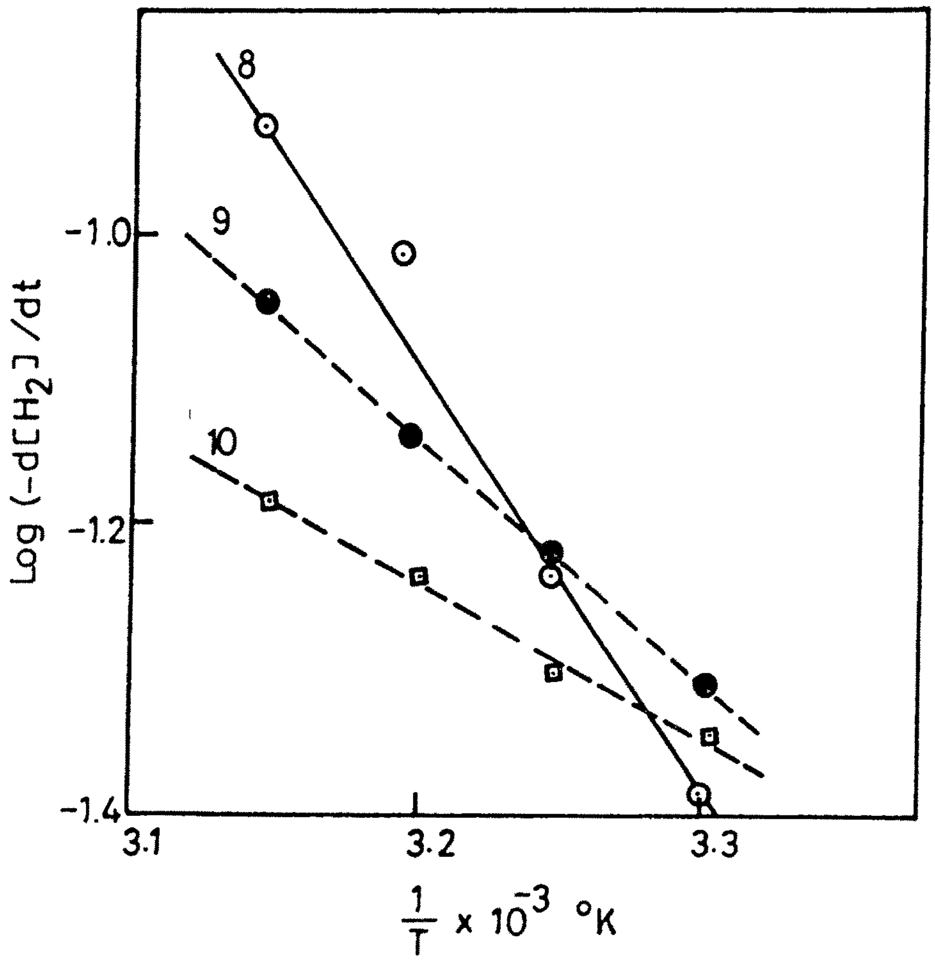

Fig. 4.3.8 Arrhenius plot for catalysts
8. 5PRu(III)DAP 9. $[RuDAPCl_2]Cl$ 10. $[PdDAP]Cl_2$

Table 4.3.11

The values of energy of activation for various catalysts

Catalyst	Energy of activation (Kcal/mol)
5PRu(III)DAP	13.53
15PRu(III)DAP	8.98
2XRu(III)DAP	9.90
8XRu(III)DAP	9.43
5PPd(II)DAP	7.30
15PPd(II)DAP	7.09
2XPd(II)DAP	8.60
8XPd(II)DAP	5.72
[RuDAPCl_2]Cl	7.94
[PdDAP]Cl_2	4.58

The influence of five different solvents (methanol, ethanol, dioxane, THF and benzene) on the rate of hydrogenation reaction has been studied.

It was observed that as the polarity of the solvent increases the rate of hydrogenation also increases. In the case of benzene the rate was found to be 0.70×10^{-2} ml/min while in the case of methanol it was 2.11×10^{-2} ml/min with 5PRu(III)DAP catalyst. The results are summarized in Tables 4.3.12 to 4.3.15.

A knowledge of solubility of gases in liquid is very essential in interpretting the gas-liquid-solid reactions. It is therefore necessary to know the solubility of gases especially in the reaction medium(96).

A detailed study of the solubility of hydrogen in methanol has been made at various pressures and temperatures(97).

Figures 4.3.9 to 4.3.11 illustrate the influene of hydrogen in methanol on the rate of reaction for all the catalysts at a constant concentration of catalyst and that of the substrate at 35°C. As the amount of reaction medium i.e., methanol is increased the amount of hydrogen available for the reaction in the liquid phase increases. The effect of the amount of methanol in the cyclohexene hydrogenation

Table 4.3.12

Solvent dependence for the hydrogenation of cyclohexene by supported catalysts at atmospheric pressure.

Reaction temperature = 35^{o}C
Qty. of solvent used = 20 ml

[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Ru present mol/lit	Solvent	Rate of reaction (ml/minx10^{2})
5PRu(III)DAP	3.71×10^{-5}	Methanol	2.11
		Ethanol	1.98
		Dioxane	1.50
		THF	1.20
		Benzene	0.70
15PRu(III)DAP	3.22×10^{-5}	Methanol	3.70
		Ethanol	3.65
		Dioxane	2.98
		THF	1.42
		Benzene	0.73
2XRu(III)DAP	3.16×10^{-6}	Methanol	2.12
		Ethanol	2.08
		Dioxane	1.72
		THF	1.21
		Benzene	0.60

Table 4.3.13

Solvent dependence for hydrogenation of cyclohexene by supported catalysts at atmospheric pressure.

Reaction temperature = 35^{o}C
Qty. of solvent used = 20 ml

[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Ru/Pd present mol/lit	Solvent	Rate of reaction (ml/min$\times 10^{2}$)
8XRu(III)DAP	1.55×10^{-6}	Methanol	2.22
		Ethanol	2.11
		Dioxane	1.82
		THF	1.41
		Benzene	0.63
5P Pd(III)DAP	4.08×10^{-5}	Methanol	3.73
		Ethanol	3.65
		Dioxane	2.80
		THF	1.50
		Benzene	0.84
15PPd(II)DAP	3.66×10^{-5}	Methanol	5.35
		Ethanol	5.20
		Dioxane	4.32
		THF	3.11
		Benzene	0.86

Table 4.3.14

Solvent dependence for hydrogenation of cyclohexene with supported catalysts at atmospheric pressure.

Reaction temperature (^{o}C) = 35
Qty. of solvent used (ml) = 20

[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Pd present mol/lit	Solvent	Rate of reaction (ml/min$\times10^{2}$)
2XPd(II) DAP	2.06×10^{-6}	Methanol	2.26
		Ethanol	2.21
		Dioxane	1.83
		THF	1.17
		Benzene	0.72
8XPd(II) DAP	1.97×10^{-6}	Methanol	8.40
		Ethanol	8.02
		Dioxane	6.41
		THF	5.23
		Benzene	0.94

Table 4.3.15

Solvent dependence for hydrogenation of cyclohexene with homogeneous catalysts at atmospheric pressure.

Reaction temperature = 35°C
Qty. of solvent used = 20 ml

[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Ru/Pd present mol/lit	Solvent	Rate of reaction (ml/min$\times 10^2$)
$[RuDAPCl_2]Cl$	1.6×10^{-3}	Methanol	2.04
		Ethanol	1.98
		Dioxane	1.61
		THF	1.20
		Benzene	0.87
$[PdDAP]Cl_2$	1.8×10^{-3}	Methanol	2.75
		Ethanol	2.69
		Dioxane	1.92
		THF	1.44
		Benzene	0.90

are given in Tables 4.3.16 to 4.3.19. Thus on increasing the volume of methanol from 10 to 40 ml at a constant concentration of cyclohexene and the catalyst, the rate was found to increase from 1.57×10^{-2} to 3.22×10^{-2} ml/min in the case of 5PRu(III)DAP catalyst while for 5PPd(II)DAP the rate varied from 2.54×10^{-2} to 6.28×10^{-2} ml/min under similar condition. Similar results are obtained with Pd complex catalysts.

Similar results have been observed in case of homogeneous systems. Thus for $[RuDAPCl_2]Cl$, the values of rate of reaction obtained were in the range of 1.92×10^{-2} to 3.71×10^{-2} ml/min when the volume of methanol increased from 10 to 40 ml at 35°C with a substrate concentration of 9.42×10^{-3} mol/lit of cyclohexene. In the case of $[PdDAP]Cl_2$ the rate changes from 2.05×10^{-2} to 4.00×10^{-2} ml/min under similar conditions.

4.3.5 **Life cycle of catalysts**

The main objective of supporting metal ions onto a polymer support is for its re-use. Since the metal ions are costly, it is necessary to use the catalyst without losing its catalytic activity as much as possible. But it is found that polymer bound catalyst can lose its activity by loss of metal ions, which is brought about by leaching of the active component or reduction to free metal. Usually the metal ion gets leached into the solutin (98,99).

Table 4.3.16

Effect of amount of hydrogen in methanol on the rate of hydrogenation of cyclohexene at atmospheric pressure.

Reaction temperature = 35^{o}C
Qty. of solvent used = 20 ml

[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Ru present mol/lit	Qty. of methanol (ml)	Rate of reaction (ml/minx10^{2})
5PRu(III)DAP	3.71×10^{-5}	10	1.57
		20	2.11
		25	2.34
		30	2.82
		40	3.22
15PRu(III)DAP	3.22×10^{-5}	10	2.92
		20	3.41
		25	3.65
		30	4.25
		40	4.88
2XRu(III)DAP	3.16×10^{-6}	10	1.80
		20	2.12
		25	2.31
		30	2.80
		40	2.95

Table 4.3.17

Effect of amount of hydrogen in methanol on the rate of hydrogenetion of cyclohexene at atmospheric pressure.

Reaction temperature = 35 °C

[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Ru/Pd present mol/lit	Qty. of methanol (ml)	Rate of reaction (ml/minx10^2)
8XRu(III)DAP	1.55×10^{-6}	10	1.66
		20	2.22
		25	2.34
		30	2.75
		40	3.18
5PPd(II)DAP	4.08×10^{-5}	10	2.54
		20	3.73
		25	4.14
		30	4.78
		40	6.28
15PPd(II)DAP	3.66×10^{-5}	10	5.26
		20	5.35
		25	5.88
		30	6.05
		40	6.76

Table 4.3.18

Effect of amount of hydrogen in methanol on the rate of hydrogenetion of cyclohexene at atmospheric pressure.

Reaction temperature (^{o}C) = 35

[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Ru present mol/lit	Qty. of methanol (ml)	Rate of reaction (ml/minx10^{2})
2XPd(II)DAP	2.06×10^{-6}	10	1.95
		20	2.26
		25	2.47
		30	2.65
		40	3.18
8XPd(II)DAP	1.97×10^{-6}	10	8.30
		20	8.40
		25	8.60
		30	8.80
		40	8.95

Table 4.3.19

Effect of amount of hydrogen in methanol on the rate of hydrogenetion of cyclohexene at atmospheric pressure.

Reaction temperature = $35^{o}C$

[Cyclohexene] (mol/lit) = 9.42×10^{-3}

Catalyst	Ru/Pd present mol/lit	Qty. of methanol (ml)	Rate of reaction (ml/minx10^{2})
[$RuDAPCl_2$]Cl	1.6×10^{-3}	10	1.92
		20	2.04
		25	2.81
		30	3.20
		40	3.71
[PdDAP]Cl_2	1.8×10^{-3}	10	2.05
		20	2.75
		25	3.30
		30	3.75
		40	4.00

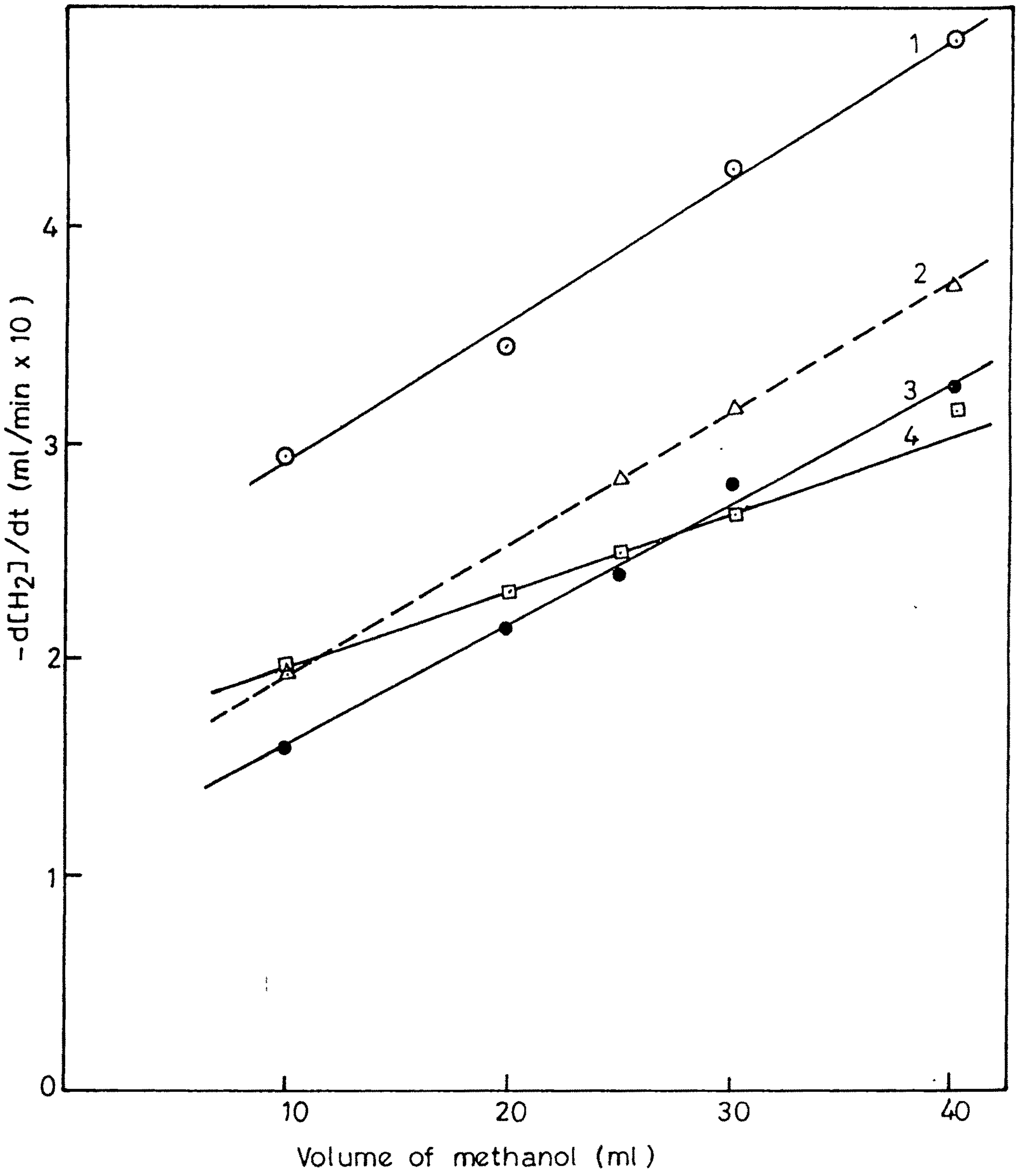

Fig. 4.3.9 Influence of solvent on the rate of hydrogenation of cyclohexene for catalysts

1. 15PRu(III)DAP 2. $[RuDAPCl_2]Cl$
3. 5PRu(III)DAP 4. 2XPd(II)DAP

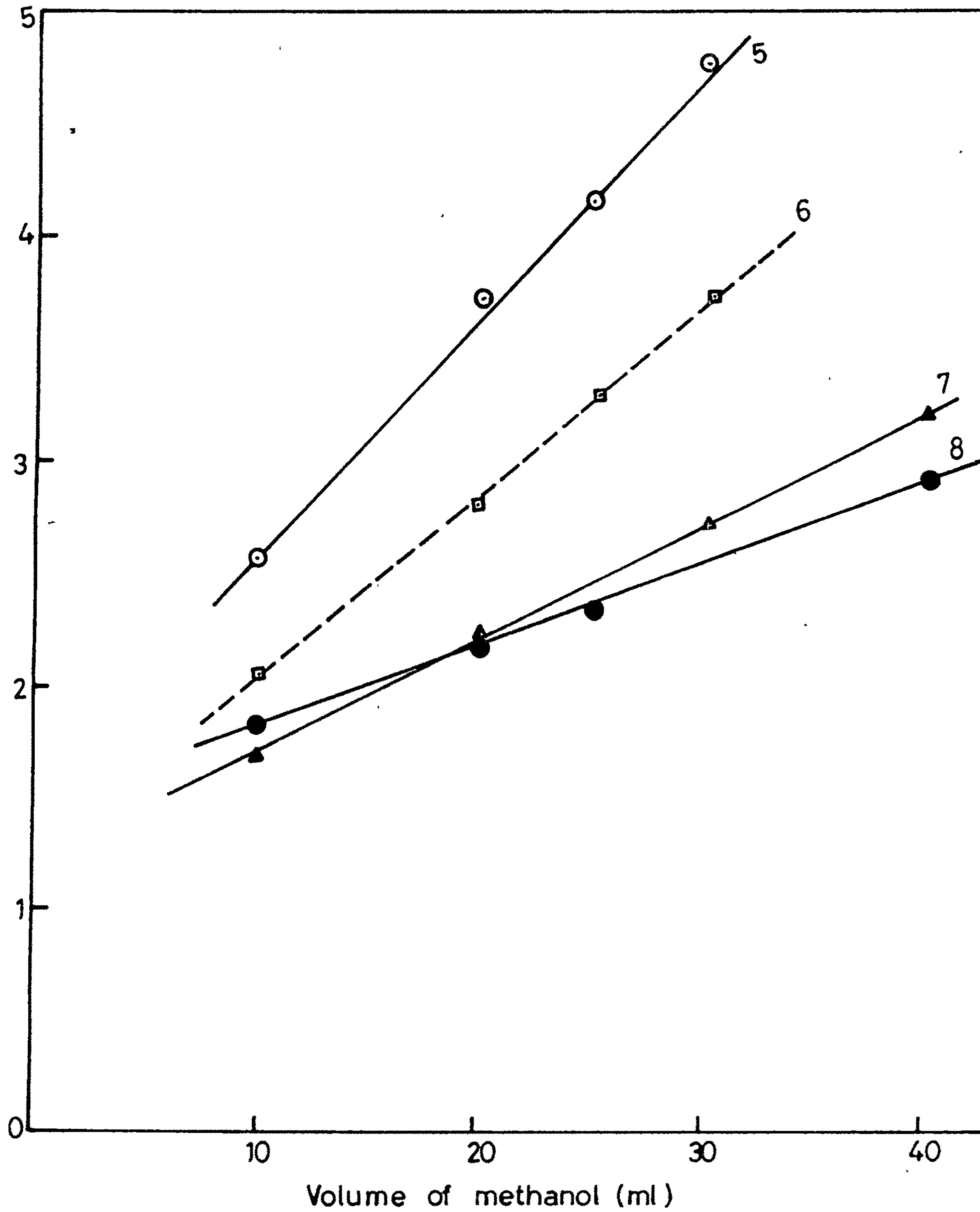

Fig. 4.3.10 Influence of solvent on the rate of hydrogenation of cyclohexene for catalysts

5. 5PPd(II)DAP 6. [PdDAP]Cl_2

7. 8XRu(III)DAP 8. 2XRu(III)DAP

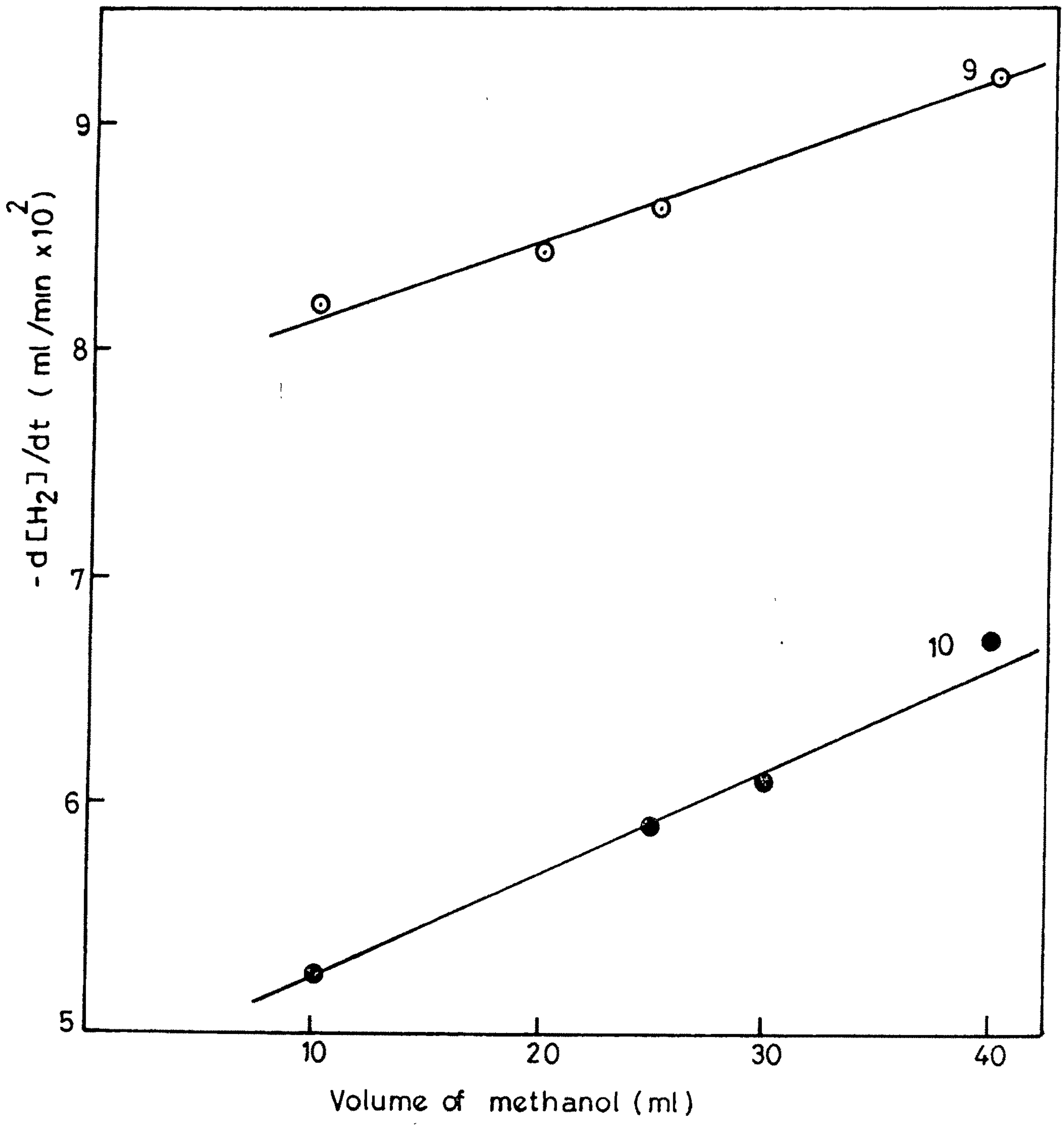

Fig. 4.3.11 Influence of solvent on the rate of hydrogenation of cyclohexene for catalysts

9. 8XPd(II)DAP 10. 15PPd(II)DAP

The leaching of metal ions can be controlled by attaching it to the support through a chelating ligand. Drago et. al have reported that polymer anchored complexes through chelating ligands are more stable(107). Pittman et. al have synthesized the rhodium diphosphine chelating complexes bound to resins and used them in the hydroformylation of styrene (100) and pent-1-ene (101). The recycling of the catalysts has been carried out to probe into the stability of the catalyst.

The experiment was carried out at 35°C for about 16 hours. In each cycle 10 μl of the substrate was injected. After completion of the reaction, 60 minutes were allowed to lapse before the next injection was made. The rate of hydrogenation was measured as a function of time for both the used and the fresh catalysts. The results are summarized in Tables 4.3.20 to 4.3.23.

It is evident from the results that in the case of poly (Sty-DVB) supported catalysts, the rate is unaltered for about 10 hours after which it decreases slowly. The estimation of metal content at the end of the reaction showed a loss of about 50% of the metal from the support.

In the case of commercially available support (XAD-2, XAD-8), the maximum rate of reaction is maintained for four hours after that the rate decreases slowly. The metal loss at the end of the reaction was found to be 63%. This loss in catalytic activity may be due to low mechanical strength of the polymer support and 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

4.3.6 **Rate equation**

In the present investigation the partial pressure of hydrogen and the concentration of hydrogen in solution is kept constant. Thus the reaction is carried out at a fixed amount of the catalyst and at constant amount of hydrogen. The actual quantity of hydrogen consumed is obtained by saturating the solvent along with the catalysts with hydrogen before injecting the olefin.

The mechanism of olefin hydrogenation using ruthenium catalysts in homogeneous medium has been studied by several workers (20,26,73). The formation of hydrido species and preferential attack of olefin on the hydrido complex of ruthenium has been established by several authors (26,28) on the basis of various experimental studies and thermodyamic properties. On the basis of the available literature evidence, the following mechanism is proposed (102).

Table 4.3.20

Life cycle study for the catalysts.

Reaction temperature = 35 °C
Qty. of methanol used = 20 ml

Fresh Catalysts		Used Catalyst	
Time (min)	Rate of reaction ml/minx10^2	Time (min)	Rate of Reaction ml/minx10^2
	5PRu(III)DAP[a]		
120	3.80	120	3.78
340	3.80	340	3.76
550	3.79	560	3.58
720	3.51	760	3.42
940	3.29	900	3.02
	15PRu(III)DAP[b]		
90	7.20	90	7.16
140	7.20	140	7.14
300	7.17	390	7.03
540	7.09	540	6.69
690	6.82	690	6.48
840	6.51	840	6.07

a Amount of catalyst 0.4 gm (7.42×10^{-5} Ru mol/lit).
Total time on stream 15.6h (15.00h)*

b Amount of catalyst 0.4gm (6.43×10^{-5} Ru mol/lit)
Total time on stream 14.00h (14.00)*

* Values given in parentheses indicate data for used catalyst.

Table 4.3.21

Life cycle study for the catalysts.

Reaction temperature = 35 ^{o}C
Qty. of methanol used = 20 ml

Fresh Catalysts		Used Catalyst	
Time (min)	Rate of reaction ml/min$\times 10^{2}$	Time (min)	Rate of Reaction ml/min$\times 10^{2}$
	5PPd(III)DAP[c]		
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
	15 P Pd(II)DAP[d]		
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

c Amount of catalyst 0.4 gm (8.17×10^{-5} Pd mol/lit).

Total time on stream 15.6h (14.00h)*

d Amount of catalyst 0.4 gm (7.33×10^{-5} Pd mol/lit)

Total time on stream 15.60h (14.00)*

* Values given in parentheses indicate data for used catalyst.

Table 4.3.22

Life cycle study for the catalysts.

Reaction temperature = 35 °C
Qty. of methanol used = 20 ml

Fresh Catalysts		Used Catalyst	
Time (min)	Rate of reaction ml/minx10^2	Time (min)	Rate of Reaction ml/minx10^2
	2XRu(III)DAP[e]		
60	3.22	60	3.20
200	3.22	220	2.68
350	3.18	300	2.00
480	3.11		
	8XRu(III)DAP[f]		
80	4.20	80	4.02
200	4.16	220	3.28
360	3.98	350	2.91
420	3.22		

e Amount of catalyst 0.4 gm (6.33×10^{-6} Ru mol/lit).

Total time on stream 8.0h (5.00h)*

f Amount of catalyst 0.4gm (3.1×10^{-6} Ru mol/lit)

Total time on stream 7.00h (5.8)*

* Values given in parentheses indicate data for used catalyst.

Table 4.3.23

Life cycle study for the catalysts.

Reaction temperature = 35 ^{o}C
Qty. of methanol used = 20 ml

Fresh Catalysts		Used Catalyst	
Time (min)	Rate of reaction ml/minx10^2	Time (min)	Rate of Reaction ml/minx10^2
	2Pd(II)DAP[g]		
60	5.30	60	5.20
200	5.26	200	5.05
350	5.12	260	4.93
480	4.98	-	-
	8XPd(II)DAP[h]		
80	16.00	80	15.97
200	15.89	200	15.82
360	15.60	360	15.55
480	14.90	-	-

g Amount of catalyst 0.4 gm (4.13 x 10^{-6} Pd mol/lit).

Total time on stream 8.00h 15.00h (4.33h)*

h Amount of catalyst 0.4gm (3.94 x 10^{-6} Pd mol/lit)

Total time on stream 8.00h (6.00)*

* Values given in parentheses indicate data for used catalyst.

$$[RuDAPCl_2]Cl + H_2 \xrightleftharpoons{K_1} [RuDAP(H)Cl]Cl + HCl$$

$$[RuDAP(H)Cl]Cl + S \xrightarrow[slow]{k'} [RuDAP(HS)Cl]Cl$$

$$[RuDAP(HS)Cl]Cl + H_2 \xrightarrow{fast} [RuDAP(H)Cl] + Alkane$$

Where K_1 represents the equilibrium constant, k' the rate constant, S is the cyclohexene and C is the catalyst (i.e.,$[RuDAPCl_2]Cl$). Then rate law can be written as

$$\text{Rate (R)} = \frac{K_1 k'[C][H_2][S]}{1+K[S]}$$

Where K is a constant.

A similar mechanism could be applied in the case of palladium metal complex.

In order to study the mechanism by which the reaction occurs, experiments were carried out by increasing the concentration of the catalyst and by keeping other parameters constant. It is found that the rate of reaction increases with increase in catalyst concentration and attains an equilibrium in each case. Similar results have been observed with the substrate concentration, keeping other factors constant. It may be concluded on the basis of the above findings that reaction follows a mechanism as suggested by Langmuir and Reidel (103).

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