CHAPTER # 2

EXPERIMENTAL

2.0 INTRODUCTION

A polymer anchored metal complex catalyst consists of two parts, a transition metal complex and a polymer. The synthesis of such catalysts envolves three steps (i) preparation and functionalization of polymer support (ii) attachment of a ligand group and (iii) introduction of metal ions. (1) The different routes by which the polymerization may be performed are shown in fig. 2.1

In order to achieve a specific effect of polymer in polymer anchored catalyst, the design of polymeric support is very important. Thus, a support with specific microstructures and/or specific ligands with a given ratio available for substitution may be prepared by homo and/or copolymerization of the monomer with the selected ligand group. When only immobilization of the homogeneous catalyst is intended, a commercial polymeric support such as polystyrene may be used to attach the ligand groups.

This chapter deals with the synthesis of polymer anchored metal chelate catalysts using commercially available polymer support of different crosslinking, their functionalization, introduction of the ligand and finally anchoring of the metal ions. The synthesis of the corresponding unbound metal complexes have also been carried out. The methods for characterization of synthesized catalysts using various conventional techniques such as chemical composition, thermal analysis, surface area measurment by BET method, bulk density, moisture content and swelling studies using various solvents are described. These catalysts have also been characterized by the use of spectroscopic methods such as far
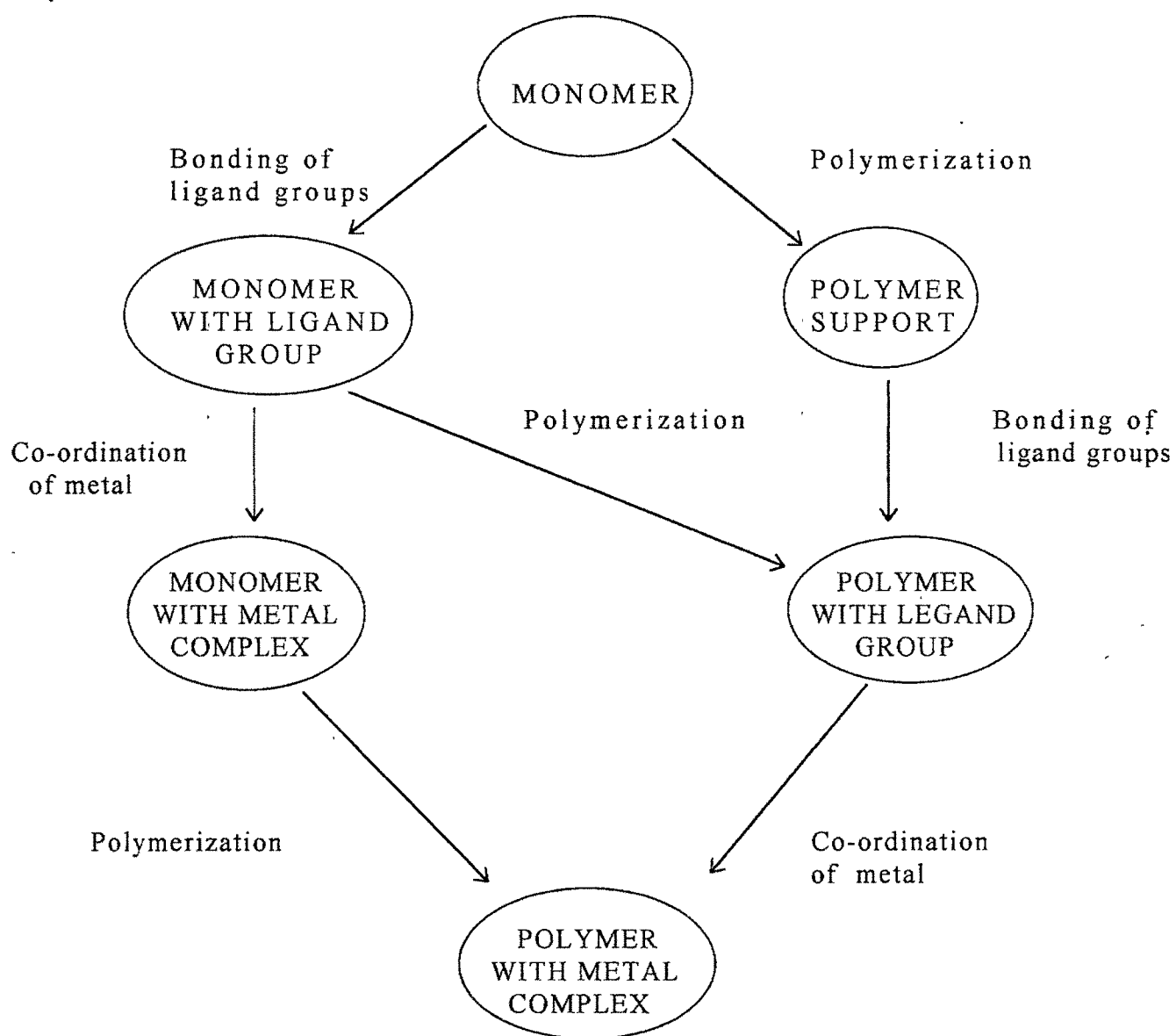
Fig. 2.1   Fundamental steps involves in the preparation of polymer anchored catalysts.

and near infrared, Ultra violet-visible spectroscopic and Scanning electron microscopy. A detailed experimental set up and procedure have been given for carrying out the hydrogenation of nitrobenzene and oxidation of toluene at normal temperature and pressure. Kinetics of both the model reactions have also been studied by varying the parameters such as temperature of the system and the concentration of the catalyst and the substrate. The study has also been made by the use of various solvents (i.e. polar and non-polar). The recycling efficiency of the catalysts has been carried out to see the stability of the catalysts.

2.1   SYNTHESIS OF THE CATALYSTS

2.2   CHLOROMETHYLATION

Commercially available styrene-divinyl benzene copolymer beads [XAD-2 and AM-24 (supplied by Ion Exchange India Ltd)] were purified by soxhlet extraction method using Benzene-Ethanol (1:1) mixture as a solvent. 1,2 dichloroethane (SRL) was distilled before use and aluminium chloride (Anhydrous AR grade) was purified by sublimation. The 8% chloromethylated (PS - DVB) beads were received as a gift sample from Ion-exchange (India) Ltd., Bombay. The chloromethylation was carried out using following method (2).

25.0g of beads were kept in contact with 100 ml of 1,2 dichloroethane in a three necked flask of 500 ml capacity fitted with a water cooled reflux condenser for an hour for the swelling purpose. 18.0g of P-formaldehyde and 3.0 g of $AlCl_3$ were dissolved in 80 ml of 1,2 dichloroethane separately and was added slowly in the above reaction mixture with constant

stirring. After complete mixing the mixture was kept at 40°C in an oil bath and dry HCl gas was bubbled through the system. The temperature was then raised to 80°C and the reaction was allowed to continue for 48h. The beads were filtered and washed sequentially with 50% aqueous dioxane, aqueous dioxane containing 10% HCl (V/V) and finally with conductivity water till the complete removal of chloride ions.

The extent of chloromethylation was determined by fusing a fixed amount of chloromethylated beads with Na_2O_2 and then estimating the chlorine content as silver chloride by the standard gravimetric method. A 1.0 g of chloromethylated sample was mixed with 2.0 g of Na_2O_2 and the mixture was fused in a platinum crucible over a gas flame, initially slowly follwed by a strong heating at least for three hours, to ensure the complete fusion of polymer with sodium peroxide. The crucible was cooled to room temperature and the mass was treated with minimum quantity of deionised water for the dissolution of sodium chloride produced during the reaction and unreacted Na_2O_2 (if any). It was filtered in 100ml volumetric flask and made up to the mark. 25ml of the aliquote was pipetted out, neutralised with dilute nitric acid and the pH of the solution was adjusted ~6. To this, 4% $AgNO_3$ (25.0ml) solution was added and was kept over night to ensure the complete precipitation of AgCl. The precipitate was filtered, washed with deionized water till the complete removal of chloride ions and finally dried at 50-60°C for ~10h. Finally, the percentage of the chloride ion was determined gravimetrically. A detailed procedure followed for gravimetric analysis has been described earlier (3)

2.3 LIGAND INTRODUCTION

25.0g of chloromethylated polymer beads were refluxed with 180.0ml of acetone-dioxane (3:1 V/V) mixture containing 20.0g of sodium iodide for four days in order to enchance the activity of the beads (4). The resin was cooled, filtered, soxhlet extracted using acetone as a solvent for 24h and finally it was dried at 80°C for 10h in vacuum.

In order to introduce the ligands, the quantity of functionalized polymers, solvent and ligand taken in the reaction are given below :

cross-linking (%)	polymer (g)	THF (ml)	Acetone (ml)	Water (ml)	Glycine (g)	L-2Amino butanol (ml)
2	25.0	180	-	-	-	10
8	25.0	180	-	-	-	10
14	25.0	180	-	-	-	10
2	25.0	60	60	60	10.0	-
8	25.0	60	60	60	10.0	-
14	25.0	60	60	60	10.0	-

The dried beads were added to the ligand solution as given above, refluxed for 4 days, cooled and finally extracted with THF untill the filtrate was colourless.

The attachment of glycine and L-2 amino butanol (L-2AB) was confirmed by elemental analysis The results for nitrogen percentage are given in Chpater 3 (Tables3.2, 3.3).

2.4 INTRODUCTION OF METAL IONS ON LIGANDED POLYMER

A weighed quantity (25.0g) of the liganded polymer was kept in contact with 80.0ml ethanol for 30 minutes in a round bottom flask. An ethanolic metal chloride solution (0.25g in 20.0ml) was added to the above mixture with help of an addition funnel fitted to the reaction vessel over a period of 30 minutes. The reaction mixture was initially refluxed for 4h and after that it was kept at room temperature for completion of reaction for 7 days. A colour change was observed from pale yellow to light grey in case of ruthenium while golden in case of palladium catalysts which is an indicative of the formation of the metal complexes on the surface of the polymer matrix.

A brief summary of the synthesis of the polymer supported metal complex catalysts is shown below :

Polymer type *	Support (g)	Ethanol (ml)	$RuCl_3.3H_2O$ (g)	$PdCl_2$ (g)	Refluxed time (h)
2 P(Gly.)	25.0	100	0.25	-	3
2 P(L2AB)	25.0	100	0.25	-	3
2 P(L2AB)	25.0	100	-	0.25	3
8 P(Gly)	25.0	100	0.25	-	3
8 P(Gly)	25.0	100	-	0.25	3
8 P(L2AB)	25.0	100	0.25	-	3
8 P(L2AB)	25.0	100	-	0.25	3
14 P(Gly)	25.0	100	-	0.25	3
14 P(L2AB)	25.0	100	-	0.25	3

* Nomenclature : NP(Gly), NP(L2AB)

Where, N : Percent crosslink, P: Co-polymer of styrene-divinyl benzene, Gly : Glycine & L2AB : L-2 amino butanol

The anchored catalysts so obtained were filtered, washed throughly with ethanol, finally dried at 70°C for 24h in vacuum and stored in vacuum desiccator.

Estimation of metal content in each case was determined as follows :

0.2g of catalyst was refluxed with 10.0ml of conc. HCl(AR grade) for 3 hours. The resulting metal chloride solution was transferred to a beaker of 100ml capacity by giving the wash with deionized water. The collected filtrate was concentrated on waterbath for half an hour and the pH of solution was adjusted to ~1.8 by means of aqueous ammonia. To this 12.5 ml of complexing agent (0.01M, prepared in 0.02N HCl) was added and heated on water bath for one hour. Nitroso-R-Salt was used as a complexing agent for Pd(II) while 2,4,6 triamino pyrimidine for the estimation of Ru(III) A colour change was observed due to formation of metal complex in solution. The solution was then transferred in 50 ml volumetric flask and made up to the mark. The metal content was determined spectrophotometrically. The procedure described by singh et al (5) was followed.

2.5 SYNTHESIS OF UNBOUND METAL COMPLEX

In order to study the catalytic activity in homogeneous medium, unbound complexes of Ru(III) and Pd(II) with L-2 amino butanol were synthesized as follows.

In order to synthesize [Ru(L2AB)Cl$_3$] complex in the solution phase, RuCl$_3$ 3H$_2$O (0.01M in 100ml methanol) was placed in a round bottom flask and L2AB (0.01M in 100ml

methanol) was added by addition funnel with a constant stirring for 4h at room temperature. The complex so formed could not be isolated. Therefore, it was used as such in the solution medium to investigate the catalytic activity of the reaction under study.

The method adopted for the synthesis of [Pd(L2AB)Cl$_2$] complex in the solution phase, was the same as in case of ruthenium complex. An equimolar mixture of palladium and L2AB was employed for this purpose The complex so formed in solution phase was used to investigate the catalytic activity for the reaction studied.

The catalysts thus synthesized are as follows :

Nomenclature of catalysts

NPML

Where, N :Percent crosslink, P:Co-polymer of styrene-divinyl benzene, M : Metal ion & L : Ligand.

Catalyst A : 2P[Ru(L2AB)Cl$_3$]
Catalyst B : 2P[Pd(L2AB)Cl$_2$]
Catalyst C : 2P[Ru(Gly)Cl$_3$]
Catalyst D : 8P[Ru(L2AB)Cl$_3$]
Catalyst E : 8P[Ru(Gly)Cl$_3$]
Catalyst F : 8P[Pd(L2AB)Cl$_2$]
Catalyst G : 8P[Pd(Gly)Cl$_2$]
Catalyst H : 14P[Pd(L2AB)Cl$_2$]
Catalyst I- : 14P[Pd(Gly)Cl$_2$]
Catalyst X : [Ru (L2AB)Cl$_3$] (Homogeneous)
Catalyst Y : [Pd (L2AB)Cl$_2$] (Homogeneous)

Elemental analyses for carbon, hydrogen and nitrogen were carried out using Coleman carbon and hydrogen analyser and Dumas method for nitrogen analysis.

The surface area and pore volume of all the supports and catalysts were carried out using Carlo-Erba sorptomatic series 1900, Model SO-19 (Italy) instrument at liquid nitrogen temperature using N_2 gas as absorbate. The calculation of surface area and pore volume was based on BET equation.

2.6 CHARACTERIZATION OF THE CATALYSTS

The following methods are used for the characterization of the catalysts.

2.6.1 APPARENT BULK DENSITY

The apparent bulk density refers to the mass of catalyst which packs into a specified and relatively large volume. The apparent bulk density depends on the efficiency with which a working catalyst such as grains, tablets or beads packed in space. It is easily evaluated by the ratio of the weight of the catalysts ant its direct measurment of volume of dried catalyst in a standard graduated measuring cylinder

$$d(Abd) = \frac{\text{Weight of catalyst}}{\text{Volume of the catalyst bed}} \text{ , g. ml}^{-1}$$

For catalyst using rigid supports it is an important practical parameter because it indicates the mass of catalyst which will pack into a reactor of specified volume. However it

is of little importance for polymer anchored catalyst wherein the volume of catalyst bed changes when it comes in contact with the reactant/solvent due to swelling.

In a typical experiment 1.0g of dried polymer bound catalyst was taken in graduated standard measuring cylinder of capacity 10ml and the volume was measured when it remained constant after continuous agitation. The experiment was repeated for five different weights and the mean of the five was calculated.

2.7   MOISTURE CONTENT OF THE CATALYSTS

A known weight of the catalyst was dried in an oven at 70°C to a constant weight. Five different weights of catalysts were taken for this purpose at a time and from the average of five the percentage of moisture content was calculated by the use of the following equation .

$$\% \text{ Moisture } = \frac{A - B}{A} \times 100$$

Where,   A :   Weight of catalyst before drying

B :   Weight of catalyst after drying

2.8   SWELLING STUDIES

0.5g of dried polymer anchored catalyst was taken into a glass filtered tube and immersed in the solvent under study for 30 minutes at room temperature. The tube was then inserted

into a centrifuge tube of 15ml capacity, closed with a teflon cap and centrifuged for about fifteen miniutes at 1200 rpm. The tube was weighed immediately and dried overnight at 100°C in vacuum to a constant weight. By knowing the difference in weight before and after drying, mole percent of swelling was calculated by use of the following equation (6).

$$Swelling \ (S) = \frac{(C-D)}{W \times M} \times 100$$

Where, C : Weight of catalyst after centrifugation

D : Weight of catalyst after drying

W : Weight of catalyst taken for study

M : Molecular weight of solvent under study

2.9 SPECTRAL STUDIES

UV-Vis reflectance spectra of the solid catalysts were recorded on a shimadzu UV-240 spectrophotometer with reference to a non absorbing standard $BaSO_4$. The electronic spectra of the unbound complex was recorded in solution with 1cm matched quartz cell using methanol as a reference solvent.

Infrared spectra of polymer anchored catalysts were scanned using KBr pellets in the range of 200-4000 cm^{-1} on Perkin-Elmer 883 spectrometers.

Scanning electron microscopic (SEM) measurments were made on a Jeol, JSM-T300 electron microscope. In order to

study SEM of supports and catalysts they were sprayed on a double adhesive tape mounted on a stud and were coated with gold before taking micrographs.

Electron Spin Resonance (ESR) spectrum was scanned on Bruker ESP-300, X-ray band spectrometer using a 100 KHz field modulation. The experiments were carried out on powder samples at 25°C in nitrogen atmosphere.

2.10   THERMAL ANALYSIS

Thermal stability of supports and supported catalysts were studied in the range of 30-500°C by thermogravimetry (TG) and differential thermal analysis (DTA) on shimadzu DT-30 Thermal analyzer.   Sample weight was recorded by programming the temperature upto 500°C at a rate of 10°C per minute in nitrogen atmosphere.

2.11   KINETICS OF CATALYTIC HYDROGENATION REACTION

2.11.1   EXPERIMENTAL PROCEDURE

The kinetics of hydrogenation reaction was carried out at atmospheric pressure in a magnetically stirred three necked semi batch glass reactor using methanol as the reaction medium. The experimental set up is shown in Fig. 2.2.   A known amount of the catalyst with methanol (freshly distilled and saturated with hydrogen at the reaction temperature) was kept in the reaction vessel. The air present in the system was removed by applying vacuum, opening the stopcock S3 and closing the stopcock S1 and S2.   The reaction vessel was
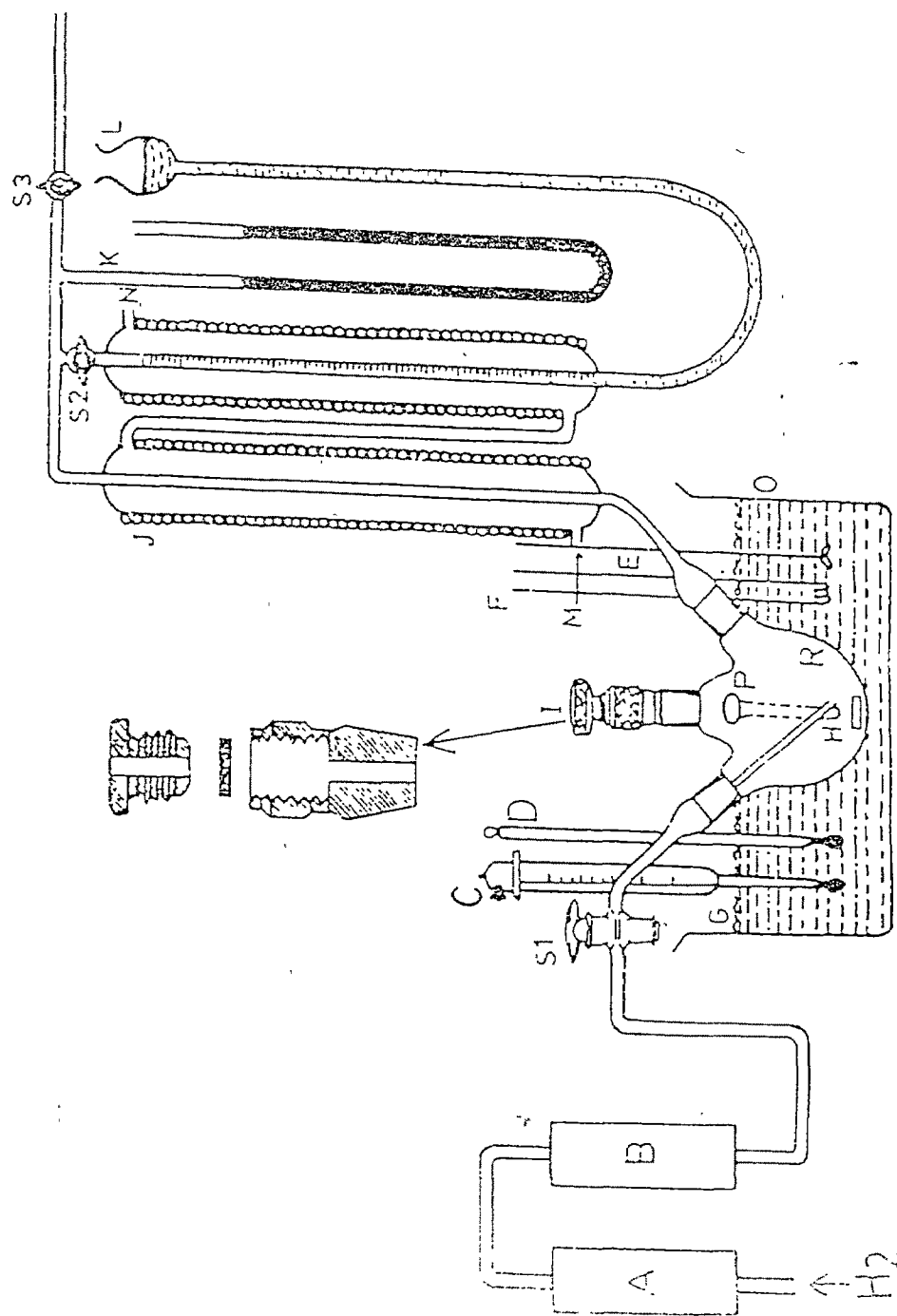
FIG. 2 2   HYDROGENATION APPARATUS

[A]   Deoxo trap   [B]   Molecular sieve trap   [C]   Contact thermometer
[D]   Thermometer   [E]   Mechanical stirrer   [F]   Heating coil
[G]   Thermocole   [H]   Magnetic bar   [I]   Injection port
[J]   Asbestos rope   [K]   Manometer   [L]   Liquid reservior
[M] H_2O from thermostat [N] H_2O to thermostat   [O]   China clay vessel
[P]   Thermowell   [R]   Reaction vessel, S_1, S_2, S_3 - Quickfit stop cocks

flushed with H_2 gas two to three times by opening stopcock S1. The air present in the gas burette was removed by raising the paraffin reservior (L) to the maximum before evaluation. Adequate amount of hydrogen gas was stored in the gas burette by carefully opening the stopcock S2, when there was positive pressure in the mercury manometer (K) keeping S3 closed. By passing molecular hydrogen, the system was made saturated at the reaction temperature by starting the magnetic stirrer (H) keeping stopcock S1 and S3 closed. After saturation, stirring was stopped and the pressure in the system was adjusted to atmospheric pressure by opening stopcock S2 and adjusting the level of reservior (L). A known amount of nitrobenzene was injected into the reaction vessel through the injection port (I) using hypodermic syringe. The arrangement was made in such a way that the temperature of reactor as well as the jacketed burette was maintained at $35\pm 0.1°C$. The hydrogenation reaction was initiated by starting the stirrer. The progress of the reaction at atmospheric pressure was followed by adjusting the level of reservior (L) at various intervals of time and measuring the hydrogen uptake. Necessary corrections were applied for the vapour pressure of the solution.

2.12 KINETICS OF CATALYTIC OXIDATION REACTION

The oxidation of toluene was carried out using molecuar oxygen. The appartus used for oxidation reaction is the same as described above. The system was flushed with medicinal grade oxygen gas before injecting the substrate and the progress of oxidation reaction was followed by measuring the oxygen uptake at different intervals of time.

The products of hydrogenation and oxidation reactions were analysed by shimadzu GC 7AG chromatopac CE1B chromatograph using FID detector. For the analysis 15% carbowax on 20M chromosorb-W column was used. The typical chromatograms are shown in Figs. 2.3 and 2.4 for hydrogenation and oxidation reactions respectively.
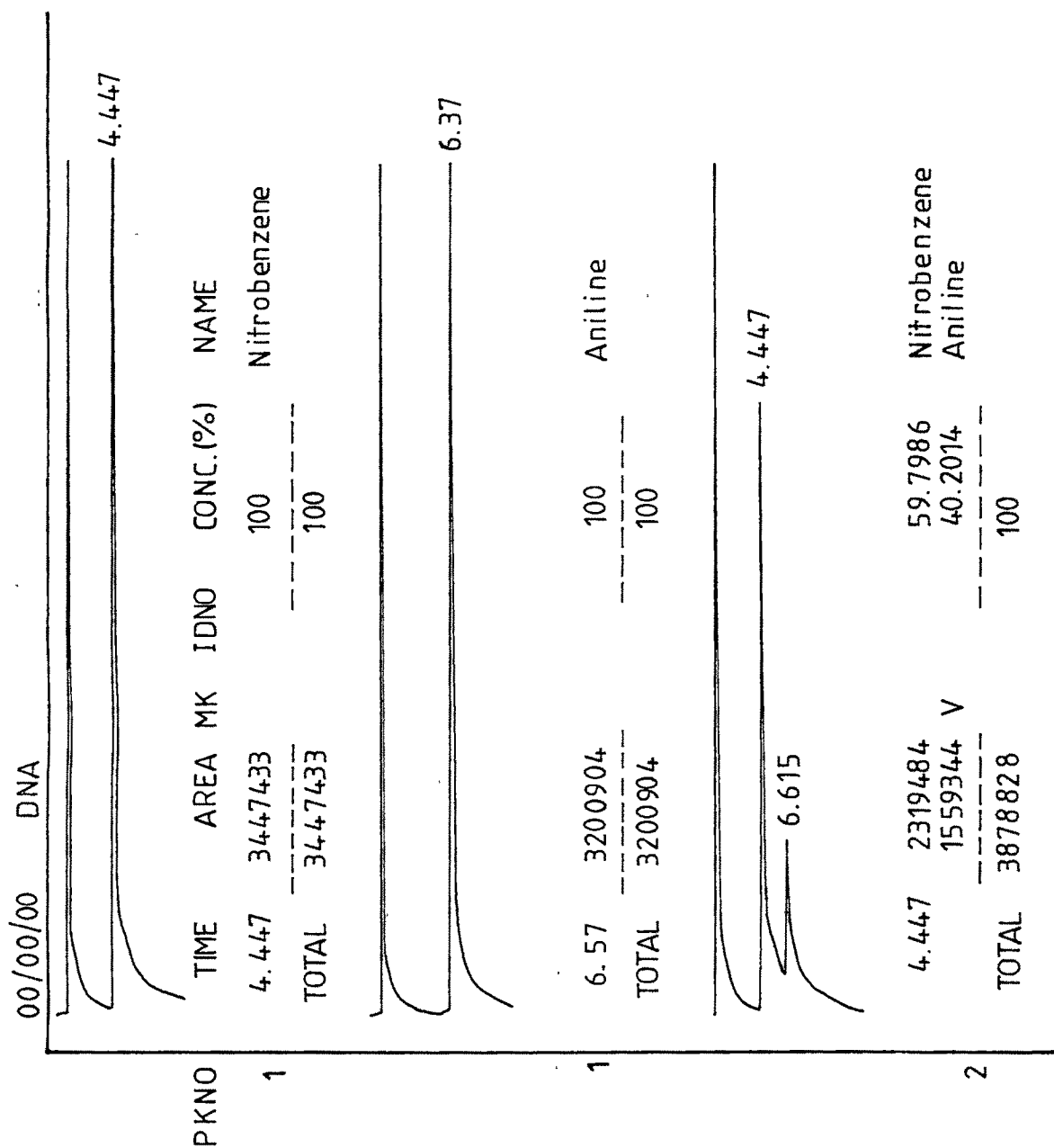
Fig. 2.3 Gas-chromatograph for hydrogenation of nitrobenzene

00/00/00   DTB

PKNO	TIME	AREA	MK	IDNO	CONC.(%)	NAME
1	5.775	23199200	S		91.2185	Toluene
2	8.908	18351	T		0.0722	
3	12.242	2214998	T		8.7093	Benzaldehyde
	TOTAL	25432546			100	

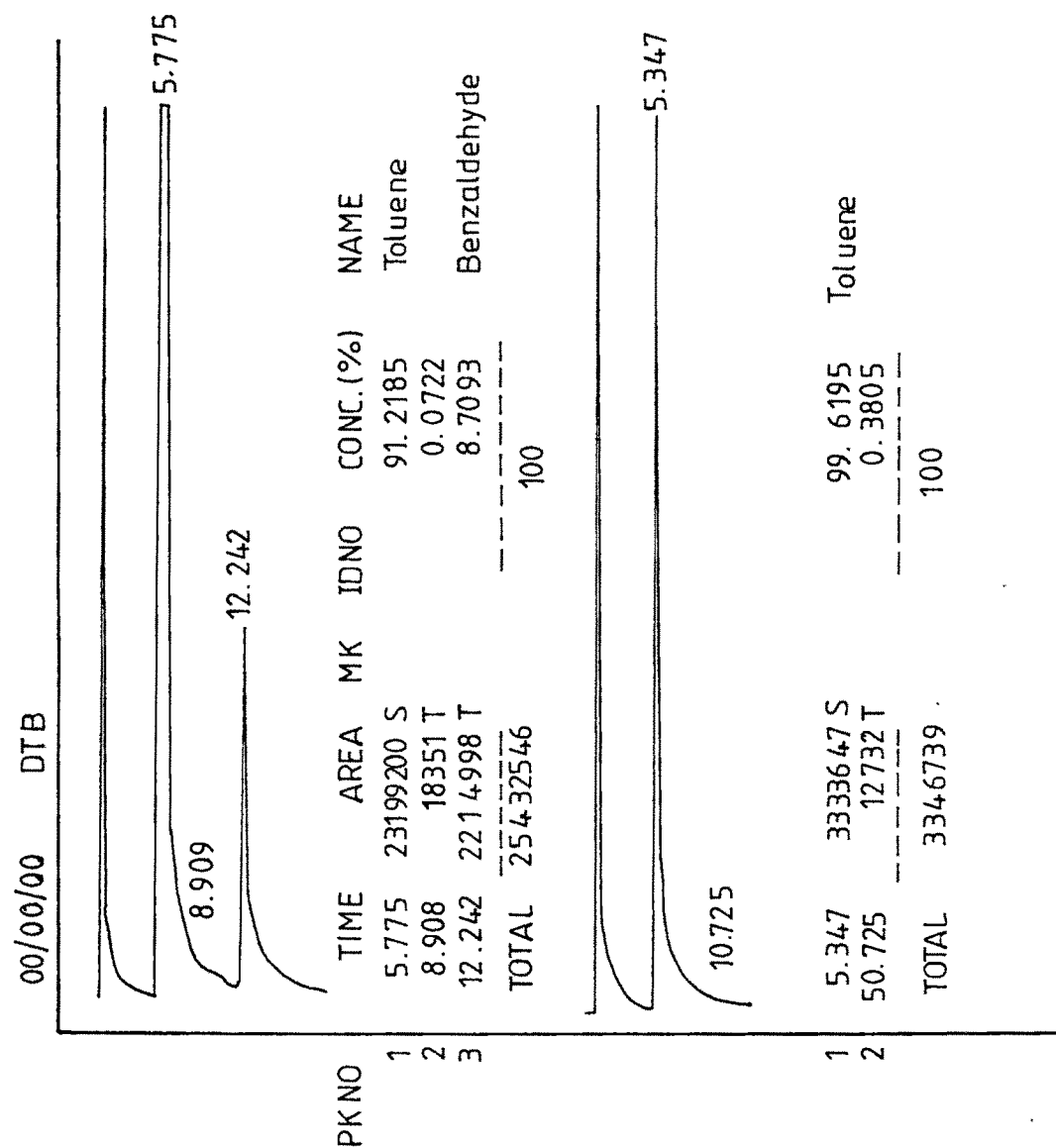| PKNO	TIME	AREA	MK	IDNO	CONC.(%)	NAME
1	5.347	3336647	S		99.6195	Toluene
2	50.725	12732	T		0.3805	
	TOTAL	3346739			100	

Fig. 2.4 Gas-chromatograph for oxidation of toluene

2.13   REFERENCES

1.   H. Hirai and N. Toshina in " Tailored metal catalysis " Ed. Y. Iwasawa ; D. Reidel Publ. Co., Dordrecht, Holland (1986) 87.

2.   J. D. Spivak and S. Vaney, N. Y. US Pat., 3281505 (1966).

3.   A. I. Vogel In "A text book of quantitative inorganic analysis" 3rd Ed., ELBS and Longmann (1975).

4.   R. S. Drago, J. Gaul, A Zombeck and D. K. Straub, J. Am. Chem. Soc., 102 (1980) 1033.

5.   A. K. Singh, M. Katyal and R. P. Singh, J. Ind. Chem. Soc., 53 (1976) 691.

6.   Jacob John, Ph. D. thesis " Some studies on anchored metal complex catalysts " M. S. University of Baroda, Baroda (1993).