Chapter - 2

EXPERIMENTAL

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2.1 INTRODUCTION

The preparation of polymer-anchored catalysts entails three steps: polymerization, bonding of a ligand group and coordination of metals (1). Polymerization may be performed initially, after bonding of a ligand group or after coordination of the metals as shown in Figure-2.1.

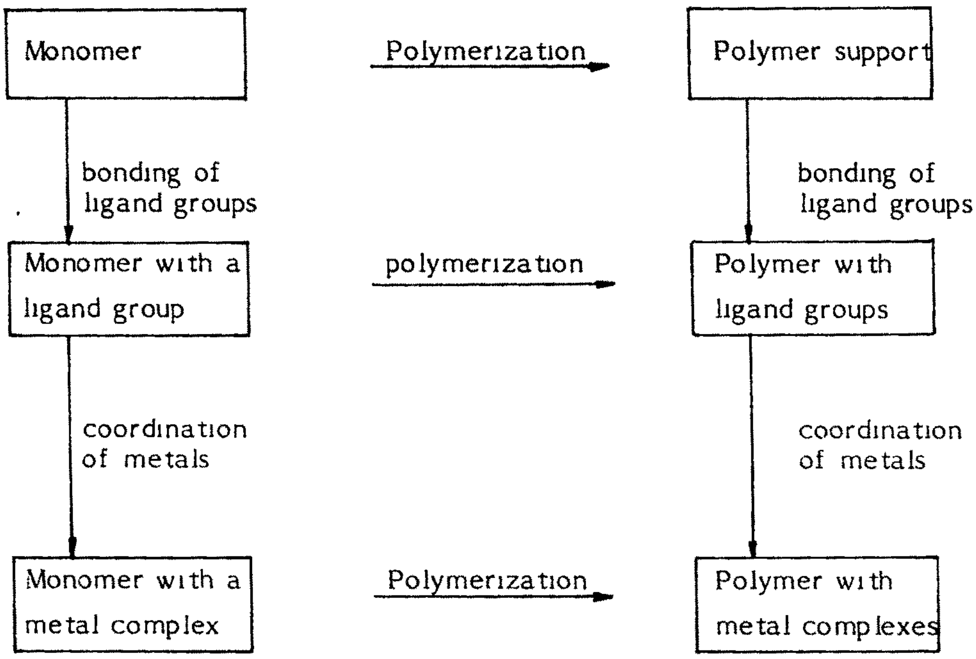

Figure-2.1 Fundamental steps in the preparation of polymer-anchored catalysts.

If a specific effect of the polymer is desired in the polymer-anchored catalyst, then the design of the 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 monomers 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 description of the method of preparation of the macroporous polymer supports, their functionalization and anchoring of the metal complexes. Synthesis of unbound [RuTMDACl_2]Cl complex and characterization of both the catalysts i.e. polymer supported and homogeneous catalysts using various experimental techniques such as chemical and thermal analysis, measurement of surface area by BET method using N_2 as an adsorbate, bulk density, moisture content, swelling studies and crushing strength have been discussed. These catalysts have also been characterized by the use of electronic spectra, far-IR, IR, SEM, X-ray, EPR and ESCA instruments. A detailed experimental set-up and procedure have been given for carrying out the hydrogenation reaction of cyclohexene and nitrobenzene at normal temperature and pressure. Kinetic study of hydrogenation has also been included in this chapter.

2.2 Preparation of Poly(styrene-divinylbenezene) supports, (PS-DVB)

The crosslinking (weight fraction of DVB) and the volume fraction Fm have a predominant effect on the texture of the porous polymers. Fm is the ratio of volume of monomer to the total volume of monomers and the diluent. The pore structure and the specific surface area depend mainly on the crosslinking and Fm. A series of porous polymers were prepared keeping Fm constant at 0.61 (2) with a variation of degree of crosslinking between 3 and 30.

2.2.1 Synthesis of beads (3,4)

All the chemicals used were of GR grade except styrene (99.5%) obtained from S.D.fine-chem. Pvt. Ltd., Boisar (India) and divinylbenzene (DVB), 50% ethylvinyl benzene supplied by Fluka AG, Chemische Fabrik CH-9470 Buchs. The inhibitor present in styrene and DVB was removed by treating with 2% sodium hydroxide solution. It was then washed with distilled water to remove sodium hydroxide and finally dried under anhydrous sodium sulphate. Monomer mixture was prepared by adding appropriate quantities of styrene, DVB, heptane as well as benzoyl peroxide (1-1.5% of the monomer mixture) and was mixed thoroughly. The ethylvinyl- benzene content in the divinyl benzene has been considered as styrene and appropriate corrections were made while calculating the crosslinking of polymers. This is the standard method used in the preparation of commercial ion exchangers (4).

The aqueous layer of the reaction was prepared by mixing (twice the amount of monomers), sodium chloride (3% salt solution) and sodium laurayl sulphate (0.3-0.4%) of aqueous layer. The polymerization was carried out in a four necked Quickfit polymer raction vessel. The stirring was achieved using a motor driven stirrer fitted through a mercury seal. The temperature of the kettle was maintained in a thermostatic water bath with an accuracy of ±0.2°C using a mercury contact thermometer. The aqueous layer was initially taken into the reaction vessel and the temperature was raised to 50°C. Keeping the stirrer speed at about 20-25 rpm the monomer mixture was run into the reaction vessel and the speed of the stirrer was adjusted to give the desired size of the beads, and the temperature was raised to 80°C. At the sticky stage, which came nearly after 90 minutes, the stirrer speed was raised slightly. The polymerization was allowed to continue for 18 hours keeping the temperature constant at 80±0.2°C. After polymerization, the contents were cooled to room temperature, filtered, washed with distilled water, water-ethanol (1:1) mixture and finally with ethanol. Any adsorbed material was removed by soxhlet extraction with ethanol-benzene mixture (1:1) for 10 hours. The beads were dried for 24 hours at 70°C under vacuum.

2.3 **Chloromethylation** (5)

The dried beads (10-20 mesh, BSS) were taken for chloromethylation reaction using chloromethylmethylether (CMME) in the presence of $AlCl_3$ as a catalyst. CMME (Merck) was distilled before use and aluminium chloride (anhydrous, GR grade) was purified by sublimation.

CAUTION is advised in chloromethylation and in handling of CMME, because of the related compound monochloroether which is carcinogenic (6).

30 gm of beads and 60 ml of CMME were kept in contact with each other in a three-necked round bottom flask of one litre capacity fitted with a water cooled reflux condenser. The flask was kept in an ice bath to get it cooled and beads were allowed to swell for one hour. 10 gm of $AlCl_3$ dissolved in 70 ml of ice-chilled CMME was added slowly in the reaction vessel with a constant stirring. The reaction was carried out at 20°C for 12 hours and the excess of CMME was removed by filtra-

tion. The beads were washed sequentially with 50% aqueous dioxane, aqueous dioxane containing 10% HCl (v/v) and finally with dry dioxane, until the washing were free from chloride ions.

2.3.1. Chloride analysis

The extent of chloromethylation was determined by fusing the chloromethylated beads with sodium peroxide and then estimating the chloride as silver chloride by the standard gravimetric method (7). A known amount of the polymer with twice the amount of sodium peroxide was fused in a platinum crucible over a gas flame, initially slowly followed by a strong heating to ensure the complete fusion of polymer with sodium peroxide. The crucible was cooled to room temperature and the mass containing sodium chloride and unreacted sodium peroxide were extracted with deionized water and filtered. The filtrate was collected in a 100ml volumetric flask and made upto the mark. In order to estimate the chloride, a known amount of filtrate was pipetted out in a beaker. The unreacted sodium peroxide present as sodium hydroxide was neutralized by the addition of dilute nitric acid. The pH of the solution was adjusted to $\simeq$ 6. Rest of the procedure as described by Vogel (7) was followed.

2.4 Ligand introduction

2.4.1 Ligand introduction on Poly(sty-DVB) supports

Chloromethylated polymer beads were kept in contact with ethanol for 30 minutes in a three necked 500 ml round bottom flask fitted with a condenser, mechanical stirrer and addition funnel. The amount of polymer, ethanol and ligand taken in the reaction are given below:

Crosslinking (% DVB)	Polymer (gm)	Ethanol (ml)	Trimethylenediamine (ml)
3	25	200	15
10	25	200	15
30	25	200	10

Trimethylenediamine (TMDA) was added dropwise into the reaction vessel over a period of 15 minutes using the addition funnel. The reaction mixture was refluxed for 4 hours with occasional stirring. After reaction the mixture was cooled and beads were filtered. The beads were initially washed with 0.5 N sodium hydroxide and then with deionized water till the complete removal of sodium hydroxide. It was finally dried at 70°C for 24 hours under vacuum.

The number of moles of TMDA attached to the polymer was calculated from the results of micro analysis. These results were further confirmed by gravimetric estimation of chloride present as unreacted chloromethyl group on the polymer support.

2.4.2 Ligand introduction on Zeo-Karb 226 resin (8)

In another series of the experiments, Zeo-Karb 226, cation exchange resin (H^+form) supplied by the Permutit Company Ltd.,London was used as support. Zeo-Karb 226 is a crosslinked polymethacrylic acid (PMA) with divinylbenzene (DVB). For this purpose two different crosslinked

(2.5% and 20% DVB) polymer were purified by soxhlet extractor with ethanol-benzene (1:1) mixture for a total period of about 48 hours.

In order to introduce TMDA on Zeo-Karb 226 resin the procedure followed was the same as described earlier (wide supra). For this purpose, the amount of Zeo-Karb 226, ethanol and TMDA used as ligand taken for the reaction mentioned below :

Zeo-Karb (% DVB)	Polymer (gm)	Ethanol (ml)	Trimethylenediamine (ml)	Refluxed* time (h)
2.5	25	200	46	5
20	25	200	10	10

* Confirmed with the trial experiments.

After completion of the reaction the beads were allowed to cool, filtered and washed with ethanol as well as deionzed water. It was then dried at 70°C for 24 hours under vacuum.

2.5 Introduction of metal ions on polymer anchored ligand

The functionalised polymer was kept in contact with ethanol for 30 minutes in a round bottom flask. A solution of $RuCl_3.3H_2O$ in ethanol taken in an addition funnel fitted to the reaction vessel was added over a period of 30 minutes. The reaction mixture was initially refluxed for 7 hours and after that it was kept at room temperature for completion of the reaction for four days. It was observed that the colour of the supernatant liquid changed from dark orange to light orange and the polymer turned light grey. It was indicative of the formation of metal complex onto the polymer matrix.

The polymer used in the study, amount of the functionalised polymer, quantity of ethanol, amount of ruthenium chloride and the time to reflux the reaction mixture are given below :

Polymer type*	Support (gm)	Ethanol (ml)	$RuCl_3.nH_2O$ (gm)	Refluxed time (h)	Day
3PTMDA	25	200	2.5	7	3
10PTMDA	25	200	2.5	7	3
30PTMDA	25	225	1.0	8	3
2.5ZKTMDA	25	200	1.0	10	4
20ZKTMDA	25	225	1.0	12	4

* Nomenclature: NPTMDA, NZKTMDA

Where N=Percent crosslink

P=Copolymer of styrene-divinylbenzene

ZK=Copolymer of methacrylic acid-divinylbenzene

TMDA=Trimethylenediamine

The polymer beads were filtered and washed thoroughly with ethanol. The anchored catalysts thus obtained were dried at 70°C in vacuum for 24 hours and stored in vacuum desiccator.

Ruthenium content in each case was determined by refluxing a known amount of the supported catalyst with Con. HCl (A.R.) for 24 hours and then estimating the metal concentration by colourimetry. The procedure described by Singh et al (9) was followed.

2.6 Synthesis of unbound ruthenium complex, [Ru(III)TMDACl$_2$]Cl

$RuCl_3.3H_2O$ (Johnson matthey Inc., New Jersey) dissolved in a fixed quantity of ethanol was placed in a round bottom flask. Distilled trimethylenediamine (TMDA), (Riedel-de Haen An Seelze - Hannover) was added into the reaction vessel by the use of addition funnel. Ruthenium - TMDA mole ratio was maintained as 1:1. The reaction was kept for 4 hours with constant stirring maintaining the temperature at 35°C. The complex thus formed was filtered, washed repeatedly with distilled ethyl alcohol and dried at 70°C in vacuum. The method for the estimation of Ru(III) followed was described earlier (9).

	C	H	N	Cl
Calculated (%wt)	12.52	3.47	35.15	37.03
Found (%wt)	12.61	3.48	35.09	36.87

The stoichiometry of the complex is [RuTMDACl$_2$]Cl. Conductivity measurement of the Complex in water showed the ionic nature of chloride. As this complex is sparingly soluble in water and insoluble in common solvents, therefore it was planned to prepare a homogeneous [RuTMDACl$_2$]Cl complex catalyst by taking minimum concentration of $RuCl_3.3H_2O$ and TMDA in methanol in such a way that the complex did not separate or precipitate and remain in the solution phase.

In order to synthesise the $[Ru(III)TMDACl_2]Cl$ complex in the solution phase, $RuCl_3.3H_2O$ ($5x10^{-4}$ mole in 100 ml methanol) was placed in a round bottom flask and TMDA ($5x10^{-4}$ mole in 100 ml methanol) was added by the addition funnel with a constant stirring for 4 hours at 35°C. The complex thus formed was used to investigate the catalytic activity for the reactions studied.

The catalysts thus prepared were named as NPML and NZKML.

Where N = Percent crosslink

P = Copolymer of styrene-divinylbenzene

ZK = Copolymer of polymethacrylic acid-divinylbenzene

M = Metal ion

L = Ligand

Let us define

Catalyst A = 3PRu(III)TMDA

Catalyst B = 10PRu(III)TMDA

Catalyst C = 30PRu(III)TMDA

Catalyst D = 2.5ZKRu(III)TMDA

Catalyst E = 20ZKRu(III)TMDA

Catalyst H = $[Ru(III)TMDACl_2]Cl$ (Homogeneous)

Chemical anaylsis for carbon, Hydrogen and Nitrogen was carried out in our laboratory using Coleman Carbon-Hydrogen and Nitrogen anaylzer.

The surface area and pore volume of all the supports and catalysts were carried out at the Research centre, Indian Petrochemical Corporation Ltd., (IPCL) using Carlo-Erba Sorptomatic Series-1900, Model SO-19 (Italy) instrument. The samples were heated upto 70°C under vacuum and nitrogen gas was used as adsorbate at liquid nitrogen temperature. The calculation of surface area and pore volume was based on BET equation. The crushing strength of all the catalysts was studied on a Baker Mercer Type C-12 machine.

2.7 Apparent bulk density (Abd)

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 pack in space. It is easily evaluated by the ratio of direct measurement of volume of dried catalyst in a standard graduated measuring cylinder to its weight as given below :

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

In a typical experiment 1.0 gm of dried polymer bound catalyst was taken in a graduated corning measuring cylinder of capacity 10 ml and the volume was measured when it remained constant after continuous tapping. The experiment was repeated for five different weights and the mean of the five was calculated. By following careful packing technique gave reproducible results.

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 bound catalyst where in the volume of catalyst bed changes when it comes in contact with the reactant/solvent due to swelling.

2.8 Moisture content of catalyst

A known weight of the catalyst was heated in an oven at 70 ± 1°C to a constant weight. Five different weight of catalysts were heated at a time, and from the average of five, the percentage of moisture content was calculated by the use of the following method :

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

Where A = Weight of catalyst before drying

B = Weight of catalyst after drying

2.9 Swelling studies (10)

0.5 gm of dried polymer-supported catalyst was loaded into a glass filter tube and immersed in the solvent under study for 30 minutes at room temperature. The tube was then inserted into a 15 ml centrifuge tube closed with a teflon cap and centrifuged for fifteen minutes at 1200 rpm. The tube was weighed immediately and dried overnight at 100°C in vacuum to a constant weight. Knowing the difference in weight before and after drying, mole percent of swelling was calculated by use of the following equation :

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

(Mole %)

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

2.10 Spectral characterization

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 1 cm matched quartz cells using methanol as a reference solvent.

Infrared spectra of polymer supported and non-supported complexes were scanned in the range 250-4000 cm^{-1} using KBr pellets on a perkin-Elmer 883 spectrometers.

X-ray diffraction patterns in the range of 2θ = 5° to 60° at scanning rate of 2° per minutes were recorded on a Rikagu Miniflex (Japan) diffractometer with nickel filtered Cu K_{α} as a radiation source.

Scanning electron microscopic (SEM) measurements were made on a Jeol, JSM-T300 scanning electron microscope. In order to study the SEM of supports and catalysts they were sprayed on a double adhesive tape mounted on a brass stud, and were coated with carbon before taking micrographs.

Electron spectroscopy for chemical analysis (ESCA) which has been used widely in the characterization of the supported metal complex catalysts, were recorded on VG model ESCA-3 mark-II (England) with AlK_{α} and MgK_{α} as radiation source.

Electron paramagnetic resonance (EPR) spectrum was scanned on Braker ESP-300, X-band spectrometer using a 100 KHz field modulation. EPR experiments were conducted on powder samples at 298°K.

2.11 **Thermal analysis**

Thermal stability and phase change were studied in the range of 30-500°C by thermo gravimetry (TG) and differential thermal analysis (DTA) on Shimadzu DT-30 (Japan) with alpha-alumina as a reference. Sample weight was recorded by programming the temperature upto 500°C at a rate of 10°C per minute in nitrogen atmosphere. The flow of the nitrogen gas was kept at 50 ml per minute through out the experiment.

2.12 Kinetics of catalytic hydrogenation reactions

2.12.1 Experimental procedure

The kinetics of hydrogenation was carried out at atmospheric pressure in a magnetically stirred, three phase, semi-batch glass reactor using methanol as the reaction medium. The experimental set-up is shown in Figure-2.2

A known amount of the catalyst with methanol (freshly distilled, passed through activated alumina and saturated with hydrogen at the reaction temperature) was kept in the reaction vessel. The air in the system was removed by applying vacuum, opening stopcock S_3 and closing the stopcock S_1 and S_2. The reaction vessel was flushed with H_2 gas 2 to 3 times by opening stopcock S_1. The air from the gas burette was removed by raising the glycerol reservoir (L) to the maximum before evacuation. Adequate amount of hydrogen gas was stored in the gas burette by carefully opening the stopcock S_2, when there was positive pressure in the mercury manometer (K) keeping S_3 closed. By passing molecular hydrogen in methanol and the catalyst were made saturated in the reactor, at reaction temperature by starting the magnetic stirrer (H) keeping stopcocks S_1,S_3 closed. After saturation, stirring was stopped and the pressure in the system was adjusted to atmospheric pressure by opening stopcock S_2 and adjusting the level of reservoir (L). A known amount of cyclohexene/nitrobenzene (saturated with hydrogen at the reaction temperature) 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 the reactor as

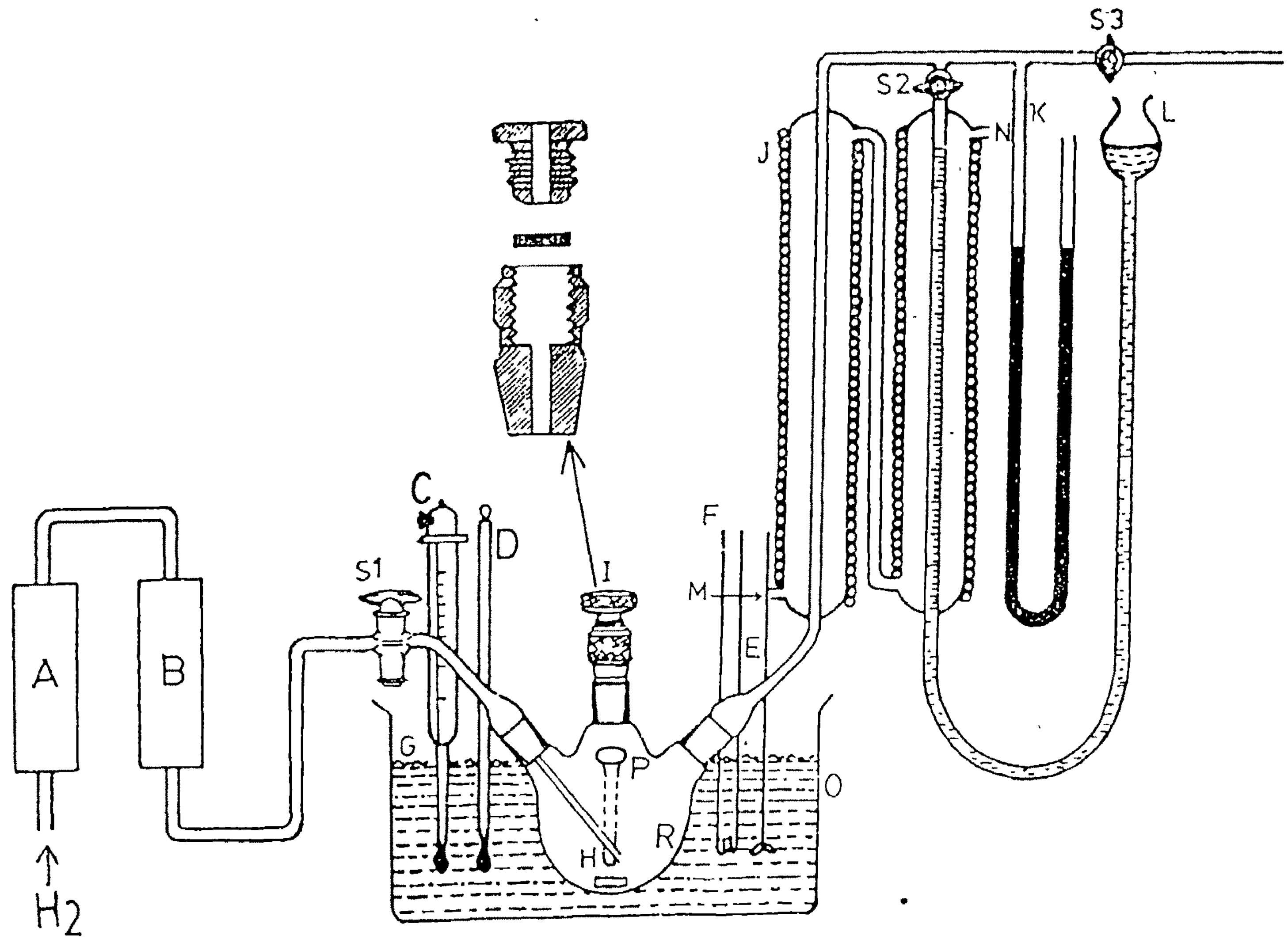

Figure-2.2 HYDROGENATION APPARATUS

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 well as the jacketed burette was maintained at 35±0.1°C. The hydrogenation experiment was then initiated by starting the stirrer. The progress of the reaction at atmospheric pressure was followed by adjusting the level of reservoir (L) at various intervals of time and measuring the hydrogen uptake. Necessary corrections for the vapour pressure of solution were applied for the calculations.

The products were analysed by Shimadzu GC-7AG Chromatopac CE 1B gas chromatograph using thermal conductivity detector. For the analysis of cyclohexene/cyclohexane 15% carbowax on 20M chromasorb-W column and 10% SE-30 on chromasorb-W for nitrobenzene/aniline were used. The typical chromatograms are shown in Figures 2.3-2.6.

A good material balance with only 1-2% deviation between H_2 consumed (measured experimentally) and that required according to the stoichiometry of the hydrogenation (i.e. one mole of hydrogen required for the hydrogenation of one mole of cyclohexene/nitrobenzene) was obtained.

2.13 References

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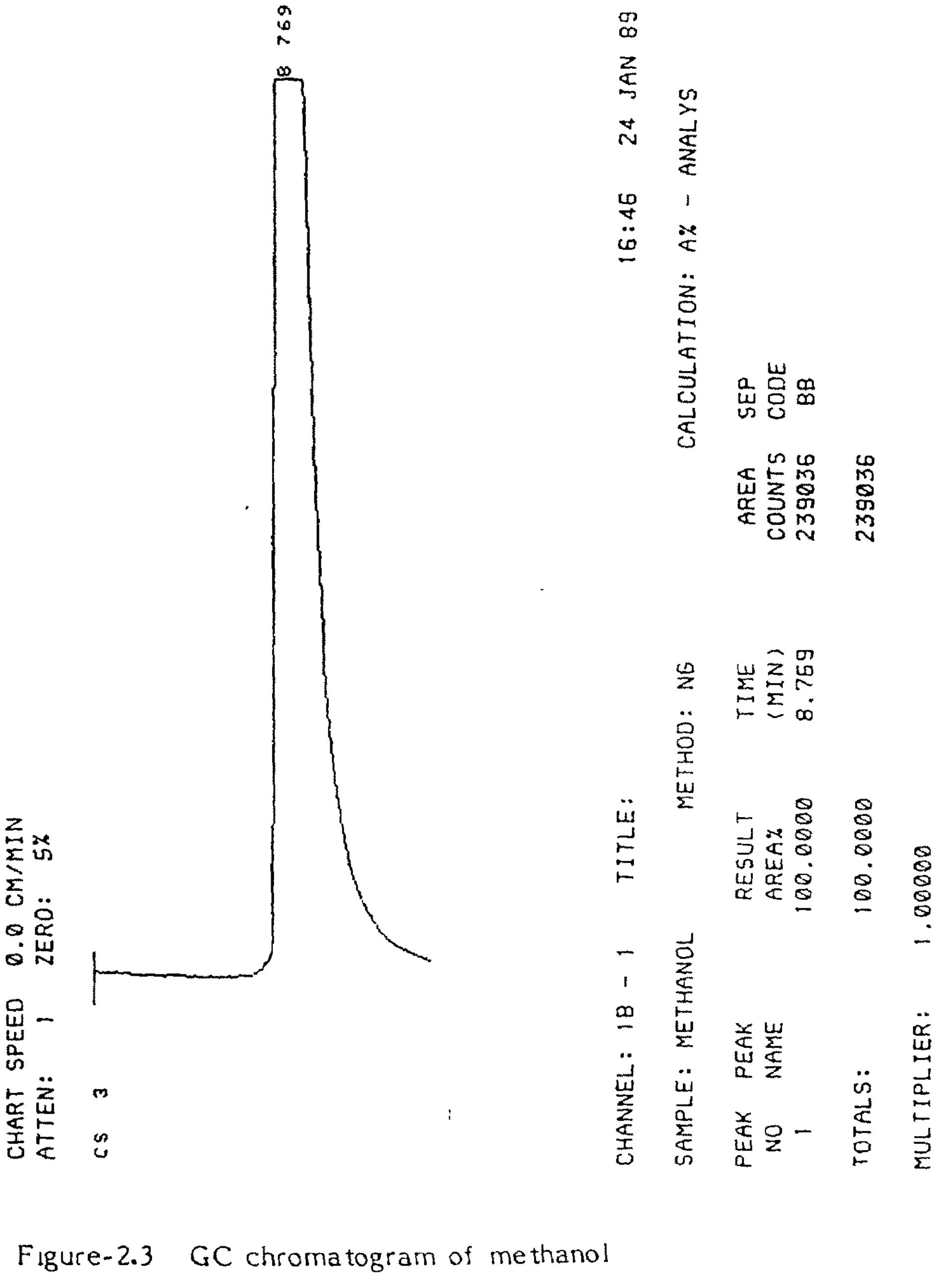


Figure-2.3 GC chromatogram of methanol

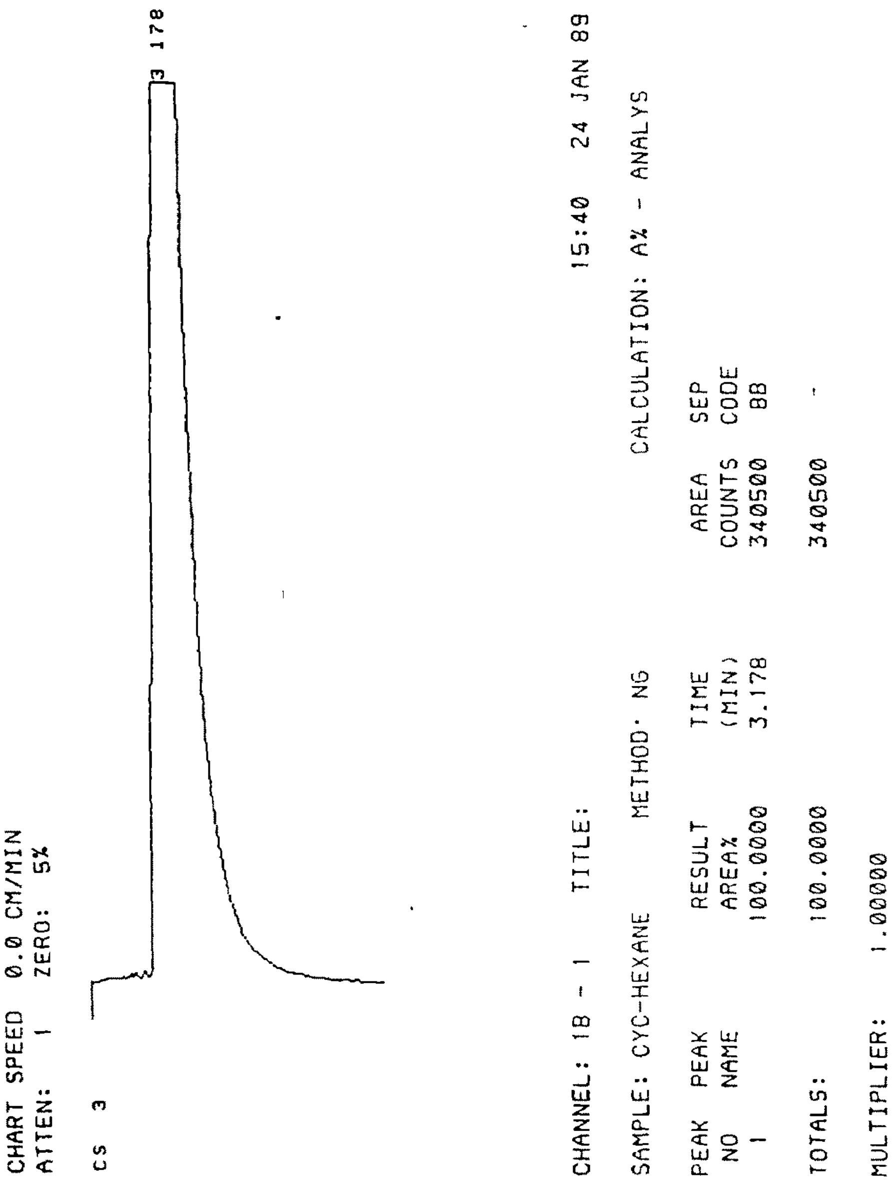
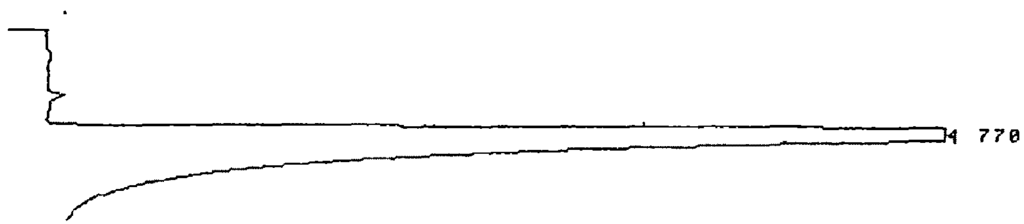


Figure-2.4 GC Chromatogram of cyclohexane

CHART SPEED 0.0 CM/MIN
ATTEN: 1 ZERO: 5%

CS 3



CHANNEL: 1B - 1 TITLE: 15:56 24 JAN 89

SAMPLE: CYC-HEXENE METHOD: NG CALCULATION: A% - ANALYS

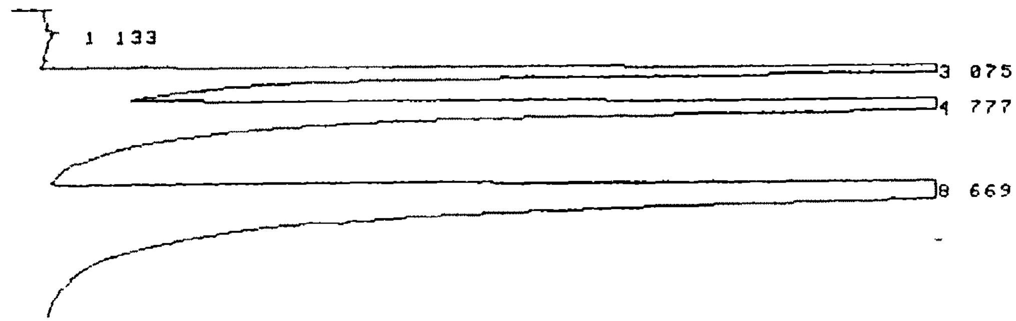
PEAK NO	PEAK NAME	RESULT AREA%	TIME (MIN)	AREA COUNTS	SEP CODE
1		100.0000	4.770	143847	BB
TOTALS:		100.0000		143847	

MULTIPLIER: 1.00000

Figure-2.5 GC Chromatogram of cyclohexene

CHART SPEED 0.0 CM/MIN
ATTEN: 1 ZERO: 5%

CS 3



CHANNEL: 1B - 1 TITLE: 17:24 24 JAN 89

SAMPLE: MIXTURE METHOD: NG CALCULATION: A% - ANALYS

PEAK NO	PEAK NAME	RESULT AREA%	TIME (MIN)	AREA COUNTS	SEP CODE
1		21.5355	3.075	137016	BV
2		36.2615	4.777	230707	VB
3		42.2030	8.669	268509	BB
TOTALS:		100.0000		636232	

MULTIPLIER: 1.00000

Figure-2.6 GC Chromatogram of cyclohexene hydrogenated products.

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