CHAPTER - II

EXPERIMENTAL

The present chapter describes in detail the experimental methods for the synthesis of polymer supported transition metal catalysts, the methods adopted to characterize the newly synthesized catalysts and evaluation of their catalytic activity.

SECTION -I

SYNTHESIS OF POLYMER SUPPORTED METAL COMPLEX CATALYSTS

Materials

Chloromethylated poly(styrene-divinylbenzene) as spherical beads with 8% and 14% crosslink [18-44 mesh, chlorine content = 14% and 22% respectively] were received from Ion Exchange India Limited, Mumbai. The chlorine content in the beads were estimated gravimetrically to ascertain the extent of chloromethylation[1]. Hydrated ruthenium trichloride[$RuCl_3.3H_2O$, Loba Chemie], 2-aminopyridine [Merck], palladium chloride [$PdCl_2$,Loba Chemie], anhydrous ferric chloride[$FeCl_3$, Ranbaxy] were used as received. Ethylenediamine (Ranbaxy), 1,4-dioxane, methanol, ethanol, acetonitrile (AR Grade) were purified by standard methods[1].

A. Synthesis of Poly(styrene-divinylbenzene) copolymer supported Schiff base liganded transition metal complexes

(i) ***Modification of chloromethyl group to an aldehydic (-CHO) functionality***

In a typical experiment, chloromethylated poly(styrene-divinylbenzene) copolymer beads(20 gm, 8% or 14% crosslink) were stirred in 170ml A.R.dimethyl sulfoxide(DMSO) with sodium bicarbonate(10gm) for 6 hours at 155°C[2]. The beads were collected on a glass filtration funnel, washed with DMSO, hot water, mixture of dioxane and water(2:1), rinsed with ethanol and finally with benzene. About 19 gms of cream coloured aldehyde functionalised beads were obtained after drying at 100°C in vacuum. The above functionalised copolymer beads were used for the synthesis of Schiff base liganded polymer.

(ii) *Preparation of Schiff base functionalised Poly(styrene-divinylbenzene) co-polymer*

The polymer beads(10 gm) bearing the -CHO group were allowed to swell in methanol (50ml) for 1hr. To this, a solution of ethylenediamine (0.5 mole in 25ml methanol) was added dropwise over a period of 45minutes with constant stirring . The contents were refluxed for 6 - 8 hrs. After cooling to room temperature, the pale yellow colored polymer beads were filtered, washed thoroughly with methanol and petroleum ether (40-60°C) and dried in vacuum at 70°C for 24 hours[3]. The Schiff base with 2-aminopyridine were similarly prepared using 0.24 mole of the amine in place of ethylenediamine.

(iii) *Incorporation of the metal ions on to Schiff base bearing resin*

The Schiff base bearing polymer beads (10gm) were allowed to swell in ethanol (50 ml) for 45 mins. To this , 5mmol of metal chloride in 50ml ethanol was added over a period of 45 mins with occasional shaking. The contents were initially heated to 50°C for 6hrs, cooled and agitated on a shaker for two weeks at room temperature. At the end of this period, the colour of the beads changed to grey in case of ruthenium, yellow for palladium and bright yellow for iron indicating the formation of metal complex on the surface of the polymer. The beads were filtered, carefully washed with ethanol and finally dried in vacuum at 70°C for 24hrs[4].

B. Synthesis of Poly(styrene-divinylbenzene) supported ruthenium(III)-2-amino-pyridyl complexes

(i)*Attachment of 2-aminopyridine to chloromethylated poly(styrene-divinylbenzene) copolymer*

2-aminopyridine (14.12gm, 0.15mole) was added slowly to a suspension of chloromethylated poly(styrene-divinylbenzene) copolymer beads (10 gm , 8% crosslink) in 150ml dioxane. The contents were heated to 120°C for 24hrs while stirring continuously [5-7]. The solution was cooled and the aminopyridyl bound polymer beads were filtered, washed successively with dioxane, water, alcohol and finally with petroleum ether(40-60°C). The functionalised polymer beads were dried in vacuum at 70°C for 12 hrs.

(ii) ***Loading of ruthenium on to the functionalised support***

10gm of functionalised polymer beads were kept in contact with ethanol (50ml) for 45mins. To this was added, 5mmole $RuCl_3 .3H_2O$ in 50ml ethanol. The contents were gently agitated on a shaker for 10 days at 25°C. The colour of the beads changed from pale yellow to grey during this period indicating the formation of the complex on the polymer matrix. After 10 days, the grey coloured polymer beads were filtered, washed thoroughly with alcohol to ensure the removal of any unreacted metal chloride and dried in vacuum at 70°C for 24hrs.

The Ru-catalyst with 14% crosslink polymer support was similarly prepared.

NOMENCLATURE

The newly synthesized polymer anchored metal complex catalysts are designated as:-

Ru-A : 8% Poly(S-DVB) Ru(III) (en-SB)

Ru-B : 14% Poly(S-DVB) Ru(III) (en-SB)

Ru-C : 8% Poly(S-DVB) Ru (III) (2ap-SB)

Ru-D : 14% Poly(S-DVB) Ru (III) (2ap-SB)

Fe-A : 8% Poly(S-DVB) Fe(III) (en-SB)

Fe-B : 14% Poly(S-DVB) Fe(III) (en-SB)

Fe-C : 8% Poly(S-DVB) Fe (III) (2ap-SB)

Fe-D : 14% Poly(S-DVB) Fe (III) (2ap-SB)

Pd-A : 8% Poly(S-DVB) Pd(II) (en-SB)

Pd-B : 14% Poly(S-DVB) Pd(II) (en-SB)

Pd-C : 8% Poly(S-DVB) Pd(II) (2ap-SB)

Pd-D : 14% Poly(S-DVB) Pd(II) (2ap-SB)

Ru-E : 8% [Poly (S-DVB)-2AP]Ru(III)

Ru-F : 14%[Poly(S-DVB)-2AP]Ru(III)

where ,

8% and 14% denote percent crosslink,

Poly(S-DVB) - poly(styrene-divinylbenzene)copolymer

(en-SB) - ethylenediamine Schiff base

(2ap-SB) - 2-aminopyridine Schiff base

2AP - 2-aminopyridine

SECTION-II

CATALYST CHARACTERISATION

Elemental analysis

The carbon, hydrogen and nitrogen present in the polymer bound metal complexes at various stages of preparation were determined using a Carlo-Erba Strumentazione microanalyser. The chlorine content in the chloromethylated poly(styrene-divinylbenzene) copolymer beads and that in the polymer supported metal complexes were determined gravimetrically as silver chloride[1]. The ruthenium and palladium contents were determined as follows :

A known amount (0.2 gm) of the complex was digested with conc. HCl (10 ml) for 24 hr. The beads were filtered and washed carefully with distilled water until the filtrate was free from chloride. The filtrate was then concentrated to about 5ml. The pH of the solution was adjusted to 1.8. To this, 12.5 ml of a standard solution of 5-nitroso-2,4,6-triaminopyridine(Nitroso R salt, 1% w/v in H_2O) and 1-nitroso-2-napthol-3,6-disulphonic acid (1% w/v in H_2O) were added as metal indicator for the estimation of ruthenium and palladium respectively[8,9]. The metal concentration was determined spectrophotometrically at 510nm(Ru) and 490nm (Pd) on a Shimadzu UV-VIS spectrophotometer.

For the estimation of iron, 0.2 gm of catalyst was digested with conc.HNO_3(10ml) for 12hrs, and finally diluted to 50ml in a volumetric flask with distilled water[10].The solution was analyzed by Atomic Absorption Spectrophotometer on a GBC 902 AAS instrument

Apparent Bulk Density

A typical procedure to determine the apparent bulk density of the polymer bound catalysts is described here :

In a 50mL graduated measuring cylinder, weighed amount of catalyst was taken. The weighed catalyst in the cylinder was tapped for 250 times on a "Ceast Volumetric Classificator" with programmer and its volume measured when it remained constant after continuous tapping[11]. The experiment was repeated for five different weights and from the mean of five readings, the apparent bulk density was calculated using the equation :

$$\textbf{Apparent Bulk Density} = \frac{\text{Mass of the catalyst}}{\text{Volume of the catalyst bed}} \text{ (gm/ml)}$$

Moisture Content of the Catalyst

A known weight of catalyst was heated in an oven at 70 ± 1°C to constant weight. The procedure was repeated on five different weights[12]. From the average of five weights, the percent moisture content was calculated using the formula:

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

Where A : Weight of catalyst before drying
B : Weight of catalyst after drying

Surface Area and Pore volume

The texture (surface/mass, pore size, structure) of pure polymer supports and supported catalysts affects the rate of transport of reactants and products from the reaction centre. The adsorption - desorption isotherms of nitrogen were recorded on a Carlo-Erba surface analyzer series 1900 at liquid nitrogen temperature (-196°C) after degassing the sample for 4 hours at 80°C. From the isotherms, the specific surface area and pore volume were calculated using BET [Brunett-Emmet-Teller] equation[12].

Swelling Studies

A systematic study on the swelling behavior of the polymer support and the anchored complexes in aliphatic, aromatic , polar and nonpolar solvents were carried out using the following procedure[13]:

Dried polymer supported catalyst (0.2 gm) was loaded into a glass filter tube fitted with a G_0 sintered disc and immersed into the solvent under study for 30 mins. The tube was then inserted into a 15ml centrifuge tube closed with a teflon cap and centrifuged for 15min. at 1200 rpm. The tube was immediately weighed and dried overnight at 100°C in a vacuum oven to constant weight. Knowing the difference in the weight before and after drying, the mole percent of the swelling was calculated using the following equation :

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

Where C = Weight of catalyst after centrifugation and before drying
D = Weight of the catalyst after drying
W = Weight of the catalyst
M = Molecular weight of solvent under study

SPECTRAL STUDIES

A major tool useful in the characterisation of catalysts is the interaction of light with catalyst particles. This involves :-

UV-Visible spectroscopy

The UV-Visible reflectance spectra (200-500nm) of the solid catalysts were recorded on a Shimadzu UV-240 spectrophotometer with reference to a non-absorbing standard $BaSO_4$. Analysis of the catalysts were carried out by spraying the powdered catalyst on a $BaSO_4$ window, to form a thin uniform film layer.

Infra-red spectroscopy

The mid I.R (4000-400 cm^{-1}) and far I.R. spectra (600-50cm^{-1}) of the functionalised polymer i.e. supports at different stages of preparation and that of anchored metal complexes were recorded on a Nicolet Magna 550 FT-IR spectrophotometer as KBr pellets.

X-ray photoelectron spectroscopy(XPS)/ Electron spectroscopy for chemical analysis (ESCA)

A Vacuum Generator's ESCALAB MKII equipment with MgKα and AlKα source was used for the surface characterisation of catalysts by XPS in which the sample is irradiated by soft X-rays resulting in knocking out of electrons from the various levels in the sample, which move with different velocities depending on the binding energies.

Scanning electron microscopy (SEM)

The morphology of the polymeric supports and the newly synthesized supported metal complexes were studied using JEOL JSM-T300 Scanning Electron Microscope. The sample under study were sprayed on a double adhesive tape mounted on brass holder and coated with gold. The micrographs were recorded at different ranges of magnification.

Thermal stability studies

The analysis of the polymer supports and the supported metal complex catalysts were studied in the temperature range of 50-600°C on a TA Instruments 2950 Thermal Analyzer at a heating rate of 10°C min^{-1} under a flow of nitrogen (10ml min^{-1}).

SECTION- III

CATALYTIC ACTIVITY STUDIES

In the present work , epoxidation of olefins such as *cis*-cyclooctene, styrene and cyclohexene was carried out using polymer supported metal complexes of Ru and Fe. Hydrogenation of *cis*-cyclooctene was studied using supported Pd- complexes.

Materials

The substrates *cis*-cyclooctene(Lancaster), cyclohexene(Fluka), and styrene [freed from stabiliser] (ABS Plastics, (India)) were distilled before use. The solvents and the other reagents were purified by literature methods prior to use[14]. TBHP (*tert*-butylhydroperoxide, 70% in water, Lancaster) was used as the terminal oxidant in the epoxidation reactions. The strength of hydroperoxide was estimated by placing 2ml of glacial acetic acid and 25ml of isopropanol in a 250ml Erlenmeyer flask. To this 10ml of freshly prepared sodium iodide- isopropanol (prepared by refluxing a mixture of 22gms of NaI in 100ml of isoproponal) was added. An accurately measured sample of TBHP solution (containing no more than 2.5 mmol of active oxygen) was added and gently refluxed for 30 secs. After dilution with 100ml of distilled water, the solution was titrated against 0.1N sodium thiosulphate till the disappearance of the yellow iodine colour using starch as the indicator[15]. The epoxidation reactions were carried out under an atmosphere of high purity nitrogen gas.

Analysis

A Shimadzu 15A Gas Chromatograph equipped with an integrator and a Flame Ionization Detector(FID) was used to analyse the products of epoxidation. The analysis of the reaction mixture was carried out using a stainless steel 15% Carbowax 20M on Chromosorb W column (1/8" x 2m) with N_2 as carrier gas at a flow rate of

30ml min^{-1} and the GC injector port temperature maintained at 220°C. The temperature programme for the analysis was :

Initial column oven temp. = 80°C, Final temp. = 150°C, Heating rate= 4°C /min.

Initial hold time = 2 mins., Final hold time = 10mins.

For the analysis of styrene epoxidation products, the final column temperature was maintained at 200°C.

Epoxidation of Olefins

A schematic representation of experimental setup is shown in **Fig.2.1.** The epoxidation of substrates such as *cis*-cyclooctene, styrene and cyclohexene using polymer anchored metal complex catalysts Ru-A to Ru-D , Fe-A to Fe-C, Ru-E and Ru-F was carried out as per the following general procedure:

The catalyst (0.25 g) was initially allowed to swell in methanol (20ml) for 30min in a two neck round bottom flask with a nitrogen inlet and a condenser. To this was added 10 mmol of the olefin followed by TBHP (5mmol). A known amount of an internal standard (chlorobenzene, 60-80mg) was added to the above solution prior to the run. The flask was stoppered and the mixture stirred magnetically at different temperatures under a blanket of nitrogen taking care to avoid any loss of solvent vapours during agitation. Aliquots(~1μL) of reaction mixture were carefully withdrawn at regular intervals and the progress of the reaction monitored by GC. Representative chromatograms are shown in **Figs.2.2 - 2.4.** Epoxidation of olefin did not take place in the absence of the catalyst. Peak positions of various reaction products were compared and matched with the retention times of authentic samples. A product profile of oxidation of different olefins is shown in **Scheme 2.1**

Hydrogenation of *cis*-cyclooctene(Kinetic study)

The kinetics of hydrogenation of *cis*-cyclooctene was studied at atmospheric pressure by measuring the hydrogen uptake at different intervals of time in a magnetically

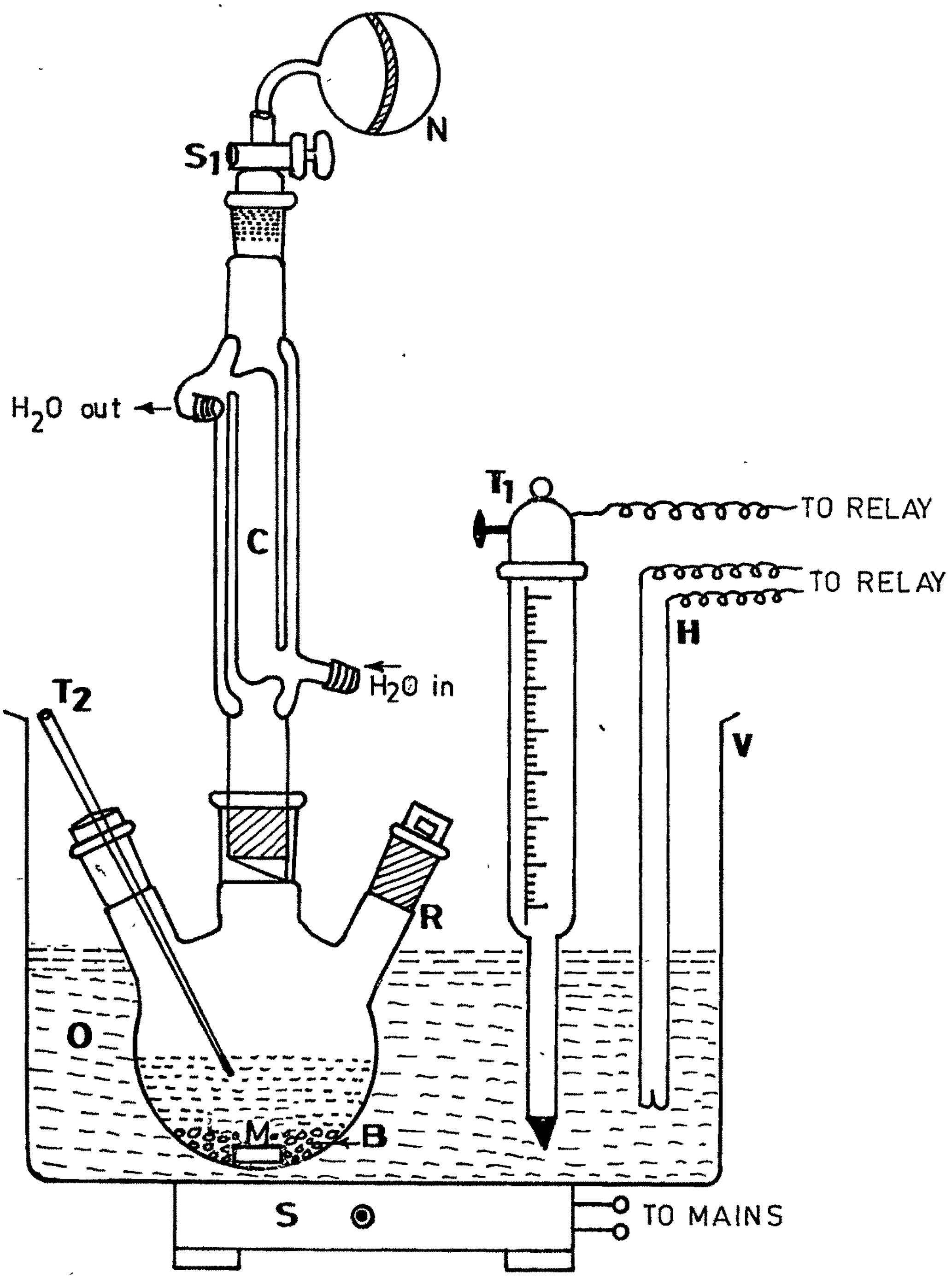
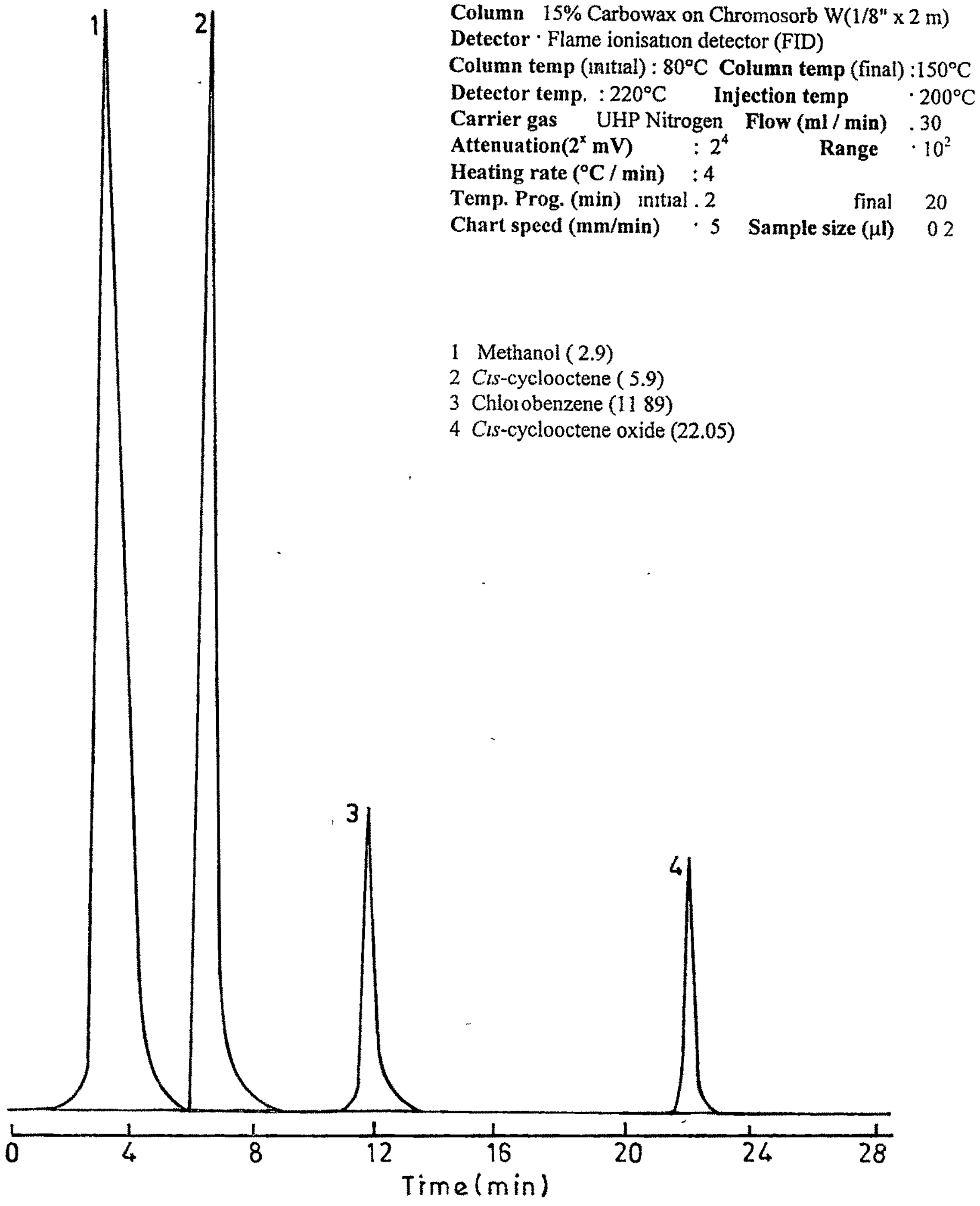


Fig. 2.1 EXPERIMENTAL SET-UP FOR EPOXIDATION OF OLEFINS

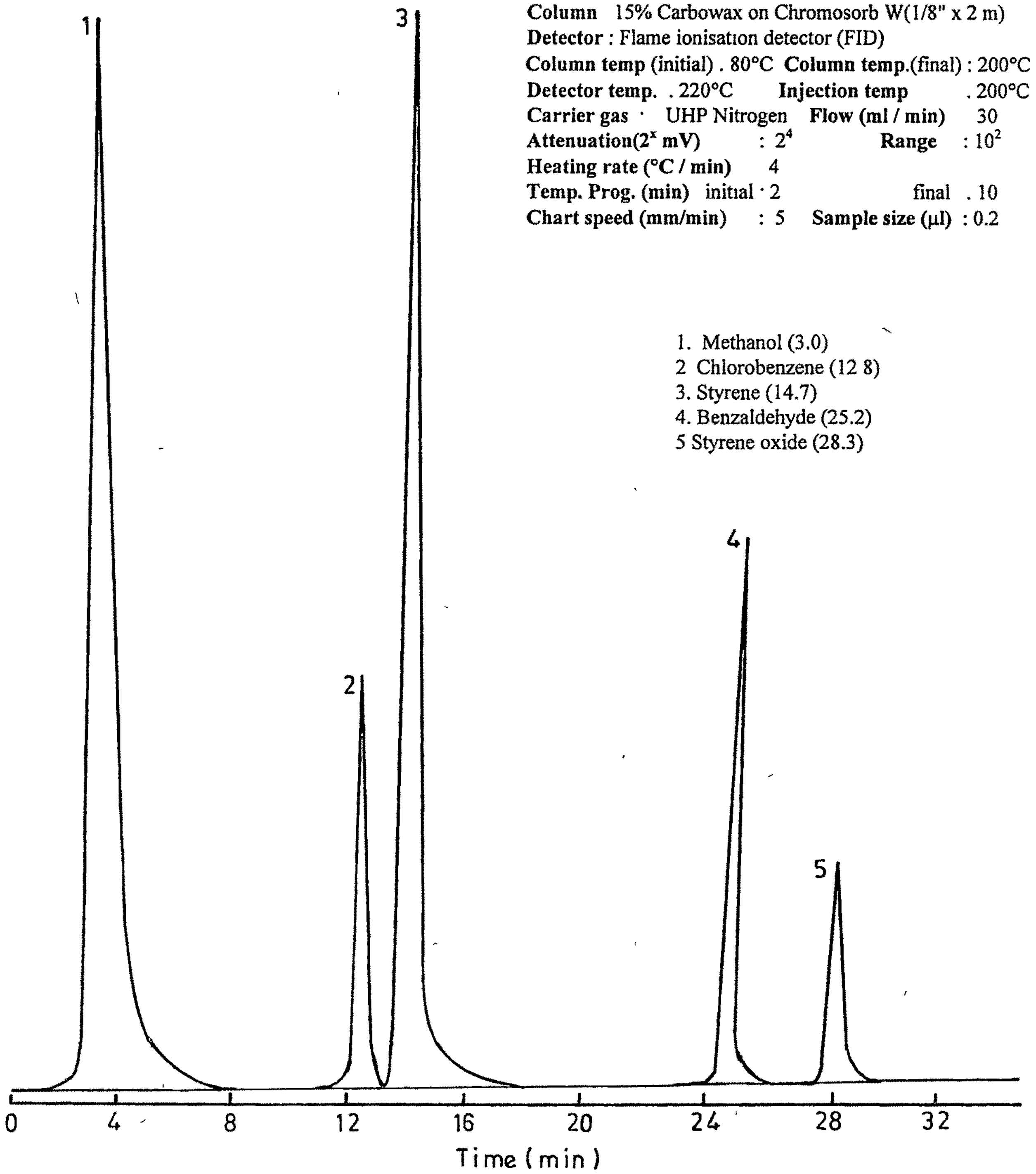
[B] Catalyst beads	[C] Condenser(jacketed)	[H] Heating coil	[M] Magnetic bar
[N] Nitrogen balloon	[O] Heating oil	[R] 3-necked Flask	[S] Stirrer
[S_1] One way stopcock	[T_1] Contact thermometer	[T_2] Thermometer	[V] Vessel



Column 15% Carbowax on Chromosorb W(1/8" x 2 m)
Detector · Flame ionisation detector (FID)
Column temp (initial) : 80°C **Column temp** (final) :150°C
Detector temp. : 220°C **Injection temp** · 200°C
Carrier gas UHP Nitrogen **Flow (ml / min)** . 30
Attenuation(2^x mV) : 2^4 **Range** · 10^2
Heating rate (°C / min) : 4
Temp. Prog. (min) initial . 2 final 20
Chart speed (mm/min) · 5 **Sample size (μl)** 0 2

1 Methanol (2.9)
2 *Cis*-cyclooctene (5.9)
3 Chlorobenzene (11 89)
4 *Cis*-cyclooctene oxide (22.05)

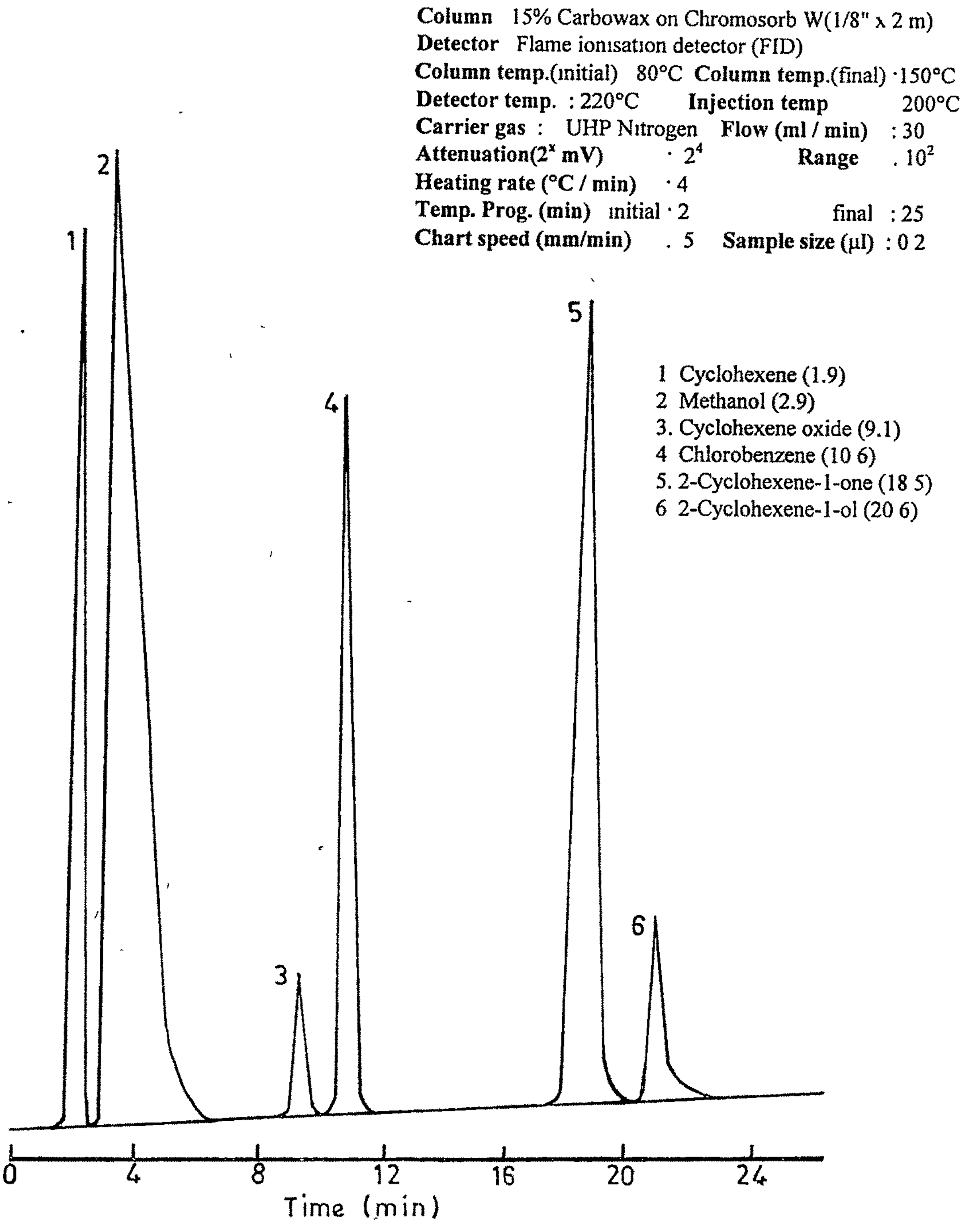
Fig 2.2.TYPICAL GC ANALYSIS OF EPOXIDATION PRODUCTS OF *CIS*-CYCLOOCTENE



Column 15% Carbowax on Chromosorb W(1/8" x 2 m)
Detector : Flame ionisation detector (FID)
Column temp (initial) . 80°C **Column temp.(final)** : 200°C
Detector temp. . 220°C **Injection temp** . 200°C
Carrier gas · UHP Nitrogen **Flow (ml / min)** 30
Attenuation(2^x mV) : 2^4 **Range** : 10^2
Heating rate (°C / min) 4
Temp. Prog. (min) initial · 2 final . 10
Chart speed (mm/min) : 5 **Sample size (µl)** : 0.2

1. Methanol (3.0)
2 Chlorobenzene (12 8)
3. Styrene (14.7)
4. Benzaldehyde (25.2)
5 Styrene oxide (28.3)

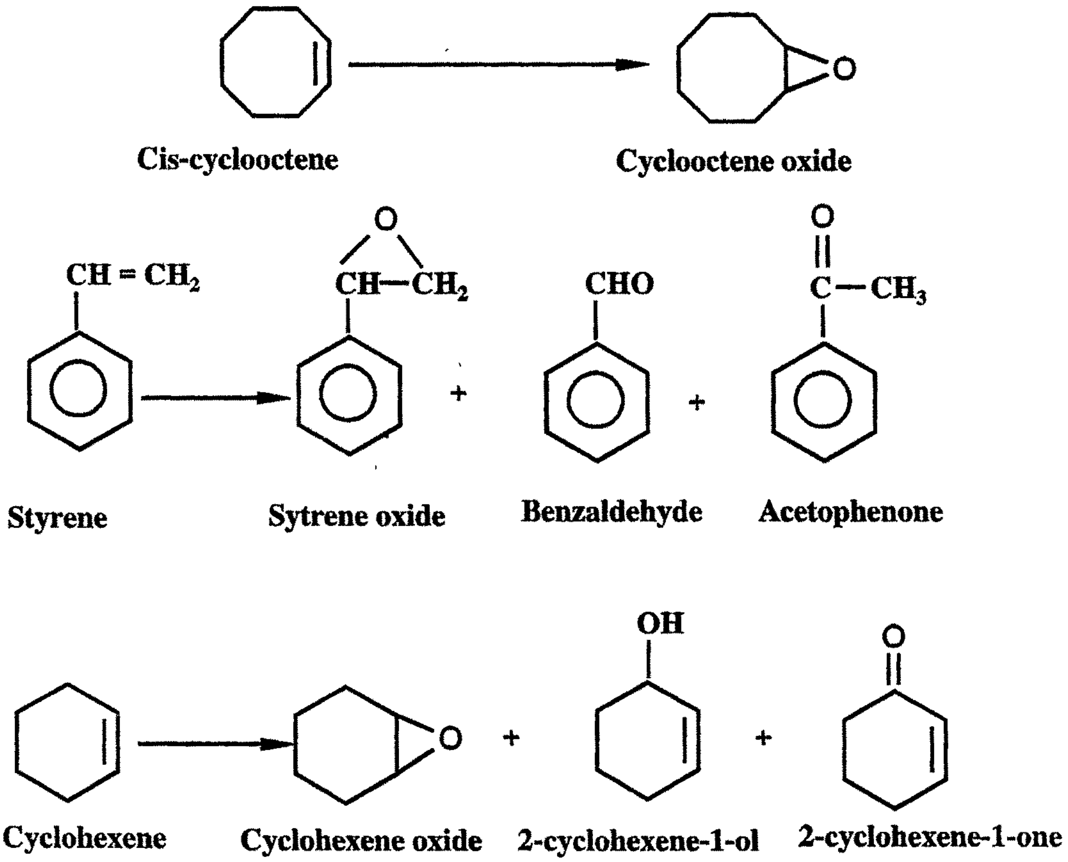
Fig 2.3. GC OF EPOXIDATION PRODUCTS OF STYRENE



Column 15% Carbowax on Chromosorb W(1/8" x 2 m)
Detector Flame ionisation detector (FID)
Column temp.(initial) 80°C **Column temp.(final)** : 150°C
Detector temp. : 220°C **Injection temp** 200°C
Carrier gas : UHP Nitrogen **Flow (ml / min)** : 30
Attenuation(2^x mV) : 2^4 **Range** : 10^2
Heating rate (°C / min) : 4
Temp. Prog. (min) initial : 2 final : 25
Chart speed (mm/min) : 5 **Sample size (μl)** : 0 2

1 Cyclohexene (1.9)
2 Methanol (2.9)
3. Cyclohexene oxide (9.1)
4 Chlorobenzene (10 6)
5. 2-Cyclohexene-1-one (18 5)
6 2-Cyclohexene-1-ol (20 6)

Fig. 2.4.GC OF EPOXIDATION PRODUCTS OF CYCLOHEXENE



Scheme 2.1 : Oxidation products of different olefins using polymer supported catalysts

stirred three necked glass reactor using methanol as solvent. The experimental set-up is shown in **Fig.2.5.**

In a typical experiment, methanol (20ml) was taken in the glass reactor and saturated with hydrogen at specified reaction temperature for 15min. A known quantity of dried catalyst(100 mg) was then introduced. The system was evacuated by applying vacuum by opening stopcock S_3 and closing S_1 and S_2. The air in the gas burette was removed by raising the paraffin reservoir **L** to the maximum. After the entire system was evacuated, stopcock S_3 was closed. The reaction vessel was then flushed with H_2 gas for few seconds by opening stopcock S_1. Sufficient amount of H_2 (about 40ml) was stored in the gas burette by carefully opening S_2. The system was allowed to equilibrate at the given temperature (± 0.1°C). On attaining equilibrium,*cis*-cyclooctene (20μL) was injected into the system through the injection port **I** using a microliter syringe(Hamilton). The hydrogen uptake was monitored by adjusting the level of the reservoir **L** periodically. The reaction was stopped when no further uptake of hydrogen was indicated from the gas burette. Necessary corrections were applied for vapor pressure of the solvent. The initial rate of reaction was calculated from the tangent of the plot of H_2 uptake *versus* time. Based on these plots, the energy of activation and the order of reaction were calculated.

Hydrogenation of *cis*-cyclooctene at high pressure

The catalytic hydrogenation of *cis*-cyclooctene at room temperature was carried out on a SS shaker type Parr hydrogenation apparatus (Model 3911) [**Plate 2.1**].

A known weight of the catalyst(100mg), *cis*-cyclooctene(10mmole) and methanol (20 ml) were sealed in a stainless steel reaction bottle(500ml) and connected to a hydrogen reservoir. Air was removed either by evacuating the bottle or by flushing with hydrogen. Hydrogen pressure in the range of 20 psig to 50 psig was applied from the reservoir and the bottle was shaken vigorously to initiate the reaction. The

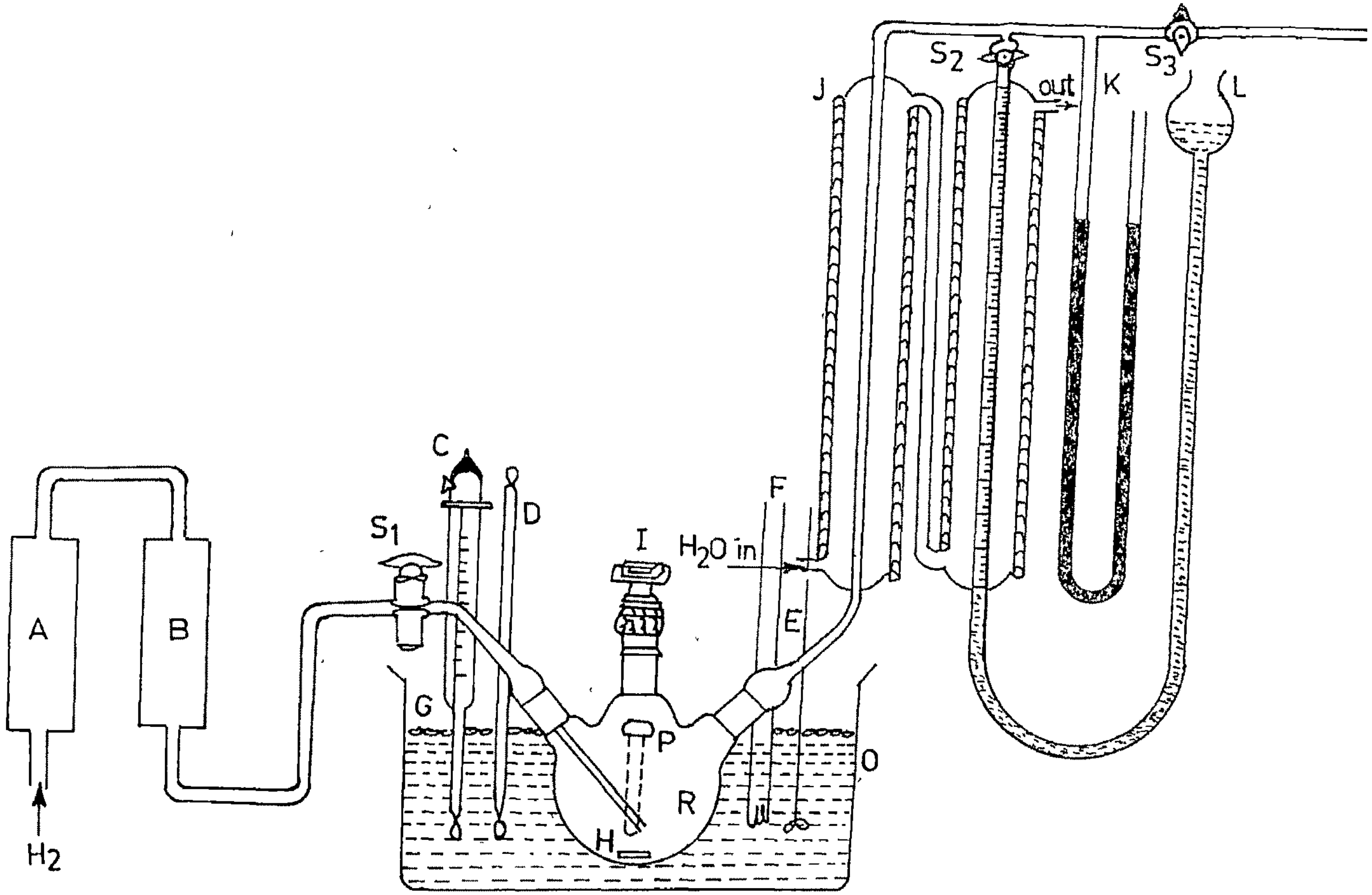


FIG.2.5EXPERIMENTAL SET-UP TO STUDY THE KINETICS OF HYDROGENATION OF OLEFINS

[A] Deoxo trap
[B] Molecular sieve(4A) 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 reservoir
[O] Vessel
[P] Thermowell
[R] Reaction vessel
[S_1,S_2,S_3] Two way stopcocks

Plate 2.1 : Low Pressure Parr Hydrogenator for hydrogenations at room temperature

Plate 2.2 : High Pressure Parr Hydrogenator for hydrogenations at elevated temperature

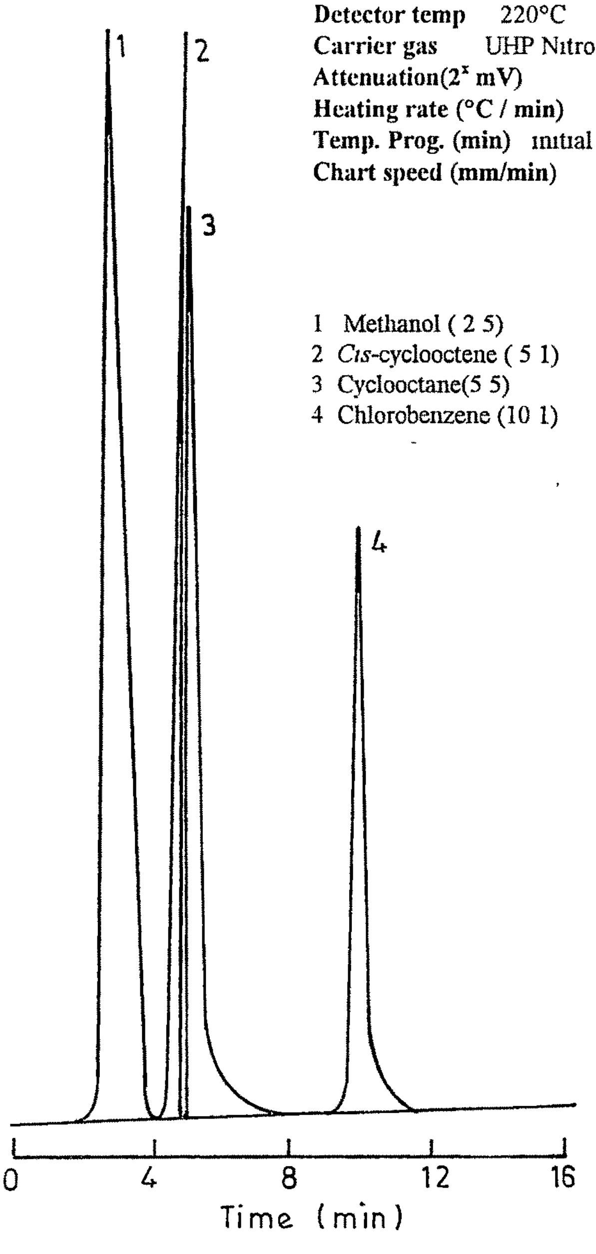
progress of the reaction was followed by observing the pressure drop in the system.After 24 hours, the reaction was stopped, bottle vented and the product collected. By adding a known quantity of an internal standard (chlorobenzene), the products were analyzed on a Shimadzu 15A Gas Chromatograph using a 15% Carbowax column (1/8" x 2m) connected to a flame ionization detector(FID). Nitrogen was used as a carrier gas with a flow rate of 30ml min^{-1}.

The high pressure hydrogenation reactions at 50°C were carried out in a 160ml Parr reactor (Model 4561) attached to a temperature controller (Model 4842) [**Plate 2.2**]. *Cis*-cyclooctene(10mmole), solvent methanol(20ml) and catalyst(100mg) were charged into the reactor. The reactor was pressurized with hydrogen in the range of 200psig to 500psig . The contents were stirred for 4 hours till no further drop in hydrogen pressure was noticed. The progress of the reaction was monitored by the fall in hydrogen pressure. After 4hrs, the reactor was cooled to room temperature, the product separated from the catalyst by filtration and the filtrate analyzed by GC as described above. A representative chromatogram of the hydrogenation reaction is shown in **Fig.2.6.**

Catalyst recycle studies

Preliminary studies on recyclablity of some of the polymer supported catalysts were carried out in the epoxidation of olefins. The procedure involved the use of *cis*-cyclooctene as the substrate , methanol as solvent, TBHP as oxidant and PhCl as internal standard. The reaction was carried out at 50°C for 24hr. After the first oxidation cycle, the catalyst was carefully separated from the reaction mixture by filtration, washed with methanol and dried. The recovery was >98%. Fresh substrate and oxidants were charged in the subsequent cycles and the oxidation reaction

Column 15% Carbowax on Chromosorb W(1/8" x 2 m)
Detector Flame ionisation detector (FID)
Column temp (initial) 80°C **Column temp** (final) 150°C
Detector temp 220°C **Injection temp** 200°C
Carrier gas UHP Nitrogen **Flow (ml / min)** 30
Attenuation(2^x mV) 2^4 **Range** 10^2
Heating rate (°C / min) 4
Temp. Prog. (min) initial 2 final 5
Chart speed (mm/min) 5 **Sample size (µl)** 0 2



1 Methanol (2 5)
2 *Cis*-cyclooctene (5 1)
3 Cyclooctane(5 5)
4 Chlorobenzene (10 1)

Fig. 2.6 GC ANALYSIS OF HYDROGENATION OF *CIS*-CYCLOOCTENE continued for the specific period. The products were analysed by GC at the end of each cycle. The experiments were extended to about 6 cycles.

To study the recyclability of polymer supported catalysts in the hydrogenation of olefins, kinetic experiments were carried out at 30°C for a period of 60mins. per cycle *Cis*-cyclooctene (20μl) was used as substrate with methanol(20ml) as solvent. The rate of hydrogenation was measured as a function of time. After each cycle, the catalyst was carefully filtered, washed with methanol and dried for further use. The catalysts were recycled for 6 cycles.

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