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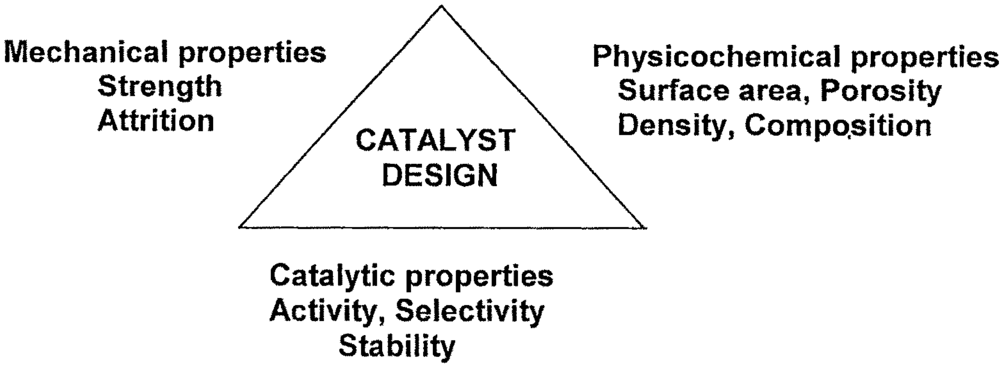
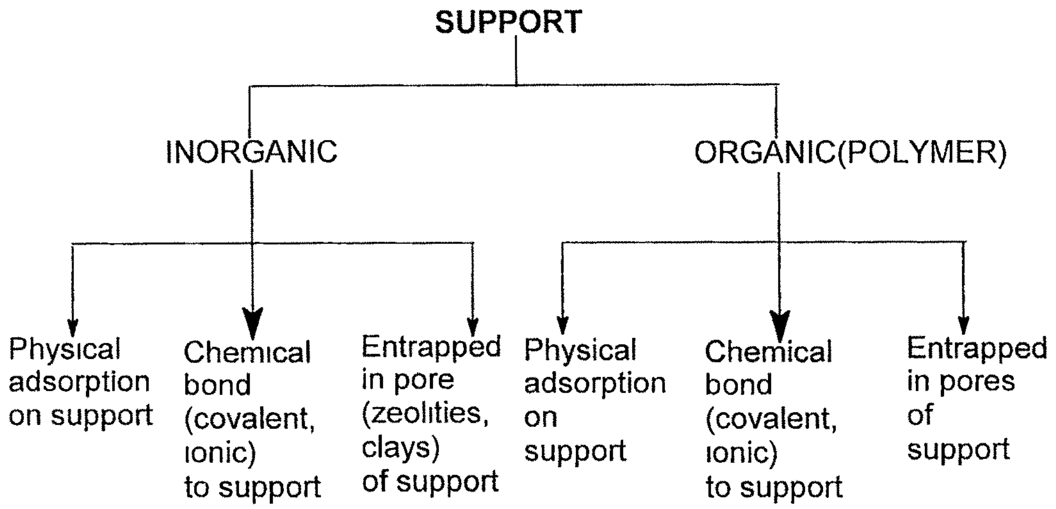
2.0 INTRODUCTION

Heterogeneous and homogeneous catalysis are integral and important techniques of modern industrial chemistry The catalyst preparation is considered to be an art The catalysts are designed with an aim to optimize a combination of interdependent physical, mechanical, chemical and catalytic properties A triangular concept of catalyst design introduced by Richardson is shown below



During the first few decades of this century, catalyst supports were derived from natural high surface area materials such as pumice, kieselguhr, asbestos, kaolin and bauxite Currently, many synthetic supports are available in a wide range of surface areas, porosities, shapes, sizes and purities. The widely used supports include both inorganic and organic materials The heterogenization of catalysts has attracted considerable attention and a summary of the various approaches that have been used is given below



The organic polymeric supports that have been most commonly used are crosslinked polymers, which are insoluble in most of the solvents Styrene and divinylbenzene (DVB) are the most frequently used monomers for synthesis of macromolecular supports as the aromatic ring in poly(styrene-divinylbenzene) copolymer can always be functionalized. In the catalyst preparation the following steps can be distinguished

monomer synthesis→ polymerization→ functionalization→ metal attachment→ activation

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

2.1 SYNTHESIS OF THE CATALYSTS

MATERIALS

Chloromethylated poly(styrene-divinylbenzene) as spherical beads (0 3 - 1 2 mm) with 5% and 8% crosslink were provided by the M/s Ion Exchange (India) Ltd , Mumbai The chloride content in the chloromethylated beads were estimated by gravimetric analysis[1] so as to ascertain the extent of chloromethylation Hydrated Ruthenium Trichloride (Loba Chemie), Manganese Chloride (Ranbaxy), Palladium Chloride (Loba Chemie), 1,3-Diaminopropane (Aldrich), 4,4'-Diaminobiphenyl (Ranbaxy), Salicylaldehyde (S d. fine-Chem Ltd), 5-Nitroso-2,4,6-Triaminopyrimidine (Ranbaxy), and 1-Nitroso-2-Napthol-3,6-Disulphonic acid (Merck) were used as supplied. A R grade 1,4-Dioxane, Methanol, Ethanol, Acetonitrile, Tetrahydrofuran (THF), and Dimethylformamide(DMF) were freshly distilled before use by adopting standard methods [1]

2.1.1 MODIFICATION OF POLYMER SUPPORT WITH LIGANDS

In a typical experiment, chloromethylated poly(styrene-divinylbenzene) copolymer beads (20 g) were kept in contact with tetrahydrofuran in a three necked round bottom flask fitted with a condenser and an addition funnel The amount of polymer, THF and 1,3-diaminopropane or 4,4'-diaminobiphenyl used for the reaction were as follows **(Table 2.1).**

Table 2.1.
Amount of polymer, solvent and ligand taken for the preparation of polymer bound 1,3-diaminopropane

Cross-linking (% DVB)	Polymer (g)	THF (ml)	1,3-Diamino propane (g)	4,4′-Diamino biphenyl (g)
5	20	125	15 8	-
8	20	125	15 8	-
5	20	125	-	39 3
8	20	125	-	39 3

Ligand was added dropwise in the reaction vessel over a period of 15 min The contents were refluxed for 6-8 h The resin beads were separated by filteration and washed with copious amount of ethanol, ethanol-water, water, water-THF and finally extracted with THF for 24 h [2] in the Soxhlet assembly to remove the impurities Elemental analysis were carried out for C, H and N using a Coleman Microanalyser The results are given in **Chapter 3**

3.1. 2 PREPARATION OF SCHIFF BASE WITH FUNCTIONALISED POLY(STYRENE- DIVINYLBENZENE) COPOLYMER [3]

The functionalized polymer beads were kept in contact with sufficient amount of benzene to make a slurry in a round bottom flask fitted with condenser and addition funnel and to it an excess amount of salicylaldehyde was added

The amount of polymer, benzene and salicylaldehyde taken for the reaction were as follows **(Table 2.2).**

Table 2.2
Amount of polymer, solvent and ligand taken for the preparation of Schiff base.

Cross-linking (% DVB)	Polymer (g)	Benzene (ml)	Salicylaldehyde (ml)
5	20	150	18
8	20	150	18

The slurry was refluxed for 6 h and water of condensation was removed in a Dean-Stark trap The resin was separated and was subjected to Soxhlet extraction with ethanol to remove the impurities and finally dried at 80^{0}C for 6 h The number of moles of ligand bound to polymer beads was calculated from the results of microanalysis The results were further confirmed by estimating chloride ions present as unreacted chloromethyl group on the polymer support

3.1.3 INCORPORATION OF THE METAL IONS ON TO THE SCHIFF BASE BEARING RESIN

The Schiff base bearing polymer beads (10 g) were allowed to swell in ethanol (50 ml) for 45 min To this, 50 ml of ethanolic solution of metal chloride (from a 1% W/V stock solution of metal chloride in ethanol), **(Table 2.3 to 2.5)** was added over a period of 45 min with occasional shaking. The contents were initially heated to 50^{0}C for 6 h, cooled and agitated on a shaker for 15 days at room temperature. After 15 days, the color of the beads changed to grey in the case of ruthenium, brown for palladium and yellow for manganese indicating the formation of respective metal complex on the surface of the polymer The beads were filtered and carefully washed with ethanol and finally dried in vacuum at 70^{0}C for 24 h [3].

The schematic representation of all the stages involved in the synthesis of poly(styrene-divinylbenzene) supported ruthenium, palladium and manganese Schiff base complexes are shown in **Scheme 2.1**

Table 2.3
Experimental details for loading ruthenium metal ions on to the Schiff base bearing polymer support.

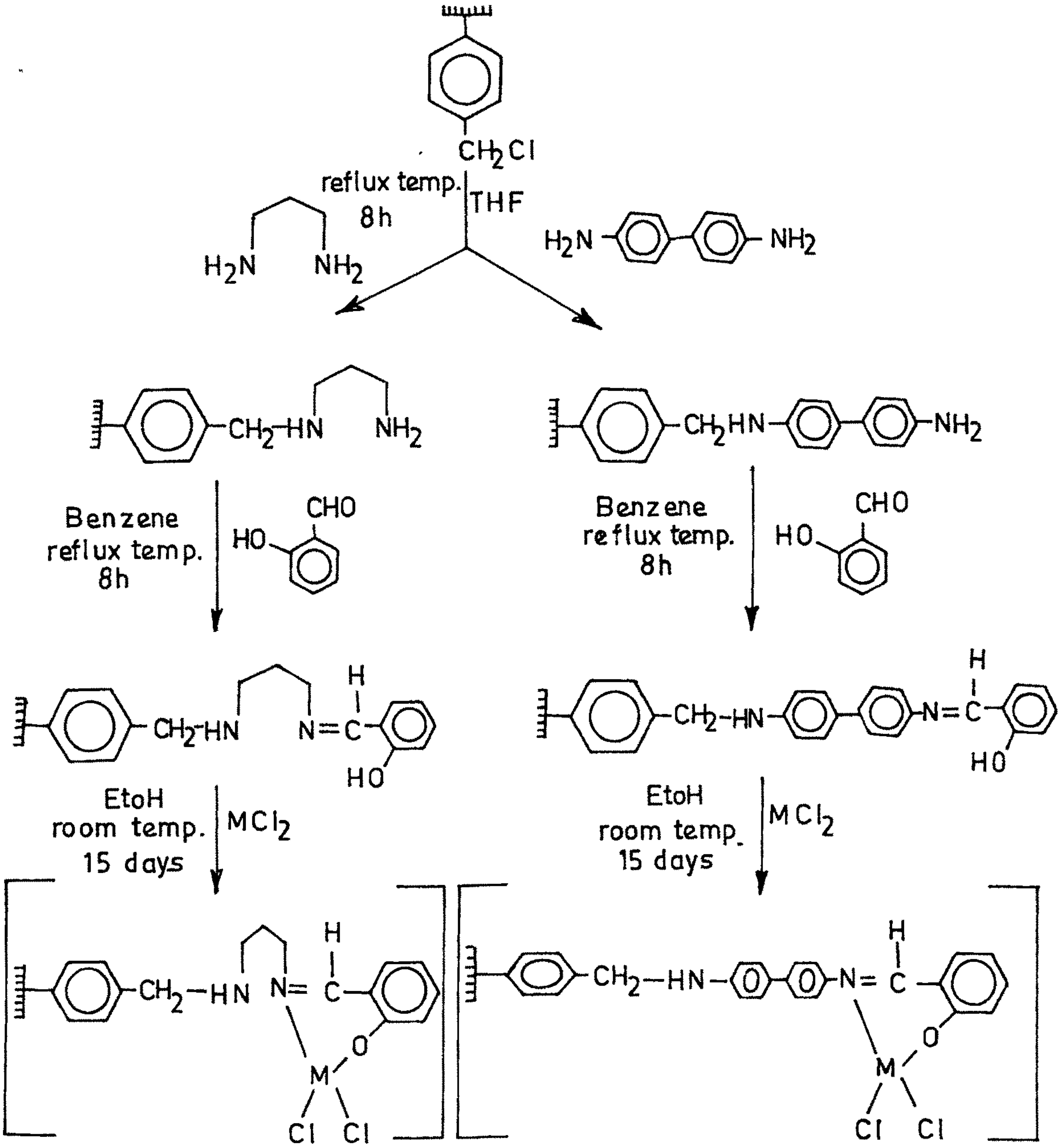
Polymer	Amount of Polymer (g)	Ethanol (ml)	$RuCl_3.3H_2O$ (g)	Time (days)
5%P(S-DVB)(1,3-dap-SB)	10	100	0.25	15
8%P(S-DVB)(1,3-dap-SB)	10	100	0.25	15
5%P(S-DVB)(4,4'-dabp-SB)	10	100	0.25	15
8%P(S-DVB)(4,4'-dabp-SB)	10	100	0.25	15

Table 2.4
Experimental details for loading palladium metal ions on to the Schiff base bearing polymer support.

Polymer	Amount of Polymer (g)	Ethanol (ml)	$PdCl_2$ (g)	Time (days)
5%P(S-DVB)(1,3-dap-SB)	10	100	0.25	15
8%P(S-DVB)(1,3-dap-SB)	10	100	0 25	15
5%P(S-DVB)(4,4'-dabp-SB)	10	100	0.25	15
8%P(S-DVB)(4,4'-dabp-SB)	10	100	0 25	15

Table 2.5
Experimental details for loading manganese metal ions on to the Schiff base bearing polymer support.

Polymer	Amount of Polymer (g)	Ethanol (ml)	$MnCl_2.2H_2O$ (g)	Time (days)
5%P(S-DVB)(1,3-dap-SB)	10	100	0 25	15
8%P(S-DVB)(1,3-dap-SB)	10	100	0.25	15
5%P(S-DVB)(4,4'-dabp-SB)	10	100	0.25	15
8%P(S-DVB)(4,4'-dabp-SB)	10	100	0 25	15



Scheme 2.1 Synthesis of polymer supported metal Schiff base complexes.

2.1.4 NOMENCLATURE

The newly synthesized polymer anchored metal complex catalysts have been named and designated as follows

Catalyst **Ru-A** : 5%poly(S-DVB)Ru(III)(1,3-dap-SB)

Catalyst **Ru-B** : 8%poly(S-DVB)Ru(III)(1,3-dap-SB)

Catalyst **Ru-C** : 5%poly(S-DVB)Ru(III)(4,4'-dabp-SB)

Catalyst **Ru-D** : 8%poly(S-DVB)Ru(III)(4,4'-dabp-SB)

Catalyst **Mn-A** : 5%poly(S-DVB)Mn(II)(1,3-dap-SB)

Catalyst **Mn-B** : 8%poly(S-DVB)Mn(II)(1,3-dap-SB)

Catalyst **Mn-C** : 5%poly(S-DVB)Mn(II)(4,4'-dabp-SB)

Catalyst **Mn-D** : 8%poly(S-DVB)Mn(II)(4,4'-dabp-SB)

Catalyst **Pd-A** : 5%poly(S-DVB)Pd(II)(1,3-dap-SB)

Catalyst **Pd-B** : 8%poly(S-DVB)Pd(II)(1,3-dap-SB)

Catalyst **Pd-C** : 5%poly(S-DVB)Pd(II)(4,4'-dabp-SB)

Catalyst **Pd-D** : 8%poly(S-DVB)Pd(II)(4,4'-dabp-SB)

where,

5% and 8% are percentage of crosslink

poly(S-DVB) : poly(styrene-divinybenzene) copolymer

(1,3-dap-SB) : 1,3-diaminopropane Schiff base

(4,4'-dabp-SB) : 4,4'-diaminobiphenyl Schiff base

2.2 CHARACTERIZATION OF THE CATALYSTS

Characterization of a catalyst refers to the measurement of its characteristics i e its physical and chemical properties which are essential for evaluation of performance in a given reaction. In order to characterize a polymer bound catalyst precisely, the constitution of the catalyst in the bulk as well as its surface has to be understood.

In the recent times, novel techniques and sophisticated instruments have been employed to characterize the catalyst before, during and after its use, which has led to a better understanding of the catalytic phenomenon However, a complete characterization of the polymer supported catalysts is extremely difficult because of their heterogeneous nature

The general procedure adopted in the characterization of a catalyst involves a careful record of the conditions under which the supported catalyst has been prepared, microanalysis of the elements present and spectroscopic techniques which are put together to arrive at a possible stoichiometry of the metal complex on the polymer

In the following sections the techniques employed to study the physicochemical properties such as elemental analysis, apparent bulk density, moisture content, surface area and swelling behavior of the catalyst in various solvents are discussed The spectroscopic investigation used to investigate the coordination of the polymer supported metal complexes and the oxidation state of the metal was carried out using UV-visible, Fourier Transform Infrared Spectroscopy (FT-IR), and Electron Spin Resonance (ESR) spectroscopy The thermal stability of the polymer supported metal complexes were studied by using thermogravimetric analysis.

2.2.1 ELEMENTAL ANALYSIS OF THE CATALYSTS

The amount of carbon, hydrogen and nitrogen present in the polymer bound metal complexes at the various stages of the preparation were determined using a Coleman microanalyser. The chloride content in the chloromethylated poly(styrene-divinybenzene) copolymer beads and that in the polymer supported metal complexes was determined gravimetrically by precipitation of chlorine as silver chloride [1] The ruthenium and palladium content in the polymer supported metal complexes were determined by refluxing a known amount (0 2 g) of the catalysts with concentrated (36%) HCl (10 ml) for 24 h. The beads were filtered and washed thoroughly with distilled water The filtrate was concentrated on a water-bath and the pH of the solution was adjusted to 1.8 The concentration of ruthenium was determined by measuring the absorbance on Shimadzu UV-VIS Spectrophotometer Model UV-265 at 510 nm using 12 5 ml of a standard solution of 5-nitroso-2,4,6-triaminopyrimidine (1% w/v in H_2O) [4] In the case of palladium the concentration was determined by measuring the absorbance at 490 nm using 12 5 ml of a standard solution of 1-Nitroso-2-napthol-3,6-disulphonic acid (1% w/v in H_2O) as metal indicator [5] The concentration of manganese in the polymer supported metal complexes was estimated using Zeeman ZL-4100 Atomic Absorption Spectrometer (Perkin Elmer) [6]

2.2.2 APPARENT BULK DENSITY

The apparent bulk density refers to the mass of the catalyst that can be packed into a specified and relatively large volume of a reactor. This parameter is of importance for catalyst based on rigid supports The typical procedure to determine the apparent bulk density of the polymer bound catalysts is described here under In a 10 ml graduated measuring cylinder, weighed amount of catalyst was taken The weighed catalyst in the cylinder was tapped 250 times on a "Ceast Volumetric Classificator" with programmer and its volume measured when it remained constant after continuous tapping [7]. The experiment was repeated for five different weights and the apparent bulk density was calculated with the mean of the five readings recorded using the equation

$$\textbf{Apparent bulk density} = \frac{\text{Mass of the catalyst}}{\text{Volume of the catalyst bed}} \text{(g/ml)}$$

2.2.3 MOISTURE CONTENT OF THE CATALYST

A known weight of the catalyst was heated in an oven at 105 ± 1^0C to constant weight The procedure was repeated on five different weights [7] Using the average of five weights, the percent moisture content was calculated as per following equation

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

where, **A** is the weight of catalyst before drying

B is the weight of catalyst after drying

2.2.4 SURFACE AREA AND PORE VOLUME OF THE CATALYST

The texture (surface/mass, pore size, structure) of the pure polymer supports and supported catalysts affects the rate of transport of reactants and of the products from the reaction centre Adsorption-desorption isotherms of nitrogen on the supports and supported catalysts were recorded on a Carlo-Erba Surface Area Analyzer Series-1900 at liquid nitrogen temperature (-196 ^{0}C) after degassing the sample for 4 h at 80 ^{0}C The isotherms were obtained and the specific surface area and pore volume were calculated by the data processor using BET (Brunauer-Emmett-Teller) equation [8]

2.2.5 SWELLING STUDIES

A systematic study on the swelling behavior of the polymer support and the anchored complexes in aliphatic, aromatic, polar and nonpolar solvents was carried out using the following procedure [9]

A dried sample (0.2 g) of polymer supported catalyst was loaded into a glass filter tube and immersed in a solvent under study for 30 min The tube was then inserted into a 15 ml centrifuge tube closed with a teflon cap and centrifuged (Remi Equipments, Mumbai, India) for 15 min at 1200 rpm The tube was immediately weighed and dried overnight at 100^0C in a vacuum oven to constant weight Knowing the difference in the weight before and after drying, the mole percent of swelling was calculated using the following equation

$$\underset{\text{(Mole \%)}}{\textbf{Swelling}\ \text{(S)}} = \frac{C - D}{W \times M} \times 10$$

where C weight of the catalyst after centrifugation and before drying

D . weight of the catalyst after centrifugation and drying

W weight of the catalyst taken for study

M molecular weight of the solvent under study

2.2.6 SPECTRAL STUDIES

A major tool useful in the characterization is the interaction of light with matter The techniques employed include UV-Vis, FT-IR and ESR

2.2.6.1 UV- VISIBLE SPECTROSCOPY

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

2.2.6.2 INFRA-RED SPECTROSCOPY

The IR spectra (4000-400 cm^{-1}) and far IR (600-50 cm^{-1}) were recorded using Fourier Transform technique The spectra of the functionalized polymer support at different stages of the preparation and that of the polymer supported metal complexes were recorded in KBr pellets on a Nicolet Magna 550 Spectrophotometer.

2.2.7 SCANNING ELECTRON MICROSCOPY (SEM)

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

2.2.8 THERMAL STABILITY STUDIES

Thermal analysis (TA) of the polymer supports and supported metal complex catalysts was investigated in the temperature range 50-600^{0}C on a TA Instruments Model 2950 Thermal Analyzer at a heating rate of 10 ^{0}C min^{-1} under a flow of nitrogen (10 ml min^{-1})

2.3 CATALYTIC ACTIVITY STUDIES

In the present work, epoxidation of the olefins such as norbornene, *cis*-cyclooctene was carried out using polymer supported metal complexes of Ru and Mn. Hydrogenation of 1-decene was studied using supported Pd-complexes .

MATERIALS

The substrates *cis*-cyclooctene (Lancaster), norbornene (Fluka) and 1-decene (Lancaster) were used as supplied. The solvents and other reagents were purified by published methods prior to use [10] Tert-butylhydroperoxide (TBHP), (70% in water, Lancaster) was used as the terminal oxidant in the epoxidation reactions

The strength of hydroperoxide was estimated by placing 2 ml of glacial acetic acid and 25 ml of isopropanol in an Erlenmeyer flask To this 10 ml of freshly prepared sodium iodide - isopropanol (prepared by refluxing a mixture of 22 g of NaI in 100 ml isopropanol) 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 sec After dilution with 100 ml of distilled water, the solution was titrated against 0.1N sodium thiosulphate till the disappearance of the yellow iodine colour using starch as an indicator [11] High purity hydrogen gas was used as a reactant in the hydrogenation reactions. The epoxidation reactions were carried out under an atmosphere of high purity nitrogen gas

ANALYSIS

A Shimadzu 9A Gas Chromatograph equipped with an integrator and a Thermal Conductivity Detector (TCD) was used to analyze the products of epoxidation The analysis of the reaction mixture was carried out using a 10% SE-30 column (packed column, 1/8" diameter, 12' length) with helium as carrier gas at a flow rate of 40 ml min^{-1} and the GC injection port temperature maintained at 200 ^{0}C **(Table 2.6)**

Table 2.6
GC column temperature programme

Substrate	Initial Temp. (^{0}C)	Initial hold Time (min)	Heating Rate (^{0}C/min)	Final hold Time (min)	Final Temp (^{0}C)
Norbornene	100	2	5	10	120
Cyclooctene	100	2	5	10	120

2.3.1 EPOXIDATION OF OLEFINS

A schematic representation of experimental setup is shown in **Fig 2.1** The epoxidation of substrates such as *cis*-cyclooctene and norbornene using

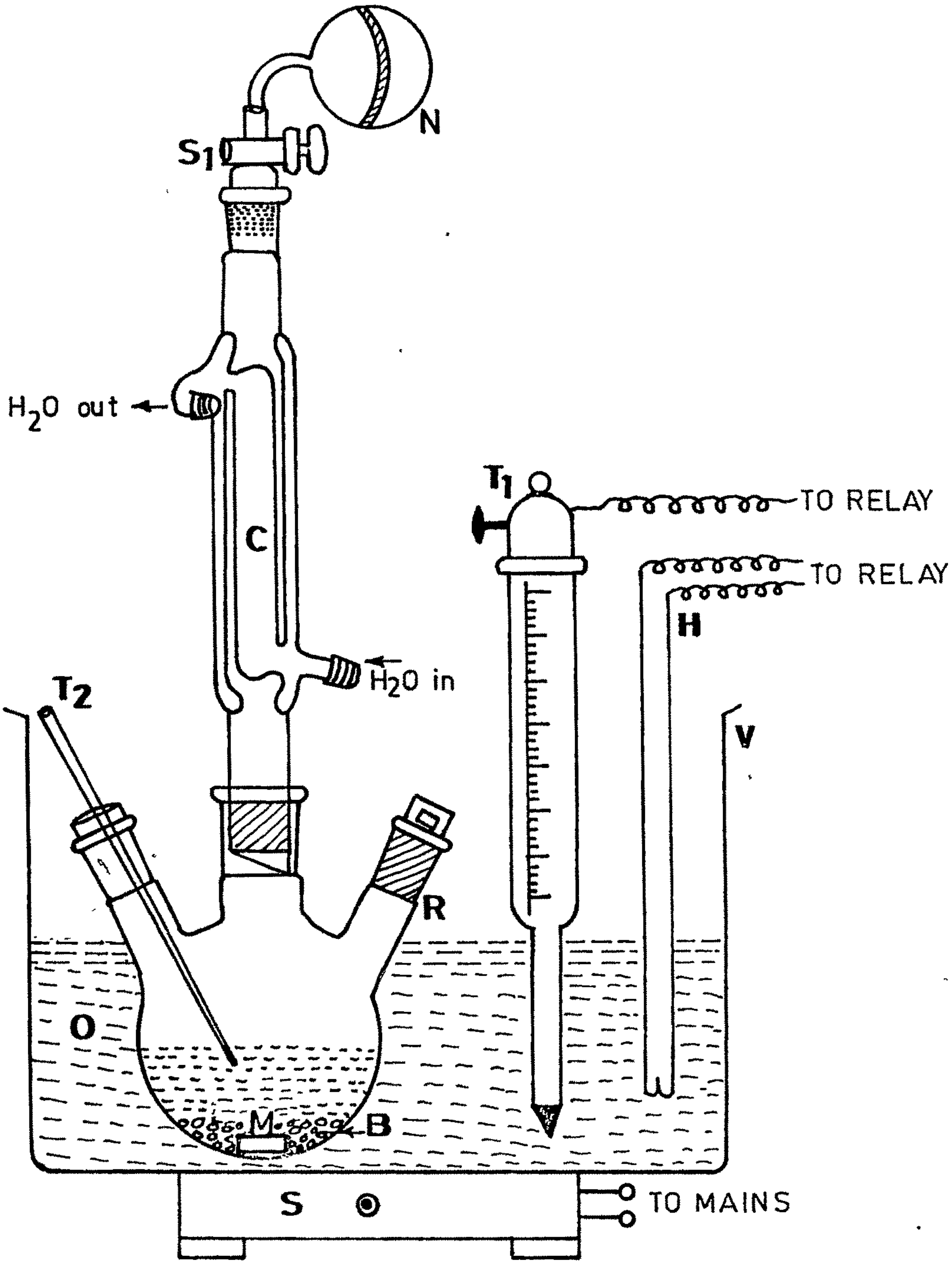


Fig. 2.1 Experimental set-up for epoxidation of olefins

[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

polymer anchored metal complex catalysts Ru-A to Ru-D and Mn-A to Mn-D was carried out as per the following general procedure

The catalyst (0 25 g) was initially allowed to swell in methylene dichloride (20ml) for 30 min in a three necked round bottom flask equipped with nitrogen inlet and a condenser. To this was added 5 mmol of the olefin followed by TBHP (2 mmol) A known amount of an internal standard (chlorobenzene, 200-300 mg) was added to the above solution prior to the run The flask was stoppered and the mixture was stirred magnetically at different temperature under nitrogen blanket taking care to avoid any loss of solvent vapours during agitation Aliquots (~5 µl) of reaction mixture were carefully withdrawn at regular intervals and the progress of the reaction was monitored by GC Representative chromatograms are shown in **Fig. 2.2**. 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 time of authentic samples. A product profile of oxidation of different olefins is shown in **Scheme 2.2.**

2.3.2 HYDROGENATION OF 1-DECENE (KINETIC STUDY)

Polymer bound Schiff base complexes of palladium(II) (Pd-A to Pd-D) have been used to study the kinetics of hydrogenation of 1-decene at atmospheric pressure The influence of various parameters such as reaction

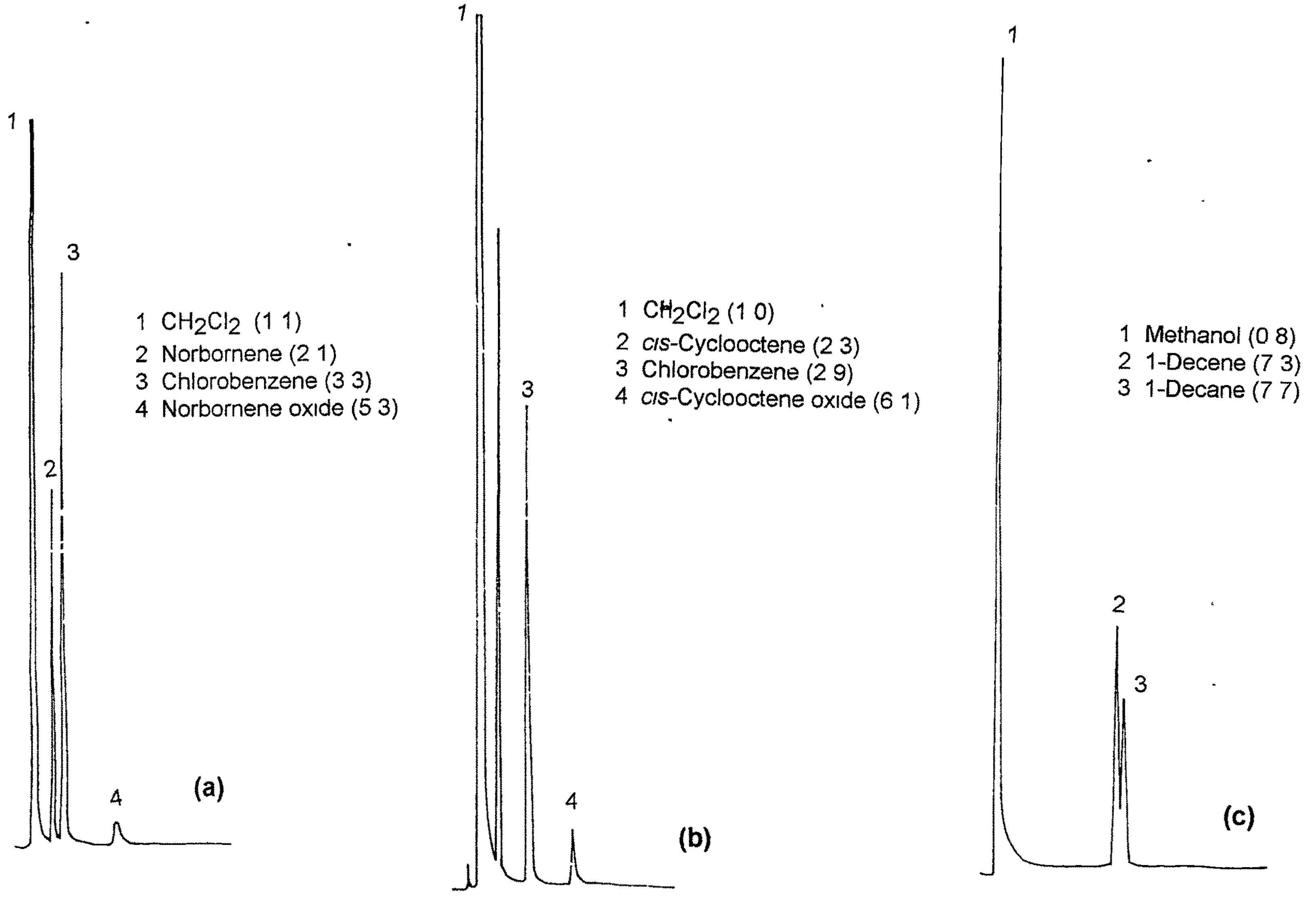
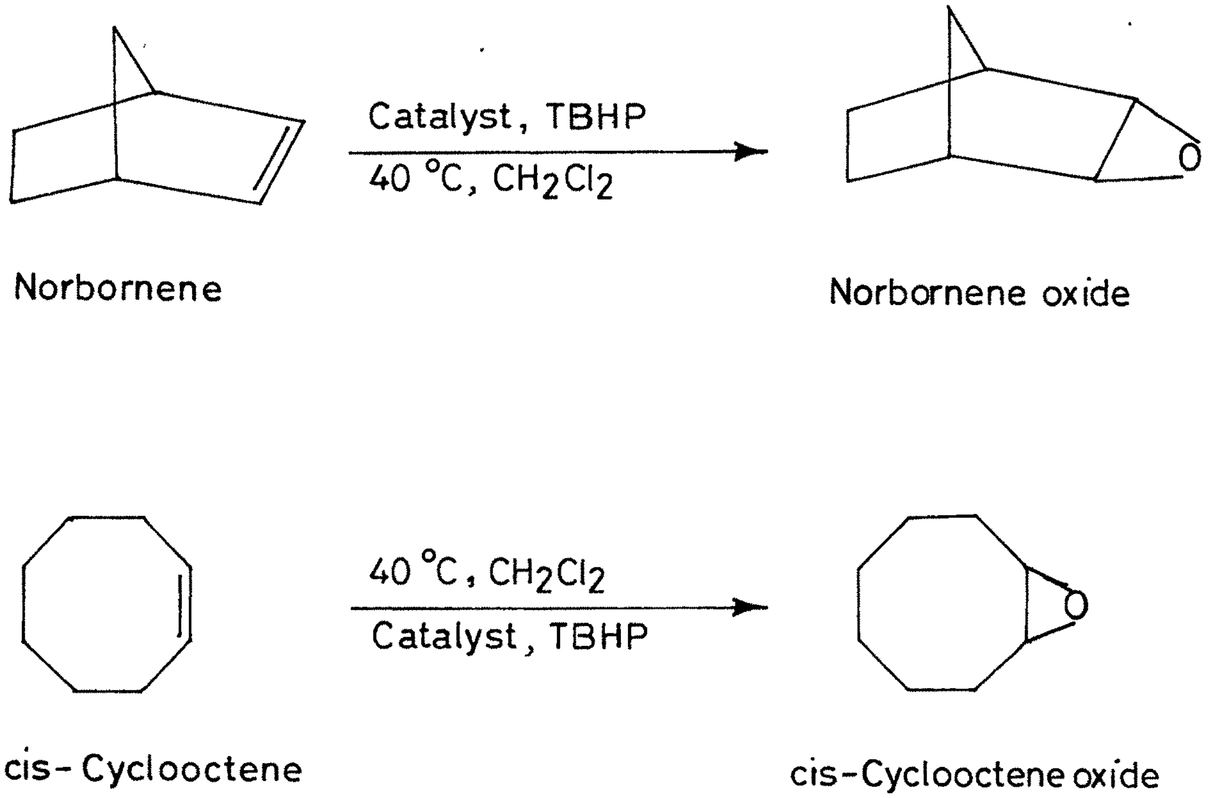


Fig. 2.2 G.C. analysis of epoxidation products of (a) norbornene (b) *cis*-cyclooctene and hydrogenation product of (c) 1-decene



Scheme 2.2 **Olefin oxidation using polymer supported catalysts.**

temperature, concentration of the catalyst, substrate and the nature of the solvent on the rate of reaction has been investigated. On the basis of above data, the thermodynamic parameters have been calculated The investigation of kinetics of hydrogenation of 1-decene was carried out at atmospheric pressure by measuring the hydrogen uptake at different intervals of time in a magnetically stirred three necked glass reactor using methanol as solvent The experimental set-up is as shown in **Fig. 2.3**. In this experiment, freshly distilled methanol (20 ml), passed through activated alumina to remove traces of impurities (if any) is taken into glass reactor and saturated with hydrogen at specified reaction temperature for 20 min To this, a known quantity of dried catalyst was introduced The system was evacuated by applying vacuum and opening stopcock S_3 and closing S_1 and S_2. The air in the gas burette was also removed by raising the paraffin reservoir (L) to the maximum After the whole system was evacuated, the stopcock S_3 was closed The reaction vessel was then flushed with H_2 by opening of stopcock S_1. After flushing the reactor vessel for a few seconds with H_2, sufficient amount of H_2 was stored in the gas burette by carefully opening S_2. The system was allowed to equilibrate at a constant temperature (+/- 0.1°C). On attaining equilibrium, a known amount of substrate, 1-decene was injected into the system through the injection port I using a hypodermic syringe. The progress of the reaction was monitored by adjusting the level of the reservoir L at various intervals of time thereby indicating the hydrogen uptake. The reaction was stopped when no further uptake of hydrogen was indicated from the gas burette Necessary corrections were applied for

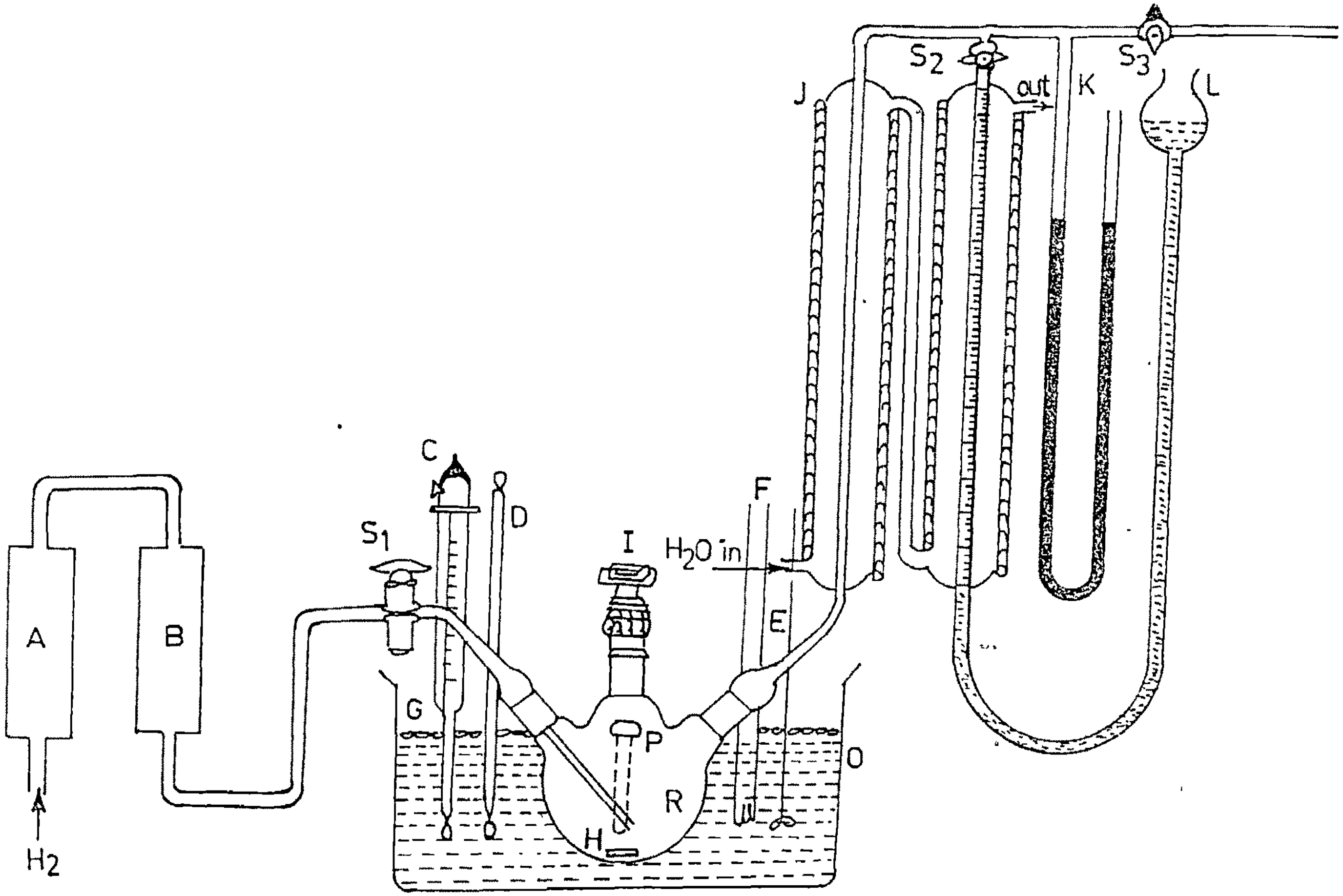


Fig. 2.3 Experimental set-up to study the kinetics of hydrogenation of olefin

[A] Deoxo trap
[E] Mechanical stirrer
[I] Injection port
[O] Vessel

[B] Molecular sieve(4A) trap
[F] Heating coil
[J] Asbestos rope
[P] Thermowell

[C] Contact thermometer
[G] Thermocole
[K] Manometer
[R] Reaction vessel

[D] Thermometer
[H] Magnetic bar
[L] Liquid reservoir
[S_1,S_2 S_3] Two way stopcocks

vapour pressure of solvent The initial rate of reaction was calculated from the tangent of the plot of H_2 uptake versus time Based on these observations, the energy of activation and order of reaction were calculated A representative Chromatogram of the hydrogenation reaction is shown in **Fig 2.2.**

2.3.3 CATALYST RECYCLE STUDIES

One of the main objectives of supporting a homogeneous metal complex onto a polymer is to enhance the life of the resulting catalyst To be a truly effective polymer supported catalyst, it is critical that recovery be simple, efficient and that the recovered catalyst retains its activity through multiple cycles It has been observed that the polymer bound catalysts may tend to loose their activity due to leaching of metal ions from the surface to solution or by reduction to free metal Preliminary studies on recyclibility of some of the polymer supported catalysts were carried out in the epoxidation of olefins The procedure involved the use of norbornene as the substrate, methylene chloride as a solvent, TBHP as oxidant and chlorobenzene as internal standard. The reaction was carried out at 40 ^{0}C for 24 h. After the first oxidation cycle of 24 h the catalyst was carefully separated from the reaction mixture by filtration, washed with CH_2Cl_2 and dried. The recovery was >97% Fresh substrate and oxidant were charged in the subsequent cycles and the oxidation reaction continued for the specific period . The formation of products was monitored by GC analysis at the end of each cycle The studies were extended to a period of 5-6 cycles

To study the reuse of the polymer supported catalysts in hydrogenation of olefins kinetic experiments were carried out at 40 ^{0}C for period of 50 min per cycle 1-Decene was used as a substrate with methanol as solvent The rate of hydrogenation was measured as a function of time in each cycle After each cycle of 50 min the catalyst was carefully filtered, washed with methanol and dried for further use. The catalysts were reused for a period of 5-6 cycles and by measuring the hydrogen uptake as a function of time with fresh substrate in each cycle and the extent of recyclability of the catalyst was determined.

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