CHAPTER 2

EXPERIMENTAL

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2.1 Introduction

Catalyst preparation is defined in the most revealing fashion by Richardson as "Catalyst preparation is the secret of achieving the desired activity, selectivity and life time (1). The definition conveys the idea that the catalyst preparation composed of unit operations is a strategic procedure which should not be disclosed or protected in the form of patents (2). Catalyst preparation is frequently described as an art (3). Proper catalyst characterization often enables to correlate catalytic behaviour with physical properties and chemical structure of the catalyst material (4). The present chapter describes synthesis of polymer supported transition metal complex catalysts and their homogeneous counterparts as well as the procedure of characterization of these catalysts.

Heterogenized homogeneous catalysts consist of two parts

1) The support (functional polymer in case of polymer-supported catalyst)
2) Transition metal complex.

These catalysts were synthesised by modifying a polymer with a suitable ligand followed by co-ordination of metal ions. The characterization of these catalysts were carried out using various techniques such as Chemical analyses, surface area measurement by BET method at liquid nitrogen temperature, evaluation of moisture content and bulk density, and swelling property studied using different solvents. The other spectroscopic techniques such as UV-visible reflectance, far infrared (IR), electron spin resonance (ESR) and electron spectroscopy for chemical analysis (ESCA) have also been described. Morphology of the polymer supports and the supported catalysts was studied using scanning electron microscope (SEM) and thermal stability was tested by thermogravimetric analysis (TGA). The experimental set-up and the procedure to carry out the kinetics of hydrogenation as well as oxidation under mild operating conditions have been included. Kinetics of hydrogenation of 1-hexene as well as styrene and oxidation of benzyl alcohol have been investigated by varying different parameters such as concentration of the catalyst and substrate, temperature of the system and the nature of the solvent. Stability of the catalysts has been seen by investigating the life cycle of the catalysts.

2.2 Modification of Polymer Supports with Ligands

Poly (styrene-divinylbenzene) is a popular polymer support because of having a wide range of physical properties where the porosity, surface area and solution characteristics may be altered by varying the degree of cross-linking.

XAD-2 (fluka AG, Chemische Fabrik CH-9470, Buchs) and AM-24 (kindly gifted by Ion Exchange (India) Ltd., Ankleshwar) were washed in sequence with distilled water, water-ethanol (1:1) mixture, ethanol and finally soxhlet extracted with ethanol-benzene (1:1) for complete removal of adsorbed material if any. The beads were dried in vacuuo at 70°C for 6 hours.

Above beads were chloromethylated with dry HCl, paraformaldehyde, acetic anhydride using $AlCl_3$ as a catalyst and 1,2-dichloroethane as a solvent. All the chemicals were purified as described earlier (5). 30 gm of polymer beads were kept in contact with 100 ml of 1,2-dichloroethane in a 500 ml three-necked flask equipepd with constant stirring device. To this, dry Hcl was bubbled and the temperature was raised upto 80°C using an oil bath. The reaction was continued for 20 hours. The beads were then washed in a sequence with 50% aqueous dioxane, aq. dioxane containing HCl (10% w/v), dry dioxane, methanol and finally with distilled water till the complete removal of chloride ion.

In a separate series of experiments, CM-800, chloromethylated P(S-DVB) with 8% cross-linking (gifted by Ion Exchange (India) Ltd., Bombay) was used as a support. The beads were washed and purified as described above.

The chlorine content was estimated in chloromethylated polymer beads by gravimetric analysis (6) in order to see the extent of chloromethylation.For this, a known amount of polymer (0.1 gm) was fused with twice the amount of sodium peroxide in a nickel crucible over a gas flame. Initially the mixture was heated slowly followed by a strong heating to enable complete fusion of polymer with Na_2O_2. The crucible was then allowed to cool at room temperature. The contents were extracted with deionized water, filtered in 100 ml volumetric flask and finally diluted with deionized water. A known volume of the filtrate was treated with dil. HNO_3 to neutralise the unreacted Na_2O_2 as NaOH and the pH of the solution was adjusted to ~6. The chloride ion was precipitated as silver chloride and the chloride content was estimated gravimetrically (6).

2.2.1 Introduction of schiff base salen on to the polymer support

In order to functionalise the chloromethylated polymer with schiffbase salen, it was sequentially treated with ehtylenediamine (en) and salicylaldehyde (Sal).

The chloromethylated polymer beads were kept in contact with tetrahydrofuran (THF), in a three necked 500 ml round bottomed flask fitted with a condenser and an addition funnel. The amount of the polymer, THF and ethylenediamine used for the reaction are as follows:

Table 2.1 : Amount of polymer, solvent and ligand taken for the preparation of polymer-bound ethylenediamine

Cross-linking (% DVB)	Polymer (gm)	THF (ml)	Ethylenediamine (ml)
2	25	117	8.4
8	25	117	8.4
14	25	117	8.4

Ethylenediamine was added dropwise in the reaction vessel over a period of 15 min. The reaction was kept at room temperature for 48 hours with occasional stirring (7) The beads were finally washed with deionized water, methanol and dry dioxane and dried at 60°C for 10 hours. Elemental analyses were carried out for C, H and N. The results are given in Tables 3.3 and 3.4 (Chapter 3).

The above polymer beads were kept in contact with sufficient amount of benzene to make a slurry in a round bottom flask fitted with a condenser and addition funnel and finally an excess amount of salicylaldehyde was added (8). The amount of the polymer, benzene and salicylaldehyde taken for the reaction are as follows:

Table 2.2 Amount of polymer, solvent and ligand taken for the preparation of polymer-bound salen

Cross-linking (% DVB)	Polymer (gm)	Benzene (ml)	Salicylaldehyde (ml)
2	15	110	08
8	23	175	10
14	23	175	10

The slurry was refluxed for 6 hours and water of condensation was removed in a dean-stark trap. Resin was cooled, soxhlet extracted with ethanol and finally dried at ~80°C for 6 hours. The no. of moles of ligand bound to polymer beads were calculated from the results of microanalysis. The results were further confirmed by estimating chloride ions present as unreacted chloromethyl group on the polymer support.

2.2.2 Introduction of ethylenediaminetetraacetic acid (EDTA) onto the polymer support.

Chloromethylated polymer beads were kept in contact with freshly prepared EDTA solution prepared in 1:1 water-dioxane mixture with a little pyridine to enhance the reactivity at room temperature with ocassional heating. The amounts of polymer, dioxane, deionized water and EDTA taken for the reaction are as follows:

Table 2.3 Amount of polymer, solvents and ligand taken for the preparation of polymer-bound EDTA

Cross-linking (%DVB)	Polymer (gm)	Dioxane (ml)	Deionized water (ml)	EDTA (gm)
8	10	500	500	0.25
14	10	500	500	0.25

The beads were filtered, washed with aq. dioxane, dry dioxane and deionized water and finally dried in vacuum for 6 hours.

2.3 Introduction of the metal ions

A fixed quantity of liganded polymer beads was kept in contact with a constant volume of ethanol for 30 minutes for swelling purpose in a round bottom flask. A solution of metal ions, $RuCl_3.3H_20$ and $PdCl_2$ (Lobachemie, Bombay) prepared in minimum quantity of ethanol taken in an addition funnel, fitted to the reaction vessel was added over a period of 30 minutes. However, the total volume of solution was maintained as shown in Tables 2.4 and 2.5. The reaction was kept at room temperature with occasional stirring for 7 days. A change in colour of the supernatent liquid from dark orange to light orange and that of the polymer beads from yellow to dark grey (light brown in case of EDTA loaded polymers) in case of ruthenium and yellow to golden yellow in case of palladium was indicative of the formation of metal complex on the surface of the polymer.

The amount of polymer beads, the quantity of the metal chloride taken, the volume of ethanol and time of reaction are given separately for both the catalysts in Tables 2.4 and 2.5.

Table 2.4 Preparation of Ruthenium complex catalyst

Polymer type*	Support (gm)	Ethanol (ml)	$RuCl_3.3H_2O$ (gm)	Time (days)
2PSalen	15	250	0.3	7
8PSalen	20	300	0.3	7
8PEDTA	15	250	0.3	7
14PSalen	20	300	0.3	7

Table 2.5 Preparation of palladium complex catalyst

Polymer type*	Support (gm)	Ethanol (ml)	$PdCl_2$ (gm)	Time (days)
2PSalen	15	250	0.5	7
8PSalen	20	300	0.5	7
8PEDTA	15	250	0.5	7
14PSalen	20	300	0.5	7
14PEDTA	15	250	0.5	7

* Nomenclature : NPSalen, NPEDTA

Where N = % cross-link

P = Copolymer P(S-DVB)

Salen = Schiffbase Salicylaldehyde-ethylenediamine

EDTA = ethylenediaminetetraacetic acid

2.3.1 Estimation of metal content of the catalysts

The metal content of the synthesised catalysts was estimated by refluxing a known amount of each catalyst with conc. HCl (AR) for 24 hours and then determining the metal ion concentration by spectrophotometric method. In a typical procedure, 0.2 gm of the catalyst was refluxed with 10 ml conc HCl (AR) and finally it was kept for 24 hours It was filtered and washed thoroughly. All the washings collected were heated on a water-bath to increase the concentration by minimising the volume of the solution and pH was adjusted to 1.8. The concentration of the Ru content was determined at 510 nm using 5-Nitroso-2,4,6-triaminopyrimidine by the use of Shimadzu UV-visible spectrophotometer (9). In case of Pd(II) ions, the concentration was measured at 490 nm using 1-Nitroso-2-napthol-3,6-disulphonic acid as metal indicator (10).

2.4 Nomenclature

The catalysts thus synthesised were named as NPML

where N = Percent cross-link
P = Copolymer of styrene-divinylbenzene
M = Metal i.e. Ru or Pd
L = Ligand i.e. Salen or EDTA

Let us define

Catalyst A = 2PRu(III)Salen
Catalyst B = 2PPd(II)Salen
Catalyst C = 8PRu(III)Salen
Catalyst D = 8PPd(II) Salen
Catalyst E = 14PRu(III)Salen
Catalyst F = 14PPd(II)Salen
Catalyst G = 8PPd(II)EDTA
Catalyst H = 8PRu(III)EDTA
Catalyst I = 14PPd(II)EDTA

2.5 Synthesis of homogeneous complexes

Homogeneous counterparts of synthesised catalysts were prepared to compare the catalytic activity of two systems (i.e. heterogenized homogeneous and homogeneous systems) for reactions studied.

2.5.1 Preparation of [Ru(III)Salen Cl]

Because of difficulties in separating out Ru-schiffbase complex, it was decided to prepare the same in solution. An equimolar solution (0.01M) of $RuCl_3$ and Salen in methanol were mixed in 1:1 to study the kinetics of catalytic reactions in solution.

2.5.2 Synthesis of [Pd(II)Salen]

6 ml freshly distilled ethylenediamine and 24.4 ml salicylaldehyde were mixed using benzene as a solvent in a round bottom flask. Stirring was continued for 30 minutes to allow the formation of schiffbase salicylaldehyde-ethylenediamine (Salen), shining yellow product obtained was filtered and dried at 50°C.

10 ml ethanolic solution of salen (0.5% w/v) was taken in a round bottom flask and 10 ml ethanolic solution $PdCl_2$(0.5% w/v) was added dropwise using an addition funnel Reaction was continued for 6 hours at room temperature with constant stirring. Dark yellow product obtained was separated out and dried at 50°C for 6 hours Elemental analysis of the product was carried out and the percentage of C, H, N and Cl was found to be 47.83, 5.65, 13.02 and 22.80 respectively.

The complex is sparingly soluble in water and insoluble in common solvents. It was therefore planned to synthesise [Pd(II) Salen] complex catalyst in solution. An equimolar solution (0.01 M) of $PdCl_2$ and Salen in methanol were mixed in 1:1 to study the kinetics of catalytic reactions in solution.

2.6 Physico-chemical properties of the catalysts

2.6.1 Apparent bulk density (Abd)

The Apparent bulk density refers to the mass of catalyst which packs into a specified and relatively large volume. The Abd depends on the efficiency with which a working catalyst such as grains, tablets or beads pack in a space. Abd is easily evaluated by the ratio of its weight and the direct measurement of volume of thoroughly dried catalyst in a standard graduated measuring cylinder as given below:

$$d(\text{Abd}) = \frac{\text{Weight of the catalyst}}{\text{Volume of the catalyst bed}}$$

$$= \text{g ml}^{-1}$$

In a typical experiment, a known weight of thoroughly dried polymer supported catalyst was taken in a 10 ml graduated corning measuring cylinder and the volume of the catalyst bed was measured when it remained constant after tapping. The experiment was repeated for five different weights and the mean was taken as Abd. By following careful packing technique, a remarkably reproducible result was obtained.

For catalyst using rigid supports, Abd 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 catalysts for which volume of catalyst bed changes when it comes in contact with the solvent due to swelling. Knowledge of Abd is required to determine surface area and pore volume of the polymer-bound catalyst by BET method.

2.6.2 Surface area and Pore volume measurements

The surface area and pore volume of all the polymer supports and catalysts were measured using Carlo-Erba strumentzione 1800, Model So-19, Italy. The sample was dried at ~85°C under vacuum and nitrogen gas was used as adsorbate at liquid nitrogen temperature (-196°C). The calculation of surface area and pore volume was based on BET equation [3].

2.6.3 Moisture content of the catalysts

The synthesised catalysts were dried in an oven at 70±1°C to a constant weight and the moisture content was calculated as follows:

% Moisture = A-B/A x 100

where A = Weight of the catalyst before drying

B = Weight of the catalyst after drying

Five different weights of catalysts were heated at a time and moisture content was calculated and the mean value was considered.

2.6.4 Chemical composition

Elemental analyses of C and H of all the catalysts were carried out at different stages of preparation using Coleman analyser. Percentage of nitrogen was estimated by Duma's method (11). The estimation of chlorine content and the metal ions present in the catalyst has already been described in the same chapter.

2.6.5 Swelling studies

Swelling behaviour of polymer supports as well as synthesised catalysts in different polar and non-polar solvents was studied. In a typical experiment, a known quantity of the catalyst (0.5 gm) was taken in a 10 ml 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 centifuged for 15 minutes at 1200 rpm. The tube was weighed immediately and then dried overnight at 100°C to a constant weight. The mole percent of swelling was calculated using following equation

$$\underset{\text{(mol \%)}}{\text{Swelling (s)}} = \frac{A - B}{W \times M} \times 100$$

where A = Weight of the catalyst after centrifugation

B = Weight of the catalyst after drying

W = Weight of the catalyst taken for study.

M = Molecular weight of the solvent under study.

2.7 Spectral Characterization

IR spectra of the polymer-bound catalysts were recorded in the range of 250-4000 cm^{-1} using KBr pellets and in some cases, Nujolmul, on a Perkin Elmer 883 spectrophotometer

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

The Electron spin magnetic resonance (ESR) spectra was scanned on a Beaker ESP-300, X-band spectrometer using a 100 kHz field modulation. ESR experiments were conducted on powdered samples at 298 K in N_2 atmosphere.

Electron spectroscopy for chemical analysis (ESCA) spectra were recorded on physical electronics Phi-5400, USA with MgK_α as the radiation source.

2.8 Morphology of the catalysts

Morphology of the supports and the catalysts were studied using Jeol JSM T-300 Scanning Electron Microscope. For scanning micrographs, catalysts were sprayed on a double adhesive tape mounted on a brass stud and were coated with gold.

2.9 Thermal analysis

Thermal stability of polymer supports and catalysts was studied in the range of 30-600°C by thermogravimetric analysis (TGA) on a Shimadzu DT-30 (Japan) using alpha-alumina as a reference, keeping the heating rate at 10°C per minute in N_2 atmosphere. The flow of nitrogen gas was kept at 50 ml min^{-1} throughout the experiment.

2.10 Kinetics of catalytic reactions

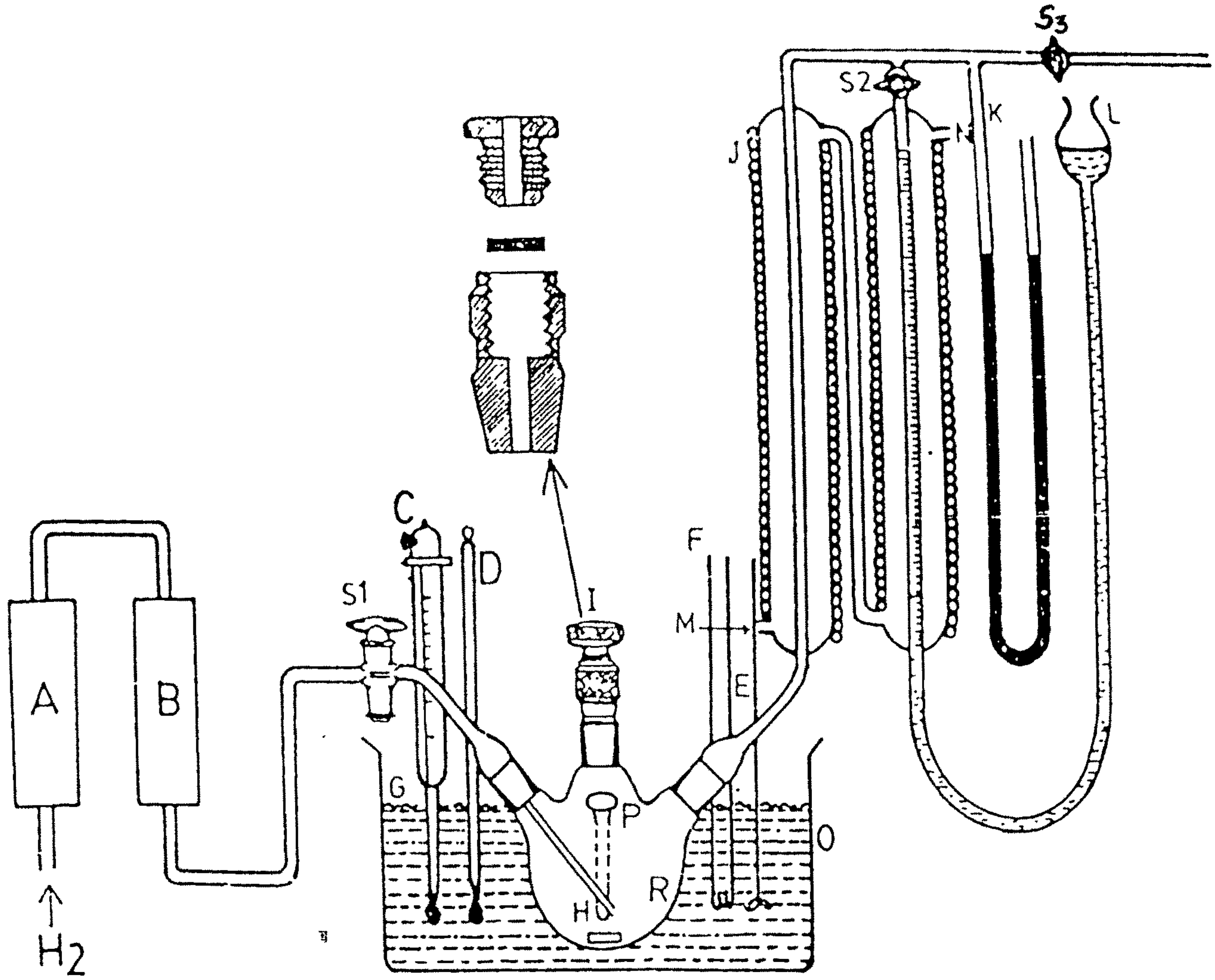
Kinetics of model reactions were studied by varying different parameters under mild conditions.

2.10.1 Experimental procedure

The investigation of kinetics of hydrogenation of 1-hexene/styrene as well as oxidation of benzyl alcohol was carried out at atmospheric pressure in a magnetically stirred three necked glass reactor using methanol as a solvent. The experimental set-up is shown in fig.2.1. Freshly distilled methanol, passed through activated alumina to remove traces of impurities (if any) and saturated with hydrogen/oxygen at the reaction temperature, was taken in the reaction vessel and a known quantity of thoroughly 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. Stopcock S_3 was then closed. The reaction vessel was then flushed with H_2/O_2 gas by opening S_1. Sufficient amount of H_2/O_2 was stored in the gas burette by carefully opening S_2. The temperature of the system was maintained constant (error ± 0.1°C). The system was allowed to equilibriate. After equilibrium, a known amount of the substrate (1-hexene/styrene in case of hydrogenation and benzyl alcohol in case of oxidation) was injected in to the reaction vessel through the injection port (I) using a hypodermic syringe. The progress of the reaction was followed by adjusting the level of reservoir (L) at various intervals of time and measuring the hydrogen/oxygen uptake. Necessary corrections were applied for solvent vapour pressure. Initial rate was calculated from the tangent of the plot of H_2/O_2 uptake against time.

2.10.2 Kinetics of catalytic hydrogenation/oxidation reactions

Kinetics of hydrogenation of 1-hexene/styrene was studied at atmospheric pressure by measuring hydrogen uptake from the gas burette at various interval of time. The rate of the hydrogenation was calculated from the slope of the tangent of the plot of hydrogen uptake against time. Influence of various parameters such as concentration of



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) Asbestus rope K) Manometer L) Liquid reservoir
M) H_2O from thermostat N) H_2O to thermostat O) China clay vessel P) Thermowell R) Reaction vessel
S1, S2, S3 - Quick fit stop cocks

Fig. 2.1 Hydrogenation/oxidation Apparatus substrate as well as catalyst, temperature and nature of the solvent on the rate of reaction was investigated. The recycling efficiency of the catalysts was studied in order to check the stability of the catalysts. The catalysts were also tested for the oxidation of benzyl alcohol to benzaldehyde at atmospheric pressure by varying parameters such as temperature of the system, concentration of the catalyst and the substrate and nature of solvent.

The products were analysed for both the reactions by Gas Chromatograph using Carbowax column and flame ionization detector. No side product was obtained for both the reactions i.e. for hydrogenation of 1-hexene to n-hexane, styrene to ethylbenzene as well as for oxidation of benzyl alcohol to benzaldehyde as observed by G.C.analysis. The Gas chromatograms are given in figs 2.2 to 2.4.

2.11 Stability test of catalysts under repeated catalytic cycles

Stability of polymer-bound catalysts was studied under repeated catalytic cycles for hydrogenation and oxidation reactions. The catalyst once taken was reused for a number of cycles and rate was measured each time. The experiment was carried out at 35°C by injecting a known amount of substrate (i.e. 20 µl) at 60 minutes intervals. The rate of hydrogenation/oxidation was measured as a function of time in each cycle. The reaction was continued till decrease in rate was observed.

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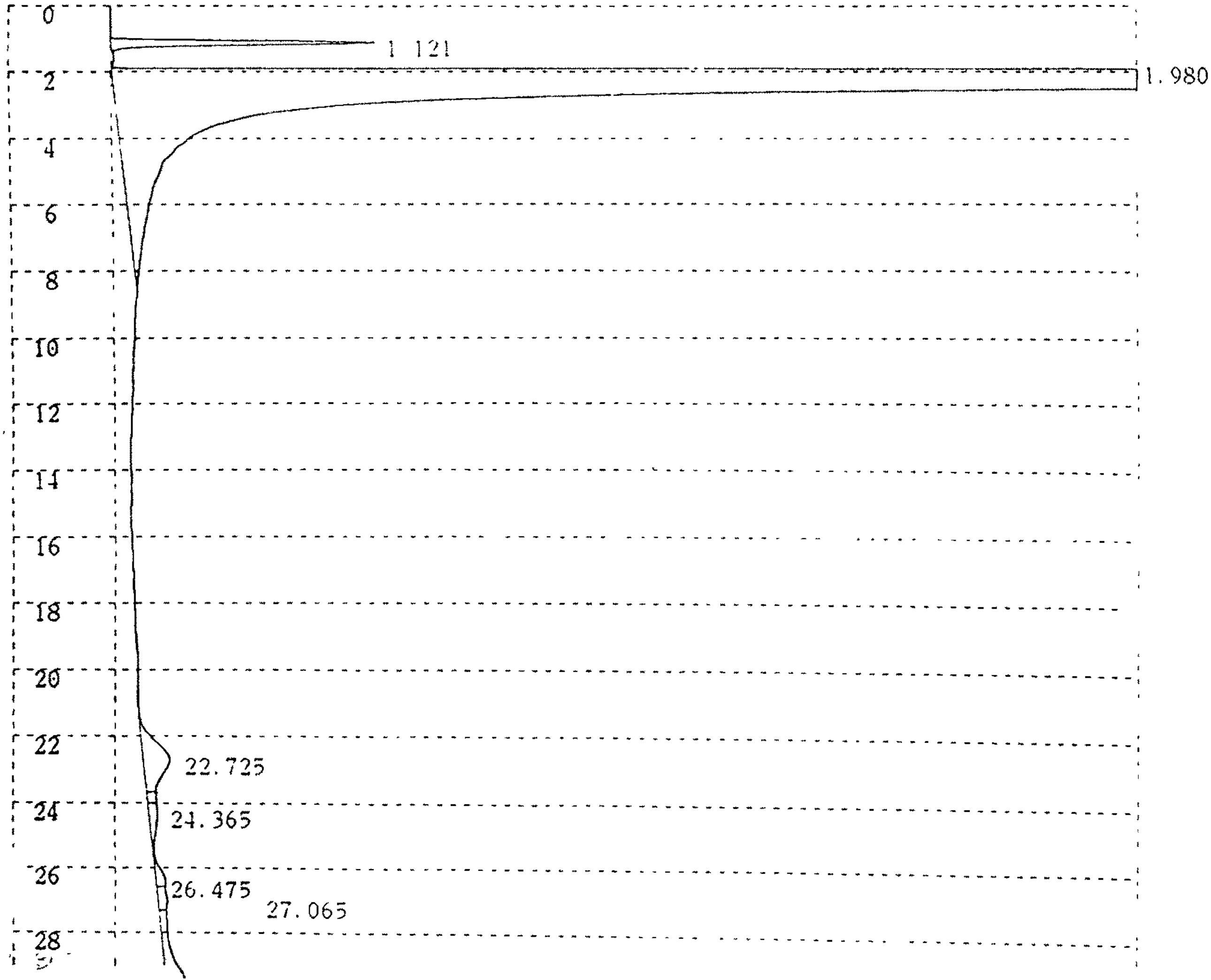
C-R4A CHROMATOPAC    CH=2    REPORT No =5    CHROMATOGRAM=1.@CHRM2.C00     98/06 18   18:13:03

Analysis File . 1:@FILER

15 %CW       2MTS.   80----2-4-16-----200 .   INJ DET---220 DEG
SAMPLE-EPO/111                     TEMP  --50 DEGREES
REACTION TIME --  24 HOURS         ANALYSED ON--SHIMADZU  7A  G C OLD
```



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**  Report ** Ch2                 98/06/18 18:13:03
PKNO  TIME         AREA    HEIGHT  MK  IDNO        Conc         NAME
   2   1.121      38234     4079                  0.6558
   3   1.98     5702876   326831                 97.8141
   4  22.725      28867      397                  0.4951
   5  24.365       9284      119   V              0.1592
   6  26.475       4582      123   V              0.0786
   7  27.065       5194      128   V              0.0891
   8  29.365      19957      256   V              0.3423
   9  29.875      11893      273   V              0.204
  10  31.196       9436      153   V              0.1618

     TOTAL      5830321   332359              100
```

Fig. 2.2 Gas Chromatogram of 1-hexene hydrogenated products

```
C-R4A CHROMATOPAC    CH=2    REPORT No.=4    CHROMATOGRAM=1:@CHRM2.C00     98 01 29  20:08:11

Analysis File : 1:@FILER.

15 %CW       2MTS.  80----2-4-16-----200 .   INJ DET-- 220 DEG
SAMPLE                                          TEMP  -  50 DEGREES
REACTION TIME -- 24  HOURS      ANALYSED ON --SHIMADZU 7A
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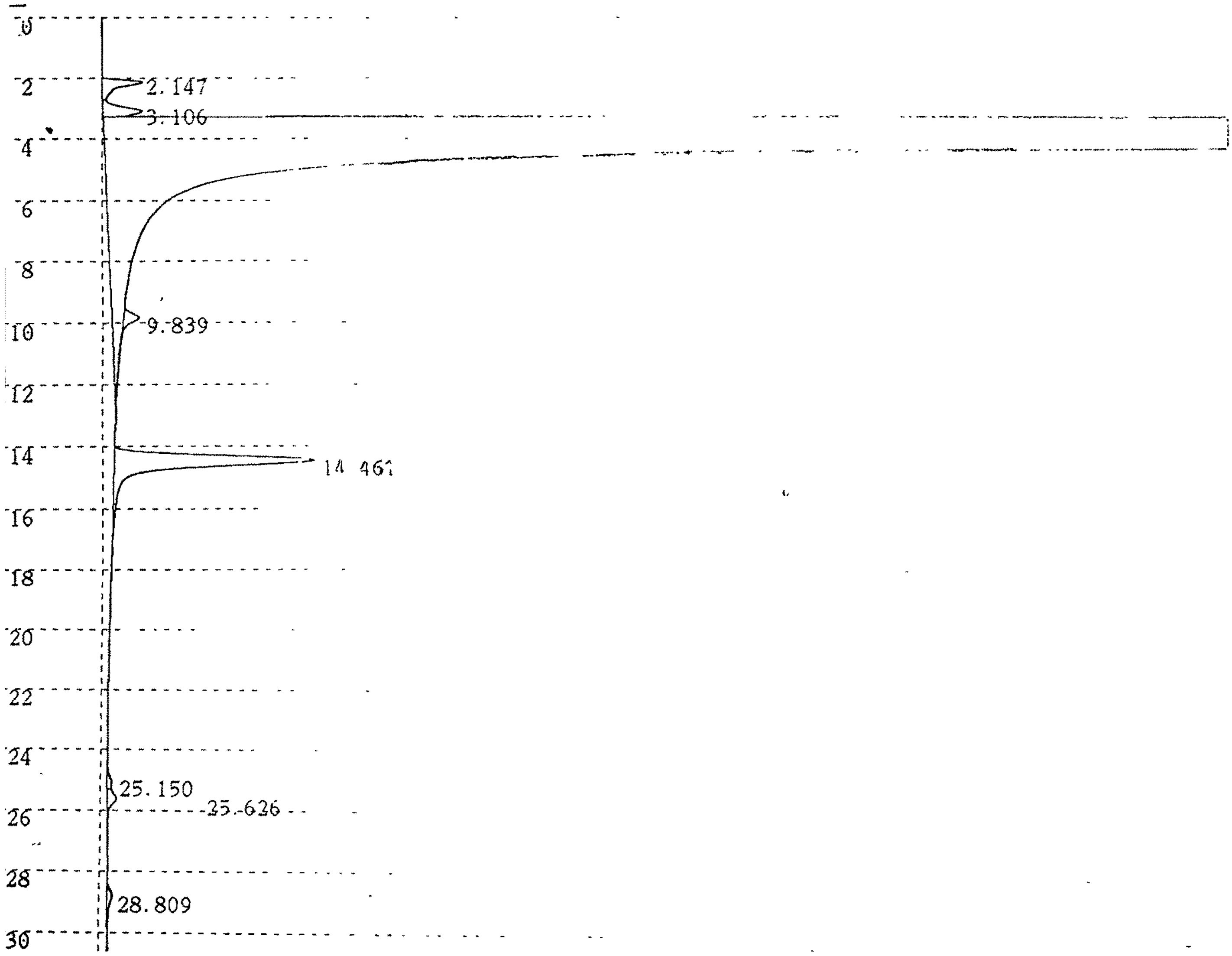

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**  Report ** Ch2              98/01/29 20:08:11
PKNO   TIME          AREA      HEIGHT  MK  IDNO       Conc            NAME
   1   2.147          9744       569                  0.111
   2   3.106         10333       554  V               0.1177
   3   3.42        8670220    373925 SV              98.7517
   4   9.839          4867       222 T                0.0554
   5  14.461         75162      2844                  0.8561
   6  25.15           1614        64                  0.0184
   7  25.626          3743       128  V               0.0426
   9  28.809          2395        71                  0.0273
  13  37.248          1744        31                  0.0199

                   8779820    378408                100
```

Fig. 2.3 Gas Chromatogram of styrene hydrogenated products

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C-R4A CHROMATOPAC   CH=2   REPORT

Analysis File : 1:@FILER.

.15 %CW      2MTS,  80----
SAMPLE==
REACTION TIME -- 24  HOURS
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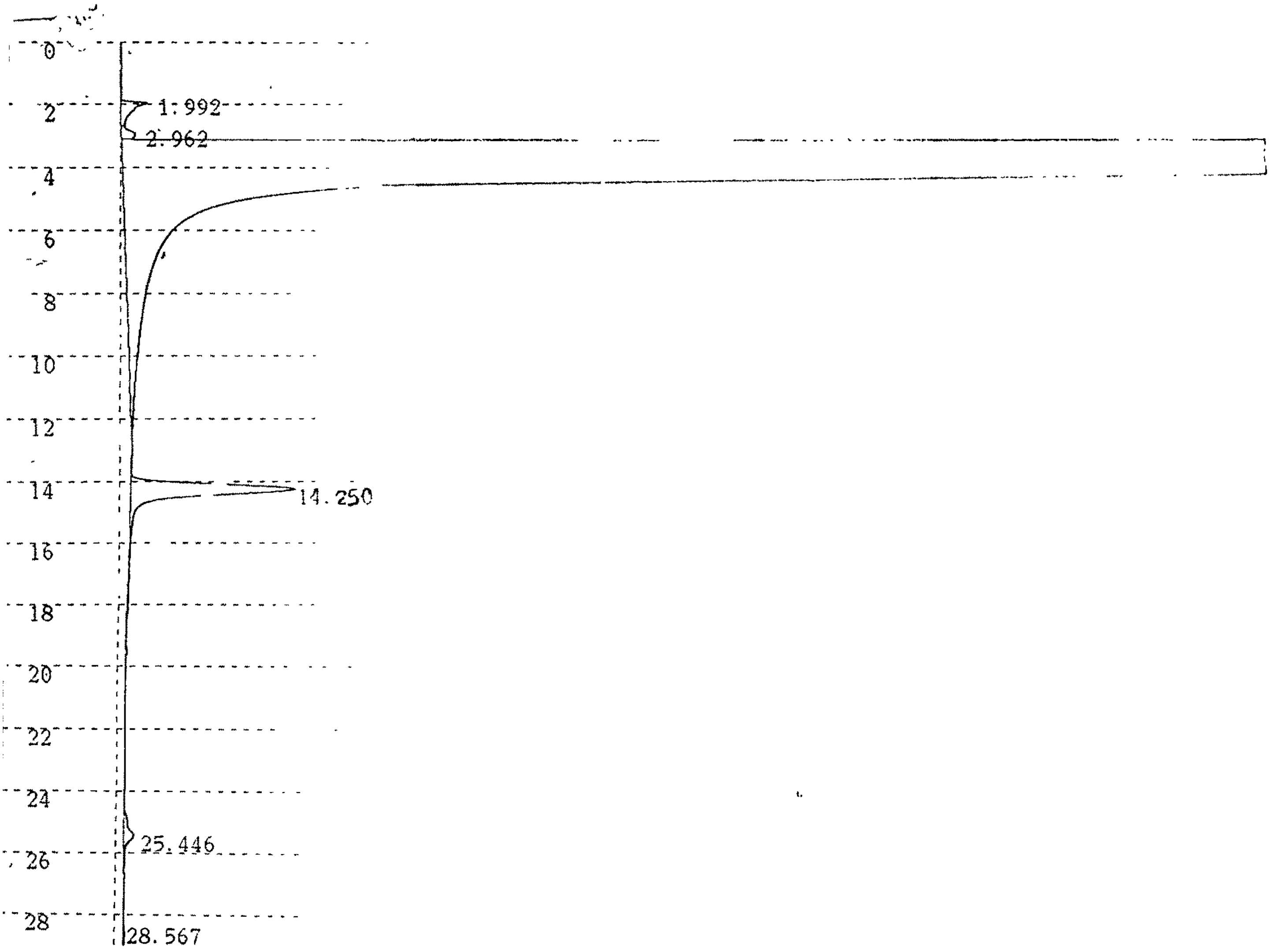

Fig. 2.4 Gas Chromatogram of Benzyl alcohol oxygenated products

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