CHAPTER II

EXPERIMENTAL

CHAPTER 2 : EXPERIMENTAL

Experimental

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 and should be protected in the form of patents(2). Catalyst preparation is frequently described as an art(3). Proper catalyst characterization often enables to correlate catalytic behavior 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.

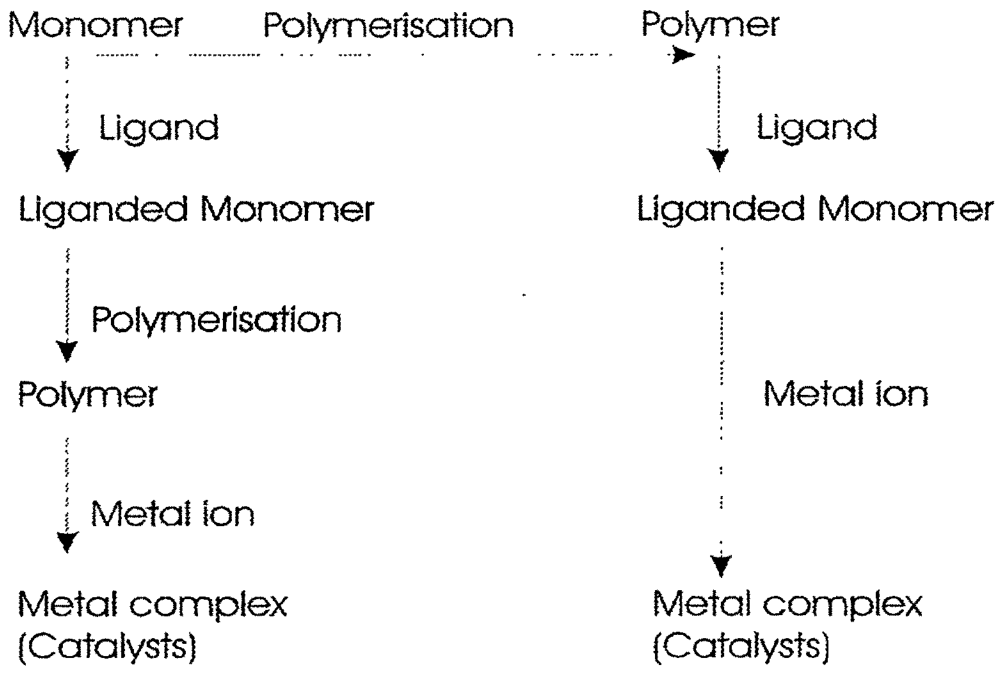
Heterogenized homogeneous catalysts consists of two parts:

1. Solid support
2. The transition metal complexes which are attached to the support by covalent bonding and the stability of the catalyst depend upon the stability of the oxides. However, only surface metals are found to be active and there is a problem of leaching of metal ions from the surface. On the other hand the organic polymer especially styrene-divinyl benzene was found to be a suitable support because of its wide variety of the properties such as surface area, pore size and controllability.

The transition metal complexes could be attached to a polymer support either first by attaching the ligand and then the metal ions or by a reaction with metal complexes synthesised separately.

The characterization of the catalyst were carried out using various techniques such as chemical analysis, surface area measurement by BET method at liquid nitrogen temperature, evaluation of moisture content and bulk density as also swelling properties were studied using different solvents.

A schematic representation is given here for synthesis of the polymer supported catalysts.



The other spectroscopic techniques such as UV-Visible reflectance, far infra red (IR), and electron spin resonance (ESR) have also been used to describe morphology of the polymer supports and the supported catalysts was studied using scanning electron microscope(SEM). The thermal stability of the catalysts was tested by thermogravimetric analysis(TGA).

The experimental set up and the procedure to carry out the kinetics of oxidation of toluene was investigated by varying different parameters such as temperature of the system, concentration of the catalysts and substrate and the nature of the solvent. The stability of the catalyst has been seen by investigating the life cycle of the catalyst.

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.(3) The chloromethylated beads (kindly gifted by Ion Exchange (India) Ltd.) of styrene-divinylbenzene were washed and purified by soxhlet extraction.(4) The chlorine content was estimated in chloromethylated polymer beads by gravimetric analysis(5) in order to see the extent of chloromethylation. For this, a known amount of polymer (0.1gm) 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 content was extracted with deionized water, filtered in 100ml volumetric flask and finally diluted with deionized water. A known volume of the filtrate was treated with dil.HNO_3 to neutralise the untreated 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.

2.2.1 Introduction of O-phenylenediamine on to the polymer support:

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

Table:

Amount of polymer,solvent and ligand taken for the preparation of polymer bound O-phenylenediamine

Cross-linking (% DVB)	Polymer (g)	THF (ml)	O-phenylenediamine (ml)
6	25	117	9.0
8	25	117	9.0
14	25	117	9.0

The slurry was refluxed for 6 h. and water of condensation was removed in a Dean –Stark trap. Resin was cooled, soxhlet extracted with ethanol and finally dried at ~80^{0}C for 6 h.

The number of moles of ligands 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 Schiff base on to the polymer support:

The chloromethylated polymer beads were kept in contact with tetrahydrofuran (THF) in a three necked 500ml round bottomed flask fitted with a condenser and an addition funnel. p-Phenylenediamine was added drop wise from the funnel in the reaction vessel over a period of 15 mins. The reaction was kept at room temperature for 48 hours with occasional stirring.(6) The beads were finally washed with deionized water, methanol and dry dioxane and dried at 60^{0}C for 10h. The loading of phenylenediamine was confirmed by the elemental analysis of nitrogen.

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 additional funnel and finally an excess amount of salicylaldehyde was added.(7) The amount of polymer, benzene and salicylaldehyde taken for reaction are as follows :

Amount of polymer,solvent and ligand taken for the preparation of polymer bound Schiff base:

Cross linking (%DVB)	Polymer (g)	Benzene (ml)	Salicylaldehyde (ml)
6	10	80	05
8	10	80	05
14	08	80	04

The slurry was refluxed for 6 h. and water of condensation was removed in a Dean-Stark trap. Resin was cooled, soxhlate extracted with ethanol and finally dried at ~80^0c for 6 hours. The number of moles of ligands 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.

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 mins for swelling purpose in a round bottom flask. A solution of metal ions $MnCl_2, 5H_2O$ and $NiCl_2, 5H_2O$ prepared in minimum quantity of ethanol taken in an additional funnel, fitted to the reaction vessel was added over a period of 30 mins. However, the total volume of solution was maintained as shown in table. 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 grey colour was observed. In case of O-phenylenediamine and Schiff based loaded polymers was indicative of the formation of metal complex on the surface of the polymer.

Preparation of manganese complex catalyst

Polymer type	Support (g)	Ethanol(ml)	$MnCl_2, 5H_2O$ (g)	Time (days)
OPDMn (II)	20	150	0.5	7
OPDMn (II)	20	150	0.5	7
PPDMn (II)	20	150	0.5	7
PPDMn (II)	20	150	0.5	7

The polymer beads were filtered and washed thoroughly with ethanol. The anchored catalyst thus synthesized were dried at 70^0C for 24 hours, and stored in vacuum desiccators. The metal content in each catalyst was determined by refluxing a known amount of the catalyst with conc. HCl (AR) for 2 days and then estimating the metal ion concentration by spectrometric method.

2.4 Estimation Of Metal Content Of The Catalysts

The Metal content of the synthesised catalyst was estimated by refluxing a known amount of each catalyst with concentrated 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. at conc. HCl (AR) and then 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 minimizing the volume of solution and pH was adjusted to 1 8 The concentration of Mn (II) content was determined at 510 nm using sodium bismuthate in a shimadzu UV-visible spectrophotometer. In the case of Ni (II) ions, the concentration was measured using dimethylglyoxime as metal indicator[6] at 490 nm wavelength.

2.5 Nomenclature

The catalysts thus synthesised were named as NPLM

where

N = Percent Cross Link

P = Co-polymer of styrenedivinyl benzene

L = Ligand i.e. O-phenylenediamine (Op) and (Schiff base of p-phenylene diamine pp)

M = Metal

OPDA = O-phenylenediamine

PPDA = p-phenylenediamine Schiff base

Let us define,

Catalyst A = 6 OPDA Mn (II)

Catalyst B = 6 OPDA Ni (II)

Catalyst C = 6 PPDA Mn (II)

Catalyst D = 6 PPDA Ni (II)

Catalyst E = 8 OPDA Mn (II)

Catalyst F = 8 OPDA Ni (II)

Catalyst G = 8 PPDA Mn (II)

Catalyst H = 8 PPDA Ni (II)

Catalyst I = 14 OPDA Mn (II)

Catalyst J = 14 OPDA Ni (II)

Catalyst K = 14 PPDA Mn (II)

Catalyst L = 14 PPDA Ni (II)

2.6 Synthesis of unbound complexes

In order to study the catalytic activity in homogeneous system unbound complexes of Mn(II) and Ni(II) with o-phenylenediamine and p-phenylenediamine (schiff base) were synthesized. The catalytic activity of these catalysts was seen under the similar condition at which the polymer supported catalysts were studied.

$MnCl_2$, $5H_2O$ (2 moles) was dissolved in a fixed quantity of ethanol placed in a round bottom flask and O-phenylenediamine dissolved in a fixed quantity of ethanol was added drop wise by using additional funnel. Manganese and O-phenylene diamine ratio was maintained as 1:1. The reaction was carried out at room temperature with constant stirring for 5h. The complex thus formed was filtered, washed repeatedly with distilled alcohol and dried at 70^0C and the metal content was estimated by spectrophotometric method. The method for estimation is already described earlier. This complex was used to investigate the catalytic activity for the reaction under study.

Synthesis of unbound Nickel complex

The method followed was same as in the case of manganese complex. The mole ratio of nickel and o-phenylenediamine was maintained as 1:1. The complex thus obtained was filtered, washed with distilled alcohol and metal content was estimated.

2.7 Physico-Chemical properties of the Catalysts

2.8 Apparent Bulk Density d(Abd)

Apparent bulk density is an important practical parameter because it indicates the mass of catalyst which will pack in to a reactor of specified volume. It depends on the efficiency with which a working catalysts such as grains, tablets or beads pack in space. It can be 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.

$$d(Abd) = \frac{\text{weight of the catalyst}}{\text{volume of catalyst bed}} \quad gml^{-1}$$

The experiment was carried out by 1.0g of dried polymer bound catalyst, which was taken in a graduated corning measuring cylinder of capacity 10 ml and the volume was measured when it remained constant after tapping The experiment was repeated for five different weights and the mean was taken as apparent bulk density. It is an important factor in the case of rigid supports but it is of little importance where the volume of catalyst bed changes when it comes in contact with the reactants / solvents.

2.9 Moisture content of the catalyst

In order to determine the moisture content, the catalysts were dried in an oven at 70^0C to a constant weight .Five different weights of catalysts were heated at a time and from the average of the five, the percentage of moisture content was calculated by the use of following equation.

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

Where A= weight of the catalyst before drying

B= weight of the catalyst after drying.

2.10 Swelling studies

A fixed quantity of the catalyst (0.5g) was taken in a glass filter tube and immersed in the solvent under study for 30 mins at room temperature.The tube was then inserted into a15ml centrifuge tube for fifteen minutes at 1200 rpm. The tube was weighed immediately and dried for overnight at 100^{0}C to a constant weight. The mole percent of swelling was calculated by the use of the following equations.

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

Where A= weight of the catalyst after centrifugation

B= weight of catalyst after drying

W=weight of the catalyst taken for study.

M=molecular weight of the solvent under study.

2.11 Spectral characterization:

UV-Vis reflectance spectra of the solid catalyst 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 a solution with 1 cm matched quartz cells using methanol as the reference solvent.

The IR spectra of the polymer bound catalyst were recorded in the range of 200-4000 cm^{-1} using KBr pellets on a Perkin Elmer 883 spectrometer.

Scanning electron micrographs (SEM) were done at IIT, Bombay. In order to study the SEM the catalysts were sprayed on a double adhesive tape mounted on a brass stud and were coated with gold.

2.12 Thermal Analysis

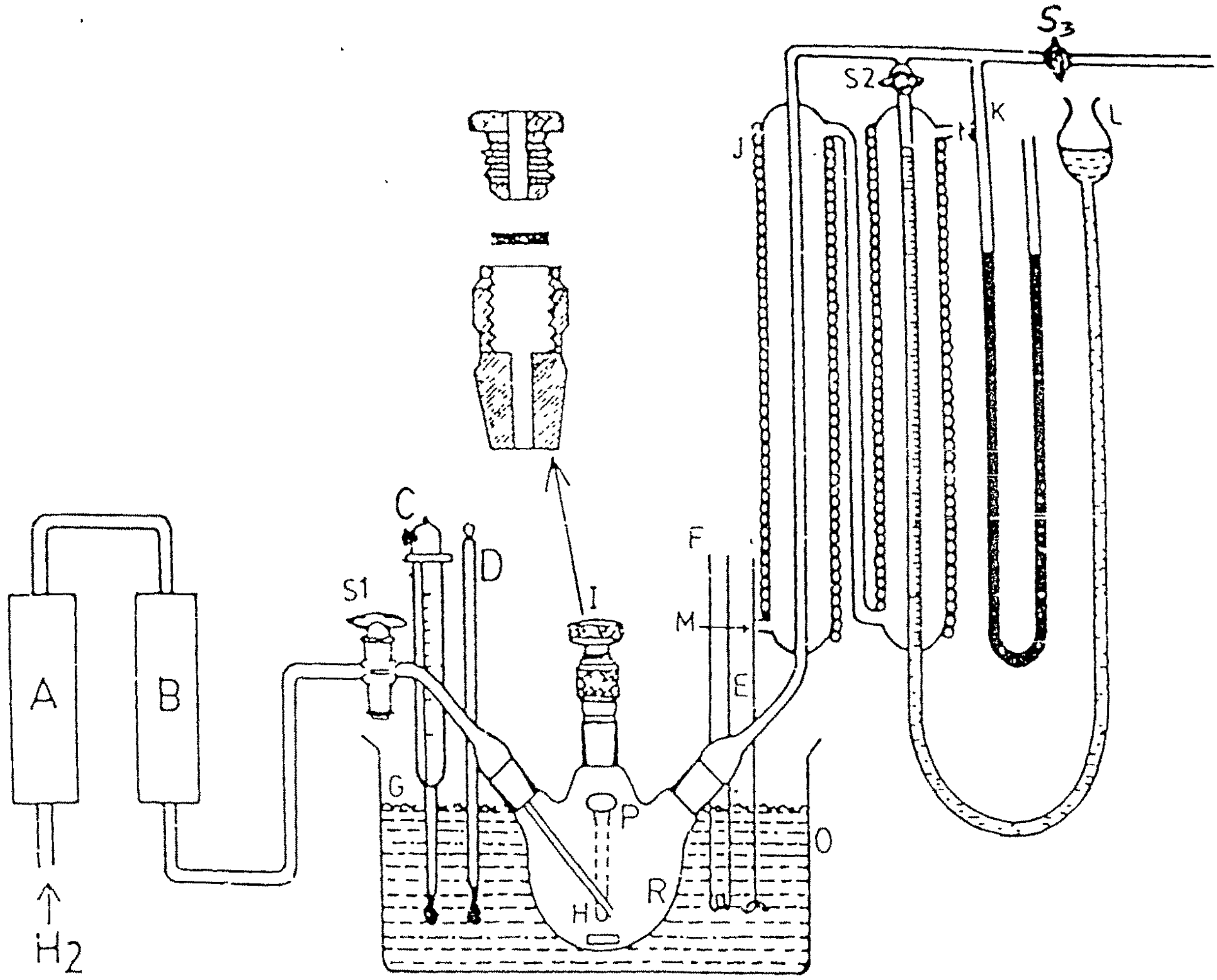
Thermal analysis (stability) and phase changed were studied in the range of 30 to 500^{0}C by thermogravimetry (TG) and differential thermal analysis (DTA) on Shimadzu-DT -30 (Japan) using alpha alumina as the reference. Sample weight was recorded by programming the temperature upto 500^{0}C at a rate of 10^{0}C per minute in nitrogen atmosphere

2.13 Kinetics of oxidation reaction

The oxidation of toluene was carried out using molecular oxygen. The apparatus used for oxidation reaction is shown in the diagram. The kinetics of oxidation reaction was carried out at atmospheric pressure in a magnetically stirred three necked semi batch glass reactor using methanol as reaction medium. A known amount of the catalyst with methanol (freshly distilled, passed through activated alumina and saturated with oxygen at the reaction temperature) was kept in the reaction vessel. The air in the system was removed by applying vacuum, opening the stopcock S3 and closing the stopcock S_1 and S_2 $_2$. The reaction vessel was flushed with O_2 gas 2 to 3 times by opening stopcock S_1. The air in the gas burettee was removed by raising the paraffin reservoir (L) to the maximum before evacuation. Adequate amount of oxygen gas was stored in the burettee by carefully opening the stopcock S_2, when there was a positive pressure in the mercury manometer (K) keeping S_3 closed. By passing molecular oxygen, the system was made saturated at the reaction temperature by starting the magnetic stirrer (H) keeping stopcocks S_1 & S_2 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 toluene was injected in to the reaction vessel through the injection port(I) using a hypodermic syringe. The arrangement was made in such a way that the temperature of the reactor as well as the injected burette was maintained at 35 ± 0.1^{0}C.

The oxidation reaction was initiated by starting the stirrer. The progress of the reaction at atmospheric pressure was followed by adjusting the level of



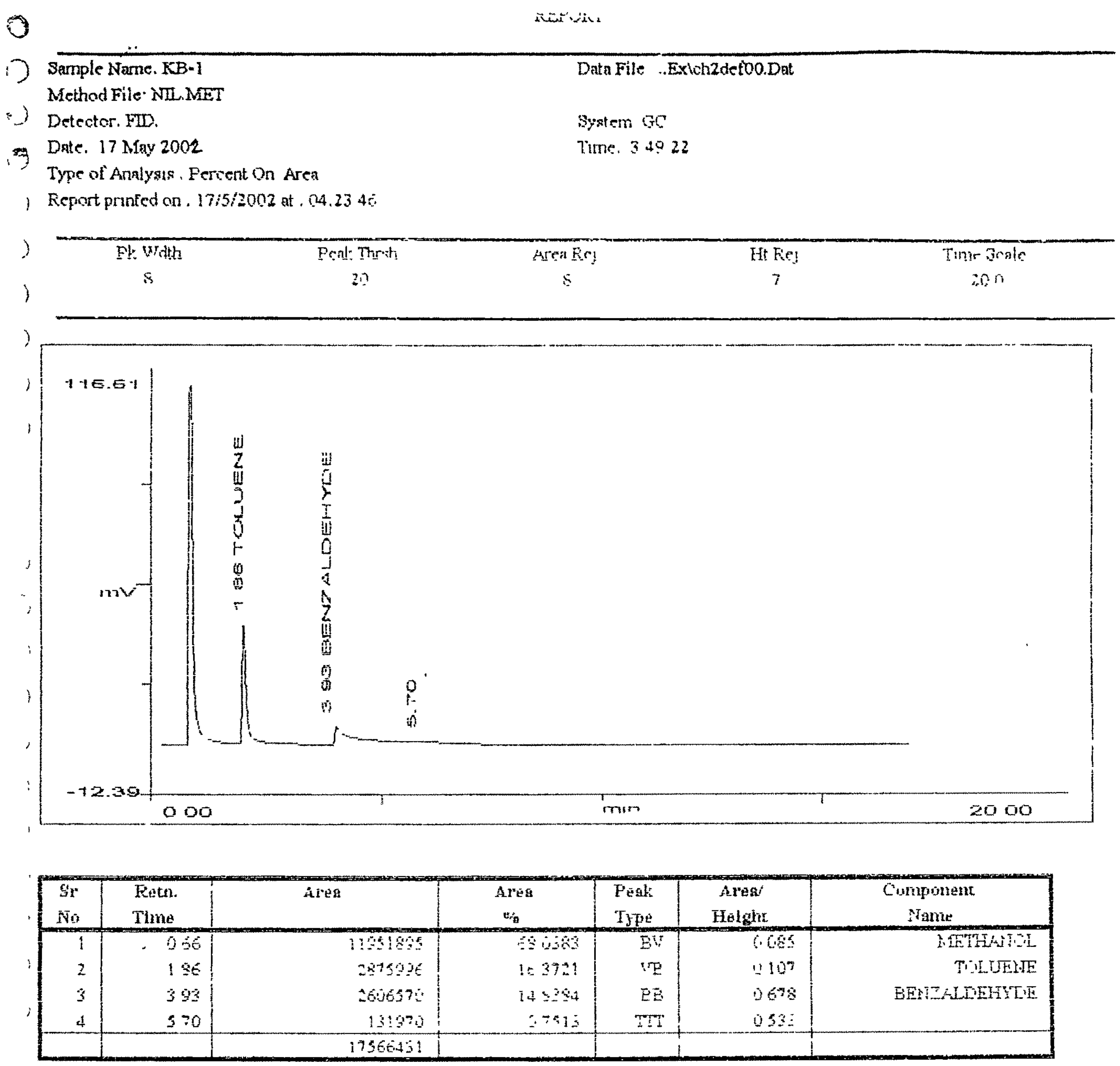
A) Deoxo trap B) Molecular sieve trap C) Contact thermometer D) Thermometer E) Mechanical stirrer F) Heating coil
G) Thermocole H) Magnetic bar I) Injection port J) Asbestus rope K) Manometer L) Liquid reservoir
M) H_2O from thermostat N) H_2O to thermostat O) China clay vessel P) Thermowell R) Reaction vessel
S1, S2, S3 - Quick fit stop cocks

Fig. 2 1 Hydrogenation/oxidation Apparatus reservoir (L) at various intervals of time and measuring the oxygen uptake. The necessary correction were applied for the vapour pressure at the solution for the oxidation of toluene the system was flushed with medicinal grade oxygen gas before injecting the substrate and the progress of oxidation reaction was followed by measuring the oxygen uptake at different intervals of time. The data have been used to determine the rate and also various thermodynamic parameters.

The products were analyzed using gas chromatograph. The chromatographs are given in Fig. 2.2 & 2.3.

2.14 Stability test of Catalysts under repeated Catalytic cycles

Stability at polymer-bound catalysts was studied under repeated catalytic cycles for oxidation reaction. The catalyst once taken was reused for a number of cycles and rate was measured each time. The experiment was carried out at 35^{0}C by injecting a known amount of substrate (i.e. 20 ml.) at 90 minutes intervals. The rate of oxidation was measured as a function of time in each cycle. The reaction was continued till decrease in rate was observed.



REPORT

Sample Name. KB-1
Method File· NIL.MET
Detector. FID.
Date. 17 May 2002
Type of Analysis . Percent On Area
Report prinfed on . 17/5/2002 at . 04.23 46

Data File ..Ex\ch2def00.Dat

System GC
Time. 3 49 22

Pk Wdth	Peak Thrsh	Area Rej	Ht Rej	Time Scale
8	20	8	7	20 0

Sr No	Retn. Time	Area	Area %	Peak Type	Area/ Height	Component Name
1	0 66	11951895	68 0383	BV	0 085	METHANOL
2	1 96	2875996	16 3721	VP	0 107	TOLUENE
3	3 93	2606570	14 8384	PB	0 678	BENZALDEHYDE
4	5 70	131970	0 7513	TTT	0 533	
		17566431				

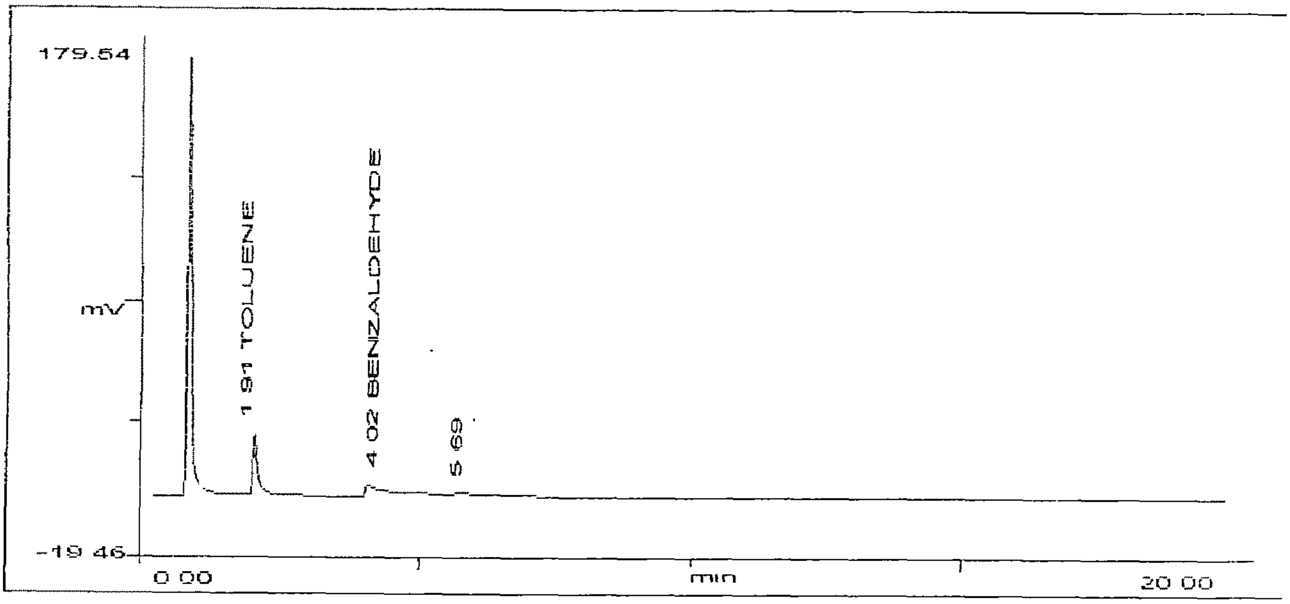
Fig. 2.2 Gas Chromatogram of Toluene Oxygenated Product

Sample Name: KB-2
Method File. .MET
Detector. FID.
Date. 17 May 2002
Type of Analysis . Percent On Area
Report printed on . 17/5/2002 at . 05.12.32

Data File. ch2def00.Dat

System. GC
Time. 5.2.50

Pk.Wdth	Peak Thrsh	Area Rej	Ht.Rej	Time Scale
8	20	8	4	2.0



Sr No	Retn. Time	Area	Area %	Peak Type	Area/ Height	Component Name
1	0.67	10602356	75.5840	BF	0.093	METHANOL
2	1.91	1515988	10.8075	PB	0.093	TOLUENE
3	4.02	1778323	12.6776	BB	0.372	BENZALDEHYDE
4	5.69	130579	0.9309	TTT	0.344	
		14027246				

Fig. 2.3 Gas Chromatogram of Toluene Oxygenated Product

Reference:

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