CHAPTER-2

EXPERIMENTAL
2.2. EXPERIMENTAL

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2.1 Materials

Neat complexes

Synthesis of copper(II) salen (CuSal)

Preparation of Salen:
Salicylaldehyde (24.4 g, 0.2 mol) was mixed with 150 ml of distilled ethanol in a 250 ml round bottom flask, which was stirred on a magnetic stirrer. Ethylenediamine (6 g, 0.1 mol) dissolved in 25 ml of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The contents were refluxed for one hour to get a yellow solid precipitate of salen, which was cooled, filtered, washed with petroleum ether and dried. The salen was then recrystallised from ethanol (yield 25 g). The melting point of the solid was 134°.

Preparation of copper salen:
Copper acetate monohydrate (2 g, 0.01 mol) and salen (2.68 g, 0.01 mol) were dissolved in ethanol separately, mixed and refluxed for five hours. The dark green precipitate of copper salen obtained was washed with hot ethanol, dried and stored in a dessicator. Yield was 2.3 g.

Synthesis of chloro manganese(III)Salen (MnSal)
Manganese acetate tetrahydrate (2.4 g, 0.01 mol) dissolved in ethanol (20 ml) was reacted with an ethanol (20 ml) solution of salen (2.68 g, 0.01 mol) by refluxing for one hour. Lithium chloride (0.635 g, 0.015 mol) was then added to the refluxing solution and the reaction continued for another 0.5 hr. Cooling
the mixture to 0° afforded ClMn (III) salen as dark brown crystals. The crystals were filtered, washed thoroughly with cold water and dried in vacuo. Yield: 2.66 g, (75%).

Synthesis of Copper (II) dichlorosalen (CuCl₂Sal)

Preparation of 5-chlorosalicylaldehyde:
Salicylaldehyde (10 g) was heated on an oil bath at 75° while passing a slow stream of chlorine gas through it for about an hour. The colour of the solid obtained on cooling was white. It was washed and recrystallised using petroleum ether. The m.p. was 100° corresponding to 5-chlorosalicylaldehyde (reported m.p 100°, Welcher).

Preparation of dichlorosalen:
5-Chlorosalicylaldehyde (3.12 g, 0.02 mol)(prepared as described above) was mixed with 150 ml of distilled ethanol in a 250 ml round bottom flask, which was stirred on a magnetic stirrer. Ethylenediamine (0.6 gms, 0.01 mol) dissolved in 25 ml of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The contents were refluxed for one hour to get a yellow solid precipitate of dichlorosalen, which was cooled, filtered, washed with petroleum ether and dried. The dichlorosalen was then recrystallised from ethanol (yield 2.52 g). The melting point of the solid was 150°.

Preparation of copper dichlorosalen:
Copper acetate monohydrate (2 g, 0.01 mol) and dichlorosalen (3.37 g, 0.01 mol) were dissolved in ethanol separately, mixed and refluxed for five hours. The dark green coloured precipitate of copper dichlorosalen obtained was washed with hot ethanol, dried and stored in a dessicator. Yield is 2.8 g.

**Preparation of chloro manganese (III) dichlorosalen (MnCl₂Sal)**

The procedure given previously for MnSalen was followed using dichlorosalen ligand instead of salen. The solid was dark brown in color.

**Synthesis of Copper (II) tetrachlorosalen (CuCl₄Sal)**

Preparation of tetrachlorosalen:

3,5-Dichlorosalicylaldehyde (Aldrich)(3.81 g, 0.02 mol) was mixed with 150 ml of distilled ethanol in a 250 ml round bottom flask, which was stirred on a magnetic stirrer. Ethylenediamine (0.6 g, 0.01 mol) dissolved in 25 ml of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The contents were refluxed for one hour to get a yellow solid precipitate of tetrachlorosalen, which was cooled, filtered, washed with petroleum ether and dried. The tetrachlorosalen was then recrystallised from ethanol (yield 3.03 g). The melting point of the solid was 215 °.

Preparation of copper tetrachlorosalen:

Copper acetate monohydrate (2 g, 0.01 mol) and tetrachlorosalen (4.05 g, 0.01 mol) were dissolved in ethanol separately, mixed and refluxed for five hours. The dark green coloured precipitate of copper tetrachlorosalen obtained was washed with hot ethanol dried and stored in a dessicator. Yield is 3.28 g.
Preparation of chloro manganese (III) tetrachlorosalen (MnCl$_4$Sal)

The procedure given previously for MnSalen was followed using tetrachlorosalen instead of salen as the ligand. The solid was dark brown in color.

Synthesis of Copper(II) dibromosalen (CuBr$_2$Sal)

Preparation of 5-bromosalicylaldehyde:

Bromine (23.97 g, 0.15 mol) in 10 ml CCl$_4$ was added drop by drop to salicylaldehyde (18.3 g, 0.15 mol) in 10 ml CCl$_4$. It was then refluxed for an hour. The solution was diluted with hexane (60 ml) and cooled. The product obtained was a silky white precipitate. When recrystallised from the same solvent, 5 - bromosalicylaldehyde was obtained. The m.p is 105°.

Preparation of dibromosalen:

5-Bromosalicylaldehyde (4.01 g, 0.02 mol) was mixed with 150 ml of distilled ethanol in a 250 ml round bottom flask, which was stirred on a magnetic stirrer. Ethylenediamine (0.6 g, 0.01 mol) dissolved in 25 ml of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The contents were refluxed for one hour to get a yellow solid precipitate of dibromosalen, which was cooled, filtered, washed with petroleum ether and dried. The dibromosalen was then recrystallised from ethanol (yield 3.18 g). The melting point of the solid was 193 °.

Preparation of copper dibromosalen:
Copper acetate monohydrate (2 g, 0.01 mol) and dibromosalen (4.25 g, 0.01 mol) were dissolved in ethanol separately, mixed and refluxed for five hours. The dark green precipitate of copper dibromosalen obtained was washed with hot ethanol dried and stored in a dessicator. Yield was 3.42 g.

*Preparation of chloro manganese (III) dibromosalen (MnBr₂Sal)*

The procedure given previously for MnSal was followed using dibromosalen instead of salen as the ligand. The solid was dark brown in color.

*Synthesis of Copper (II) tetrabromosalen (CuBr₄Sal)*

Preparation of tetrabromosalen:

3,5 Dibromosalicylaldehyde (5.6 g, 0.02 mol) was mixed with 150 ml of distilled ethanol in a 250 ml round bottom flask, which was stirred on a magnetic stirrer. Ethylenediamine (0.6 g, 0.01 mol) dissolved in 25 ml of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The contents were refluxed for one hour to get a yellow solid precipitate of tetrabromosalen, which was cooled, filtered, washed with petroleum ether and dried. The tetrabromosalen was then recrystallised from ethanol (yield 4.02 g).

Preparation of copper tetrabromosalen:

Copper acetate monohydrate (2 g, 0.01 mol) and tetrabromosalen (5.83 g, 0.01 mol) were dissolved in ethanol separately, mixed and refluxed for five hours. The dark green precipitate of copper tetrabromosalen obtained was washed with hot ethanol dried and stored in a dessicator. Yield was 4.84 g.

*Preparation of chloro manganese (III) tetrabromosalen (MnBr₄Sal)*
The procedure given for MnSal was followed using tetrabromosalen instead of salen as the ligand. The solid was dark brown in color.

*Synthesis of Copper (II)dinitrosalen (Cu(NO₂)₂Sal)*

Preparation of 5-nitrosalicylaldehyde:

In a 250 ml flask kept on a magnetic motor stirrer, 20 g of glacial acetic acid and 5 g salicylaldehyde were added. After cooling to 25°, 4 g of 98 % nitric acid were added over a period of 2.5 hrs with stirring. The temperature was kept below 15° during the addition of the nitric acid. After all the nitric acid had been added the temperature was allowed to rise to 45° and kept at that temperature for 2 hrs and then 100 ml water containing 4.5 g of cracked ice was added. The mixture was allowed to stand for 5 hrs. Mixture of 3 - nitro and 5 - nitro isomers (yield 99%) was obtained as a yellow solid. These isomers were dissolved in 3 ml of warm water containing 10 g NaOH. The mixture was allowed to stand for 24 hrs after which the 5 - nitro isomer precipitated out. The m.p. of the 5 - nitrosalicylaldehyde was 126°.

Preparation of dinitrosalen:

5-Nitrosalicylaldehyde (3.34 g, 0.02 mol) was mixed with 150 ml of distilled ethanol in a 250 ml round bottom flask, which was stirred on a magnetic stirrer. Ethylenediamine (0.6 g, 0.01 mol) dissolved in 25 ml of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The contents were refluxed for one hour to get a yellow solid precipitate of nitrosalen, which
was cooled, filtered, washed with petroleum ether and dried. The nitrosalen was then recrystallised from ethanol (yield 2.68 g).

Preparation of copper dinitrosalen:

Copper acetate monohydrate (2 g, 0.01 mol) and nitrosalen (3.58 g, 0.01 mol) were dissolved in ethanol separately, mixed and refluxed for five hours. The dark green precipitate of copper nitrosalen obtained was washed with hot ethanol, dried and stored in a dessicator. Yield was 3.16 g.

Preparation of chloro manganese(III) dinitrosalen (Mn(NO₂)₂Sal)

Manganese acetate tetrahydrate (2.4 g, 0.01 mol) dissolved in ethanol (20 ml) was reacted with an ethanol (20 ml) solution of nitrosalen (3.58 g, 0.01 mol) by refluxing for one hour. Lithium chloride (0.635 g, 0.015 mol) was then added to the refluxing solution and the reaction continued for another 0.5 hr. Cooling the mixture to 0° afforded ClMn (III) dinitrosalen as dark brown crystals. The crystals were filtered, washed thoroughly with cold water and dried in vacuo. Yield: 3.27 g.

Synthesis of chloro manganese(III) saltin complexes (saltin = salicylaldehyde 1,3-propylenediamine) (Mn(III)Saltin)

Preparation of salicylaldehyde 1,3-propylenediamine (saltin):

Salicylaldehyde (4.88 g, 0.02 mol) was mixed with 150 ml of distilled ethanol in a 500 ml round bottom flask, which was stirred on a magnetic stirrer. 1,3-propylenediamine (0.749 g, 0.01 mol) dissolved in 25 ml of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The
contents were refluxed for one hour to get a yellow solid precipitate of saltin, which was cooled, filtered, washed with petroleum ether and dried. The saltin was then recrystallised from ethanol (yield 4.23 g).

The substituted saltins were prepared using substituted salicylaldehyde instead of salicylaldehyde.

Preparation of ClMn (III) saltin:
Manganese acetate tetrahydrate (2.4 g, 0.01 mol) dissolved in ethanol (20 ml) was reacted with an ethanol (20 ml) solution of saltin (2.82 g, 0.01 mol) by refluxing for one hour. Lithium chloride (0.635 g, 0.015 mol) was then added to the refluxing solution and the reaction continued for another 0.5 hr. Cooling the mixture to 0° afforded ClMn (III) saltin as dark brown crystals. The crystals were filtered, washed thoroughly with cold water and dried in vacuo. Yield : 2.17 g.

The substituted Mn saltins were prepared using substituted salicylaldehyde instead of salicylaldehyde.

Synthesis of chloro manganese(III) salophene complexes (salophene = salicylaldehyde 1,2,phenylenediamine)(Mn(III)salophene)

Preparation of salophene:
Salicylaldehyde (4.88 g, 0.02 mol) was mixed with 150 ml of distilled ethanol in a 250 ml round bottom flask, which was stirred on a magnetic stirrer. 1,2-phenylenediamine (0.995 g, 0.01 mol) dissolved in 25 ml of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The
contents were refluxed for one hour to get a yellow solid precipitate of salophene, which was cooled, filtered, washed with petroleum ether and dried. The salophene was then recrystallised from ethanol (yield 5.14 g).

The substituted salophenes were prepared using substituted salicylaldehyde instead of salicylaldehyde.

Preparation of Cl Mn (III) salophene:

Manganese acetate tetrahydrate (2.4 g, 0.01 mol) dissolved in ethanol (20 ml) was reacted with an ethanol (20 ml) solution of salophene (3.67 g, 0.01 mol) by refluxing for one hour. Lithium chloride (0.635 g, 0.015 mol) was then added to the refluxing solution and the reaction continued for another 0.5 hr. Cooling the mixture to 0° afforded ClMn (III) salophene as dark brown crystals. The crystals were filtered, washed thoroughly with cold water and dried in vacuo. Yield: 3.15 g.

The substituted Mn salophenes were prepared using substituted salicylaldehyde instead of salicylaldehyde.

*Synthesis of chloro manganese(III) salicyhexene complexes (salicyhexene = salicylaldehyde 1,2-cyclohexanediamicine)(Mn(III)salicyhexene)*

Preparation of salicyhexene:

Salicylaldehyde (4.88 g, 0.02 mol) was mixed with 150 ml of distilled ethanol in a 250 ml round bottom flask, which was stirred on a magnetic stirrer. 1,2-cyclohexanediamicine (1.75 g, 0.01 mol) dissolved in 25 ml of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The
contents were refluxed for one hour to get a yellow solid precipitate of salicyhexene, which was cooled, filtered, washed with petroleum ether and dried. The salicyhexene was then recrystallised from ethanol (yield 5.9 g).

The substituted salicyhexene were prepared using substituted salicylaldehyde instead of salicylaldehyde.

Preparation of Cl Mn(III) salicyhexene:
Manganese acetate tetrahydrate (2.4 g, 0.01 mol) dissolved in ethanol (20 ml) was reacted with an ethanol (20 ml) solution of salicyhexene (3.75 g, 0.01 mol) by refluxing for one hour. Lithium chloride (0.635 g, 0.015 mol) was then added to the refluxing solution and the reaction continued for another 0.5 hr. Cooling the mixture to 0° afforded ClMn(III) salicyhexene as dark brown crystals. The crystals were filtered, washed thoroughly with cold water and dried in vacuo. Yield: 3 g.

The substituted Mn salicyhexenes were prepared using substituted salicylaldehyde instead of salicylaldehyde.

Encapsulated complexes

Encapsulation of complexes by the flexible ligand method

Synthesis of Cu - Y

Copper acetate monohydrate (3.5 g) was dissolved in 700 ml of warm distilled water. To that was added 7.5 g of Na - Y (ALDRICH) under stirring. The contents were heated under reflux for 8 hrs and cooled. The resulting solid was filtered and washed thoroughly with hot demineralised water till the washings
were colourless. This exchange procedure was repeated twice. The solid Cu-Y obtained after the third exchange was dried at 383 K overnight in air. The material was then dried at 383K.

*Synthesis of Cu Salen / substituted Salen - Y (Flexible ligand method) (CuSal-Y(FL))*

The syntheses of CuSalen - Y, CuCl₂Salen - Y, CuCl₃Salen - Y, CuBr₂Salen - Y, Cu(NO₂)₂Salen - Y are described below: Salen / substituted salen and Cu-Y (prepared as described below) were taken in the ratio of 3:1. Salen / substituted salen was taken in a conical flask immersed in an oil bath and heated to its melting point \( \approx 134^\circ \) under stirring by a magnetic stirrer. To the molten salen the Cu-Y was added and the temperature was maintained for 24 h. After 24 h the solid was taken out and extracted (soxhlet) with methylene chloride till all unreacted salen / substituted salens were removed i.e., until the extract was colourless. Uncomplexed Cu²⁺ ions remaining in the zeolite were removed by back exchange of the zeolite with aqueous 0.01 M NaCl solution. The solid was then washed with hot water to remove adsorbed chloride ions. The completion of chloride ion removal was confirmed with AgNO₃ solution.

**Encapsulation of complexes by the zeolite synthesis method**

Before we discuss the synthetic procedure for encapsulation, the solubility of metal complexes in the synthesis medium should be established. It has been observed that only dissolved metal salen complexes in solution can be encapsulated in microporous cavities during zeolite synthesis. Hence the
following experiments have been conducted to find out the solubility of metal complexes in zeolite medium. CuCl$_2$Salen (0.3 g)(containing 0.0478 g of Cu) was stirred in 100 g of an aqueous solution of fumed silica (4 g) and NaOH (3.2 g)(pH = 12.8) at room temperature for 24 h, before heating at 363 K for 12 h. This solution was identical to that used during synthesis of the zeolites except that the Al source was not added. The latter precaution was taken to avoid the precipitation of an aluminosilicate solid. At the end of 12 h, 0.17 g of the solid CuCl$_2$Salen (equivalent to 0.0271 g of Cu) was recovered by centrifugation (8000 rpm for 2 h) of the hot slurry. Chemical analysis of the solution (by atomic absorption spectroscopy) revealed the presence of 0.0207 g of Cu in 100 g of the solution. Since the copper content in CuCl$_2$Sal-X (ZS) was 0.01% wt (Table 3.1). (equivalent to about 0.001 g of Cu), it was concluded that the zeolite synthesis medium contained enough dissolved CuCl$_2$Salen complex to lead to the encapsulation levels observed for CuCl$_2$Sal-X (ZS).

The solubility of Mn(III)Salen complex in the zeolite synthesis medium was also carried out. Mn(III)Salen (0.3 g) (containing 4.6×10$^{-2}$ g of Mn) was stirred in 100 g of an aqueous solution of fumed silica (4 g) and NaOH (3.2 g)(pH = 12.8) at room temperature for 24 h, before heating at 363 K for 24 h. This solution was identical to that used during the synthesis of zeolite X except that the Al source was not added. At the end of 12 h, 0.15 g of the solid Mn(III)Salen (equivalent to 0.0335 g of Mn) was recovered by centrifugation (8000 rpm for 2 h) of the hot slurry. Chemical analysis of the clear, solution
(by atomic absorption spectroscopy) revealed the presence of 0.0335 g of Mn in 100 g of the clear solution. Since the manganese content in MnSal-X was 0.33% wt (Table 3.2), (equivalent to about 0.0033 g of Mn), it was concluded that the zeolite synthesis medium contained enough dissolved MnSalen complex to lead to the encapsulation levels observed for MnSal-X. Similar results were obtained for other complexes.

Synthesis of Na-X zeolite around the metal complexes

The synthesis of Cu salen / substituted salen, and Mn salen / substituted salen complexes encapsulated in zeolite NaX has been described below: Aluminium isopropoxide and NaOH were used without further purification. The silicate gel was prepared from 4.0 g of fumed silica (Sigma), 3.2 g NaOH, 0.30 g of metal complex and 8.0 ml of H$_2$O. Addition of the aluminate solution (9.0 g of Al (iOPr)$_3$, 3.2 g NaOH, 6.0 ml H$_2$O) resulted in a slurry with an intense greenish (for Cu)/ yellowish (for Mn) colour. An additional 36 ml of deionized water was added. The gel was then transferred to a polypropylene bottle. The mixture with a molar composition of SiO$_2$ : Al$_2$O$_3$ : Na$_2$O : H$_2$O : CuCl$_2$Sal = 3 : 1 : 3.6 : 141 : 0.015 was aged at room temperature with stirring for 24 h and then heated at 363 K for 15 h. It was then allowed to cool to room temperature and was diluted with copious amounts of deionized water. The solid crystals were isolated by centrifugation at 8000 rpm for 2 h. The light, greenish/yellowish solid was dried at 363 K for 24 h in air and extracted (soxhlet) first with dichloromethane and then with acetonitrile. It was finally dried at 363 K under vacuum (10$^{-3}$ Torr) for 15 h. The X-ray diffraction pattern
of the material confirmed it to be the zeolite, Na-X. The catalysts are designated by: Metal - Ligand - Zeolite - (synthesis method). Thus CuCl₂Sal-Y (FL) designates a Y zeolite containing CuCl₂Sal encapsulated by the flexible ligand method.

2.2 Procedures - Catalytic reactions

2.2.1 Catalytic runs

The catalytic runs at atmospheric pressure and using H₂O₂ as oxidant were carried out in a three necked flask (100 ml capacity) fitted with a condenser, thermometer well and a dropping funnel. The temperature of the reaction vessel was maintained using an oil bath, which was kept on a magnetic stirrer. In a typical oxidation reaction, the solid catalyst (0.05 g) was added to the substrate phenol (4.7 g). Aqueous H₂O₂ (1.13 g) (30% wt) was added to the reaction mixture after the desired temperature was attained. The reaction was carried out for one hour.

Copper, or manganese was not detected (by atomic absorption spectroscopy, Hitachi Model Z-8000) in the colourless reaction product when using any of the solid catalysts used in the present study.

In the case of styrene oxidation, the reactions were carried out in a thermostated reactor of 100 ml volume. The reactor was equipped with a reflux condenser and a gas inlet. In a typical experiment, dry air was bubbled through the reactor containing styrene (5 g), acetonitrile (5 g), catalyst (0.1 g) and tertiary butyl hydroperoxide (70% aqueous solution) (0.1 g) and the reaction was carried out for 10 - 12 hours at 343 K. At the end of the reaction,
the reaction mixture was cooled to room temperature and the products were analysed.

Aerial oxidation of p-xylene was carried out in a 300 ml Parr autoclave. P-xylene (30 g), tertiary butyl hydroperoxide (70% aqueous solution) (0.5 g) and the catalyst (0.5 g) were added to the autoclave and pressurised with air upto 450 psi. The contents were heated with constant stirring for a fixed period of time. The liquid and gaseous products were analysed by GC.

2.2.2 Product analysis

The products of the oxidation reactions were analysed by gas chromatography (Shimadzu GC 14B), employing a FID detector and using a SE-52 column or carbowax polyethylene glycol columns. The reactants and products of phenol oxidation were analysed by a gas chromatograph (Hewlett Packard) equipped with a SE 52 capillary column. The acids formed in the oxidation of styrene and p-xylene (like benzoic, toluic or terephthalic) were esterified and analysed as methyl esters by the procedure given below: 300 microliter of the reaction product sample (after filtration of the catalyst) was taken in a glass vial. 2 ml of 14% boron trifluoride (BF₃) in methanol was added to the glass vial which was stoppered with a teflon lined stopper and heated for 1 hr at 353 K. The sample was cooled to room temperature and 2 ml of Milli-Q reagent water was added with mild shaking. The ester was extracted with 2 ml of HPLC grade dichloromethane and analysed by GC. The identity of the products was further confirmed by GC-MS (Shimadzu QCMC-QP 2000A).

2.3 Procedure - Catalyst characterisation
2.3.1 Chemical analysis

A known weight of zeolite encapsulated complex was taken in a platinum crucible with lid and heated at 393 K to get the dry weight of the sample. The sample was weighed after equilibration. The difference in weights gives the loss on heating. The anhydrous sample was treated with sulphuric acid (75%) and hydrofluoric acid (40%) and was evaporated on a hot plate to remove the silicon in the form of SiF₄. This procedure was repeated three times and the sample was heated, cooled and weighed. The loss in weight gives the amount of silica present in the sample. The residue was fused with potassium pyrosulphate and dissolved in a known volume of water in a standard flask. It was then analysed for copper, manganese, silicon, sodium, potassium and aluminium by atomic absorption spectroscopy.

2.3.2 Adsorption and surface area measurements

Omnisorb 100 CX (COULTER Corporation, USA) was used for the measurements of nitrogen sorption and surface area of the samples. Prior to the adsorption measurements, the samples were activated at 373 K for 4 h, in high vacuum (1.33 x 10⁻⁶ Pa). After the evacuation the samples were cooled to room temperature and the weight was taken. The samples were then cooled to 78 K using liquid nitrogen and nitrogen gas was allowed to adsorb on them. The volume of N₂ adsorbed (cc/g at STP) and the BET surface areas were then measured.

2.3.3 ESR spectroscopy
The ESR spectra of the solid catalysts were measured at room (300 K) and liquid N₂ (77 K) temperatures using a Bruker (E-2000) ESR spectrometer (200 D) at 9.7 MHz with a rectangular cavity ST₉₄₂₄. The cavity input power was 20 Mw and the field modulation intensity was 1.25 Gpp. The instrument was calibrated with a standard sample of weak pitch (g = 2.0029). The frequency modulation was carried out at 100 kHz and a time constant of 10¹ msec was used. A standard calibration curve using different molar concentrations of CuSO₄·5H₂O (Aldrich) was drawn and the total number of spins of Cu²⁺ in the catalyst samples was estimated from the calibration curve.

2.3.4 X-ray diffraction

The solid catalyst samples were analysed for qualitative and quantitative phase identification on a computer controlled automatic X-ray powder diffractometer (Rigaku Model D/MAX III VC, Japan). Ni filtered Cu-Kα radiation (λ = 1.5404 Å) was used with a curved graphite crystal monochromator and a NaI scintillator. All measurements were made at room temperature. Data were collected in the 2θ range 4-50 degrees at a scan rate of 4°/min. Silicon was used as the internal standard for calibrating the instrument. After background correction and Kα2 stripping were done, the peak positions were marked. The ‘d’ values and the relative intensities I/I₀ of the peaks were calculated. The interplanar spacings, ‘d’, were corrected using silicon and then used for the determination of unit cell parameters. The latter were further refined by least square fitting programs. The crystalline phases were identified using a search-
match technique. The catalysts were finely powdered and sieved through a 170 mesh before they were loaded in the sample compartment.

2.3.5 Infrared spectroscopy

The infrared spectra were recorded using a Perkin Elmer 1600 FTIR spectrometer in the frequency range 4000-400 cm\(^{-1}\). Nujol was used as the mulling agent. Band intensities were expressed either as transmittance (T) or as absorbance (A). The spectra were also recorded by the KBr pellet method over the same frequency range. The samples were prepared by grinding a mixture of the catalyst and spec-pure KBr powder in an agate mortar and pressing them using a hydraulic press at a pressure of 10 tons/Sq. in

2.3.6 UV-Vis spectroscopy

The diffuse reflectance UV-Vis spectra (DRS) of the solid catalysts were recorded using a Shimadzu UV-2101 PC UV-Vis spectrophotometer in the range 200-800 nm. Barium sulphate was used as the reference material. UV spectra of liquid samples were measured in the 200-400 nm region. The computer processing of the spectra consisted of (i) subtraction of baseline (ii) conversion to wavenumber and (iii) calculation of the Kubelka-Munk function for solids. The values of the Kubelka-Munk function at the band maxima were used for quantitative diffuse reflectance spectroscopy.

2.3.7 X-ray photoelectron spectroscopy

XPS of the solid catalysts were recorded with a VG Scientific ESCA III Mark (II) with MgK\(\alpha\) (1253.6 Å) as the excitation source. AlK\(\alpha\) (1486.6 Å) was
used for excitation and photoelectron kinetic energy was measured with reference to the Fermi energy. Binding energies were corrected with respect to the peak at 285.0 eV for Carbon C$_1$, and the surface composition was determined from the observed peak intensity using known values of Scofield total cross section photoionisation constants of the individual atoms. The spectrometer was calibrated by checking the binding energies of Au 4f$_{7/2}$ (84.0 eV), Ag 3d$_{5/2}$ (368.3 eV) and Cu 2p$_{3/2}$ (932.4 eV) using spectroscopically pure metals (Johnson and Matthey, UK). The samples were ground to a fine powder and a homogeneous mixture was made with isopropanol. It was deposited on a nickel strip for analysis. All XPS spectra were recorded under similar conditions (50 eV pass energy, 4 mm slit entrance, pressure 10$^{-9}$ Torr.). In all cases, the samples were measured before and after argon ion sputtering. The peaks were resolved after background subtraction and a gaussian equation was used to fit the curves. The binding energy values were measured to a precision of ± 0.2 eV.

2.3.8 Scanning electron microscopy

Scanning electron micrographs of the solid catalysts were recorded on a Leica, Stereoscan-440, Cambridge instrument. The crystal morphology and the average particle size of the catalysts were estimated by this technique. The samples were dusted on alumina and coated with a thin film of gold to prevent surface charging and to protect the surface material from thermal damage by
the electron beam. In all analyses a uniform film thickness of about 0.1 mm was maintained.

2.3.9 Thermal analysis

Simultaneous TG-DTA-DTG analyses of the free metal complexes as well as the zeolite encapsulated metal complexes were recorded on an automatic derivatograph (Setaram TG-DTA 92). The thermograms of the samples were recorded under the following conditions:

- Weight of the sample = 30 mg
- Heating rate = 10 K min⁻¹
- Sensitivity
  - TG = 25 mg
  - DTG = 0.2 mv
  - DTA = 0.1 mv
- Atmosphere = Nitrogen

Preheated and finely powdered α alumina was used as the reference material.