CHAPTER II

MATERIALS AND METHODS
2.1 INTRODUCTION

This chapter provides details of the general reagents and other materials used in the present study. A brief account of the methods used for the synthesis of ligands, zeolite supported metal complexes and metal oxide catalysts is given. Procedures of various physico-chemical techniques employed for the characterization studies are also discussed.

2.2 REAGENTS

The following metal salts were used: MnCl₂ 4H₂O (E. Merck, GR); FeCl₃ (Qualigens); CoCl₂ 6H₂O (E. Merck, GR); NiCl₂ 6H₂O (E. Merck, GR); CuCl₂ 2H₂O (E. Merck, GR); Ce(NO₃)₂ 3H₂O (NICE, GR); Cr(NO₃)₃ H₂O (NICE, GR); Ce(NO₃)₃ (IRE, Udyogamandal); Ammonium titanyloxalate (TTP, Thiruvananthapuram)

The supports, Y-Zeolite (in powder form) and γ-Al₂O₃ (extrusions of 3 mm dia. and 10 mm length) for preparing the catalyst samples were obtained from Sud-Chemie India Ltd., Binanipuram, Cochin. Dimethylglyoxime, Salicylic acid, Hexamine, 2-hydroxy-acetophenone, 2-hydroxy-1-naphthaldehyde and ethylenediamine obtained from E. Merck were used for the synthesis of ligands.

Hydrogen peroxide (30% w/v), benzyl alcohol, ethylbenzene and 4-methoxy-benzaldehyde (E. Merck) were used for the catalytic studies on supported metal complexes. Gas cylinders for carbon monoxide (Air Products, UK), Oxygen, Nitrogen and Hydrogen (Sterling Gases, Cochin) and Helium (Speciality Gases, Bangalore) were used for catalytic studies of metal oxide catalysts.

2.3 SYNTHESIS OF LIGANDS

2.3.1 Dimethylglyoxime (dmg)

Dimethylglyoxime was purified by recrystallisation from methanol and dried in vacuum over anhydrous calcium chloride.
2.3.2 3-Formylsalicylic acid (fsal)

3-Formylsalicylic acid was synthesized by adopting the procedure reported by Duff and Bills. Salicylic acid (40.0 g), hexamethylenetetramine (27.0 g) were mixed together in water (300 ml) and then boiled under reflux for 16 hours. The solution was cooled and acidified with 4 N HCl (300 ml) to obtain a yellow precipitate. This precipitate was filtered, dried and soxhlet extracted with benzene for 8 hours. The benzene solution was evaporated and the residue was dissolved in 3 N NH₃ solution (200 ml). Subsequently, 10% BaCl₂ (100 ml) and 2 N NaOH (50 ml) solutions were added to form the precipitate of barium 3-formylsalicylic acid which was then converted to 3-formylsalicylic acid by acidifying with dil. HCl. The compound separated was collected, purified by recrystallisation from boiling water and dried in vacuum over anhydrous calcium chloride.

2.3.3 N,N'-Ethylenebis(7-methylsalicylideneamine) (Mesalen)

Mesalen ligand was synthesized as per the method reported in the literature. 2-Hydroxyacetophenone (4.1 g, 3 x 10⁻² mol.) in 50 ml methanol was mixed with ethylenediamine (0.9 g, 1.5 x 10⁻² mol.). The Schiff base was formed as a yellow precipitate. It was filtered, purified by recrystallisation from methanol and then dried in vacuum over anhydrous calcium chloride.

2.3.4 N,N'-Ethylenebis(5,6-benzosalicylideneamine) (Benzosalen)

The procedure employed for the synthesis of this ligand was reported in the literature. 2-hydroxy-1-naphthaldehyde (5.2 g, 3 x 10⁻² mol.) and ethylenediamine (0.9 g, 1.5 x 10⁻² mol.) were mixed together in 50 ml methanol. The Schiff base was separated out as a yellow powder. It was filtered, washed with methanol and was finally dried in vacuum over anhydrous calcium chloride.
2.4. SYNTHESIS OF Y ZEOLITE SUPPORTED METAL COMPLEXES

2.4.1 Modification of Y Zeolite

Metal exchanged Y zeolite support was prepared as per the following procedure:

(a). Preparation of Na exchanged zeolite (NaY)

The parent zeolite, HY (5.0 g) was ion exchanged with NaCl solution (1 M, 500 ml) under stirring for 24 hours at room temperature. It was then filtered and washed with deionised water till the filtrate was free of chloride ions. The NaY formed was dried at 120 °C for 12 hours.

(a). Preparation of metal exchanged zeolite (MY)

Zeolite, NaY (5.0 g) was stirred with metal chloride solution (0.007 M, 500 ml) of pH 4.0-4.5 at 90 °C for 8 hours. Such low concentration of metal salt solutions of pH 4.0-4.5 was used as dealumination occurs at higher concentrations and pH < 4.0. Ferric chloride solution of still lower concentration, 0.001 M, was used, as this destruction is more probable in the case of ion exchange with Fe³⁺. The slurry was filtered and washed with deionised water to remove chloride ions. It was then dried at 120 °C for 2 hours and finally dehydrated at 450 °C for 4 hours.

2.4.2 Encapsulation of metal complexes in Y zeolite

The flexible ligand method was used for encapsulating metal complexes in Y zeolite. In this method, ligand molecules are diffused through the zeolite channels and are allowed to react with the metal ions previously introduced into the supercage to form complexes in it. General procedure for this kind of encapsulation is as follows:

Metal exchanged zeolite, MY (3.0 g) was mixed thoroughly with excess of ligand (ligand to metal mole ratio ~ 2 - 4) and introduced into a glass ampule. It was then sealed and heated. The heating temperature has to be optimised so as to effect the complexation reaction. After this, the resulting material was purified from surface
complexes formed and unreacted ligand by soxhlet extraction with one or more solvents. The soxhlet extraction was continued further for 16 hours after the extracting solvent becomes colourless to ensure the complete removal of surface species. The uncomplexed metal ions in the zeolite and ionisable protons of the ligand, if any, transferred to zeolite framework were removed by ion exchange with NaCl solution (0.1 M, 250 ml) for 24 hours. It was then filtered, washed free off chloride ions and finally dried at 100 °C for 2 hours.

2.5 PREPARATION OF METAL OXIDE CATALYSTS

Alumina supported Cu or Cu-Cr based metal oxide catalysts were prepared by using the impregnation technique. This technique is particularly useful to make small crystallites of catalytically active components dispersed on a porous support. It mainly consists of three steps: (i) dipping the support in the impregnating solution containing active components, (ii) drying and (iii) activate by calcination. In the first step, the solution is sucked into the support by capillary action followed by diffusional transport of the solute to the carrier. During the drying step, the metal salt is precipitated and deposited on the surface of pores. The drying and calcination steps determine final distribution of the active components on the support. In incipient wetness impregnation method, the volume of impregnating solution is adjusted so as to get the solution fully absorbed by the support. This method is very effective for precisely controlling the concentration of active ingredients in the catalyst.

2.6 PHYSICO-CHEMICAL PROPERTIES

2.6.1 Chemical analysis

(a). Determination of Si, Al, Na and transition metal ion in zeolite samples

Chemical analyses of zeolites and zeolite encapsulated complexes were done according to the following procedure: The sample was dried at 120 °C for one hour and
was then kept in a desiccator. A known weight (w₁) of the sample was taken in a beaker and the zeolite framework was destroyed by heating with concentrated sulfuric acid (40 ml, 98%) until SO₃ fumes were evolved. It was then cooled, diluted with water and filtered using ashless filter paper. The filtrate was collected in a standard flask. The residue was taken in a platinum crucible with lid and incinerated at 1000 °C for one hour, cooled and then weighed (w₂). Hydrofluoric acid (10 ml, 40%) was added to dissolve the residue and the resulting solution was evaporated on a hot plate to remove silicon in the form of H₂SiF₆. It was again incinerated at 1000 °C, cooled and weighed (w₃). From the loss in weight, the amount of silica present in the sample can be estimated using Eq. II. 1.

\[
\% \text{SiO}_2 = \frac{(w_3 - w_2)}{w_1} \times 100
\]  
Eq. II. 1

The residue in the crucible was fused with potassium persulfate, dissolved in water and was added to the filtrate collected in the standard flask. The solution was then made up to a known volume. This solution was analysed for Al, Na and metal contents using atomic absorption spectrophotometry.

(b). **Determination of CeO₂ in Al₂O₃-CeO₂ support**

A known weight of the support, Al₂O₃-CeO₂ (~ 0.5 g), was fused with potassium hydrogen sulfate (~ 10 g) at 700 °C for one hour. The melt was cooled and then dissolved in hot water. This solution was analysed for CeO₂ by atomic absorption spectrophotometry.

(c). **Determination of TiO₂ in Al₂O₃-TiO₂ support**

A known weight of the support, Al₂O₃-TiO₂ (~ 0.5 g), was fused with KOH (~10 g) at 500 °C for one hour. The melt was cooled and extracted with hot water in a polyethylene beaker. This solution was acidified with Con. HCl and used for determining TiO₂ content by atomic absorption spectrophotometry.
(d). *Determination of Cu and Cr in metal oxide catalysts*

A known weight of the catalyst sample (~ 0.5 g) was fused with potassium hydrogen sulfate (~10 g) at 700 °C for one hour. The fused melt was dissolved in hot water after cooling. This solution was analysed by atomic absorption spectrophotometry for estimating the amount of metals present in the catalyst.

### 2.6.2 CHN analysis

The results of microanalyses for C, H and N in zeolite encapsulated complexes were provided by Central Drug Research Institute, Lucknow.

### 2.6.3 Atomic absorption spectrophotometry

Atomic absorption spectrophotometry (Perkin Elmer 3110) was used for analysing various ingredients in zeolites and metal oxide samples.

### 2.6.4 Surface area analysis

Surface area was determined by BET method of nitrogen adsorption at liquid nitrogen temperature in Micromeritics Gemini 2360. The volume of gas adsorbed by the sample was monitored at different relative pressures in the range 0.1-0.9.

Surface area was calculated using the following BET equation (Eq. II. 2):

\[
1/V_{ads}(P_o-P) = 1/V_m C + [(C-1)/V_m C] P/P_o \quad \text{Eq. II. 2}
\]

where

- \( V_{ads} \) = volume of gas adsorbed at relative pressure \( P/P_o \)
- \( P_o \) = saturated vapour pressure
- \( V_m \) = volume of gas adsorbed for monolayer coverage
- \( C \) = BET constant

By plotting left side of the Eq. II. 2 against \( P/P_o \) (upto 0.3), a straight line is obtained with a slope of \((C-1)/V_m C\) and an intercept \(1/V_m C\). From these values, \( V_m \) and hence the number of moles of \( N_2 \) adsorbed, \( X_m \), can be calculated.
BET surface area is calculated using Eq. II. 3.

\[ S_{\text{BET}} = X_m N A_m 10^{20} \]  
Eq. II. 3

where

\[ N = \text{Avogadro's number} \]
\[ A_m = \text{cross-sectional area of the adsorbate molecule in } \text{Å}^2 \]

Total pore volume of the sample at \( P/P_0 \sim 0.9 \) is computed by converting the volume of \( N_2 \) adsorbed at \( P/P_0 \sim 0.9 \) to volume of liquid equivalent to it using Eq. II. 4.

\[ V_{\text{tot}} = V_{\text{ads}} D \]  
Eq. II. 4.

where

\[ V_{\text{tot}} = \text{total pore volume at } P/P_0 \sim 0.9 \]
\[ V_{\text{ads}} = \text{volume of gas adsorbed at relative pressure } \sim 0.9 \]
\[ D = \text{density conversion factor} \]

2.6.5 Pore volume analysis

Mercury penetration method was used to measure the pore volume of metal oxide catalysts (Micromeritics Pore sizer 9320). Mercury porosimetry is based on the capillary law governing liquid penetration into small pores. This law, in the case of non-wetting liquid like mercury, is expressed by the Washburn equation, assuming pores are cylindrical.

\[ D = -\frac{1}{P} 4\gamma \cos \theta \]  
Eq. II. 5

where

\[ D = \text{Pore diameter} \]
\[ P = \text{Applied pressure} \]
\[ \gamma = \text{Surface tension (} 485 \text{ dynes/cm for Hg)} \]
\[ \theta = \text{Contact angle (usually 130°)} \]

2.6.6 X-ray diffraction spectroscopy

Zeolite complexes and Cu-Cr catalysts were analysed for powder X-ray diffraction using Rigaka D-Max C X-ray diffractometer. The analysis was carried out with a
stationary X-ray source. Ni filtered CuKα radiation (λ=1.5404) and a movable detector which measures the intensity of diffracted radiation as a function of the angle 2θ between the incident and diffracted beams.

2.6.7 Scanning electron microscopy

Scanning electron microscopy analysis of a representative zeolite complex before and after soxhlet extraction was performed at Sree Chitra Institute of Medical Science and Technology, Thiruvananthapuram.

2.6.8 Magnetic moment measurement

The magnetic susceptibility measurements were carried out at room temperature on a simple Gouy type magnetic balance. The Gouy tube was standardised using Co [Hg(SCN)₄] as suggested by Figgis and Nyholm⁹.

The effective magnetic moment was calculated using Eq. II. 6

\[ \mu_{\text{eff}} = 2.84 \left( X'_m T \right)^{1/2} \text{ BM} \]  

where

\[ T = \text{absolute temperature} \]

\[ X'_m = \text{molar susceptibility corrected for diamagnetism of all atoms present in the complex using pascals constant and that of zeolite frame work per unit metal.} \]

2.6.9 Diffuse reflectance spectra

The diffuse reflectance spectra were recorded at room temperature between 200-2000 nm against MgO as standard on a Cary Win spectrophotometer at Regional Sophisticated Instrumentation centre, Indian Institute of Technology, Chennai. The spectra were computer processed and plotted as percentage reflectance versus wavelength. A Kubelka-Munk analysis¹⁰,¹¹ was performed on the reflectance data. The Kubelka-Munk factor, F(R), is given by Eq. II. 7
\[ F(R) = \frac{(1-R)^2}{2R} = k/s \quad \text{Eq. II. 7} \]

where

\[
\begin{align*}
F(R) &= \text{Kubelka-Munk factor} \\
R &= \text{the diffuse reflectance of the sample as compared to MgO} \\
k &= \text{the molar absorption coefficient} \\
s &= \text{the scattering coefficient of the sample.}
\end{align*}
\]

### 2.6.10 Infrared spectra

Infrared spectra of the ligand and supported complexes in the region 4600 cm\(^{-1}\)-400 cm\(^{-1}\) were taken in KBr pellets using Schimadzu 8000 Fourier Transform Infrared Spectrophotometer.

### 2.6.11 EPR spectra

The X-band EPR spectra of zeolite supported Cu complexes were recorded at liquid nitrogen temperature using a Varian E-109 X/Q bands spectrophotometer. The \(g\) values were estimated relative to tetracyanoethylene (TCNE, \(g = 2.0027\)). Magnetic moment was determined\(^{12}\) from the EPR data using Eq. II. 8.

\[
\mu_{\text{eff}}^2 = g_{\parallel}^2/4 + g_{\perp}^2/4 + 3kT/\lambda_o \quad \text{Eq. II. 8}
\]

where \(\lambda_o\) is the spin orbit coupling constant for the free metal ion.

The density of unpaired electrons at the central metal atom was computed\(^{13}\) using Eq. II. 9.

\[
\alpha^2_{\text{Cu}} = (A_{\parallel}/P) + (g_{\parallel}^2-2) + 3/7(g_{\perp}^2-2) + 0.04 \quad \text{Eq. II. 9}
\]

where \(1-\alpha^2\) measures the covalency associated with the bonding of metal ion to the ligand and \(P=0.036\) cm\(^{-1}\).
2.6.12 TG analysis

Thermogravimetric analysis was performed on a Shimadzu TGA-50 in the temperature range 30-550 °C at a heating rate of 10 °C/minute in air. About 20 mg sample was taken for each analysis in a platinum crucible hanged from one arm of balance in the instrument. The TG data were computer processed and plotted the % weight against temperature at 5 °C intervals.

2. 7 CATALYTIC STUDIES

Catalytic studies over zeolite complexes and metal oxide catalysts are detailed in Chapter VII and VIII respectively. The following instruments were used for conducting catalytic experiments:

2.7.1 Gas chromatographs

Gas Chromatograph Chemito 8510 was used for analysing the reactants and products of the catalytic reactions over zeolite complexes. A SE-30 column was used for separating various components in the reaction mixture.

The analysis of CO in inlet and outlet gas streams was carried out using a Chemito 3865 gas chromatograph for determining CO oxidation activity of various catalysts. A Poropak Q column was used for separating CO₂ formed from unreacted CO in the product stream. The outlet of the column was passed through a methanator for converting CO and CO₂ to methane, which is then sensed by the FID detector.

2.7.2 Microcatalytic reactor

Chemisorption studies were carried out in a microcatalytic reactor assembly in which the reactor is heated using a temperature programmer (Century Systems CS-7533). A Chemito 8510 GC was connected on line to the reactor for the gas analysis.
REFERENCES