CHAPTER II

MATERIALS AND METHODS

2.1. INTRODUCTION

The details regarding the general reagents and other materials used in the present study, a brief account of the methods used for the synthesis of the zeolite encapsulated metal complexes, and the various analytical and physico-chemical methods employed for characterisation are given in this chapter. Procedural details about the synthesis and catalytic activity studies of the complexes are given in appropriate chapters.

2.2. REAGENTS

The following metal salts were used: MnCl$_2$.4H$_2$O (E. Merck, GR); CoCl$_2$.6H$_2$O (E. Merck, GR); NiCl$_2$.6H$_2$O (E. Merck, GR); CuCl$_2$.2H$_2$O (E. Merck, GR).

Synthetic Y-type zeolite was obtained from Sud-Chemie India Ltd., Binanipuram, Cochin. Salicylaldehyde, 2-hydroxyacetophenone, 1,2-phenylenediamine and 1,1-ethanediamine obtained from E-Merck and pyridine-2-carboxaldehyde and pyridine-3-carboxaldehyde obtained from Aldrich were used as such for preparation of the encapsulated metal complexes. The chiral amine trans-1,2-cyclohexanediamine (Aldrich) was used for the preparation of the chiral Schiff base complexes encapsulated in zeolite-Y. Commercially available styrene used for the epoxidation reactions was purified by known procedures [1]. The 1,2-epoxyethylbenzene procured from Aldrich was used as the
standard for calculating the yield. For catalytic studies, 3,5-di-tert-butyl catechol (Aldrich) and L-ascorbic acid (SRL, LR) were used. Unless otherwise specified, all the other reagents were of analytical reagent grade. Solvents employed were either of 99% purity or purified by known laboratory procedures [1].

2.3. SYNTHESIS OF Y ZEOLITE ENCAPSULATED METAL-SCHIFF BASE COMPLEXES

2.3.1. Modification of Y zeolite

Metal exchanged Y zeolite support was prepared according to the following general procedure:

One negative charge present per aluminium on the framework is compensated by loosely attached, ion-exchangeable cations. These cation exchange sites within the internal void space of the crystallite allow the straightforward introduction of active metal ions for catalysis. So at first it is exchanged with sodium ions and it can be replaced afterwards with various ions easily. The parent-powdered zeolite (5 g) was converted to the sodium form by ion exchanging with NaCl solution (0.1 M, 500 mL) under stirring at room temperature for 24 h. The zeolite was filtered and washed until the filtrate was free from chloride ions. The NaY so obtained was stored for further use after drying at 120°C for 2 h.

For introducing Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ ions, the sodium exchanged Y zeolite (5 g) was stirred in a solution of the respective metal chlorides (0.05 M, 500 mL) at room temperature for 24 h. At these very low concentrations it is assumed that all the metal ions are exchanged and situated in the super cage only. It was then filtered and made free from chloride ions. The metal exchanged zeolite samples so obtained were made active by calcining at 450°C for 2 hours.
2.3.2. Preparation of the Y zeolite encapsulated metal Schiff base complexes

The complexes were prepared using metal template method [2]. Here the Schiff base complexes were synthesized from the smaller components- aldehyde and amine- by assembling them around the transition metal ions already in the zeolite super cage. A general procedure for the preparation is as follows:

Metal exchanged Y zeolite (5g) was refluxed with the aldehyde (2 M) in appropriate solvent. The aldehyde chelates so obtained were purified by soxhlet extraction with one or more suitable solvents. These chelates were then condensed with a molar solution of the respective amines. The resulting Schiff base complexes were purified by soxhlet extraction to colourless washings. This ensures the complete removal of surface species. They were re-exchanged with 0.01M NaCl at room temperature for 24 h to remove any surface adsorbed metal ions remaining after soxhlet extraction. After filtration it was washed free of chloride ions and dried at 120°C for 2 h. before storing in vacuum over anhydrous calcium chloride.

2.4. ANALYTICAL METHODS

2.4.1. Analysis of the zeolite samples for Si, Al, Na and transition metal ions by the complete dissolution method

The chemical analysis of the zeolites and the zeolite encapsulated metal complexes were done according to the following procedure:

The zeolite sample was dried by keeping it at 120 °C for 2 hours. A known weight of the dried zeolite sample (w1 g) was transferred to a beaker and treated with conc. sulphuric acid (40 mL, 98%) and heated until SO$_3$ fumes were evolved. This is to destroy the zeolite framework. It was cooled and diluted with water (200 mL) and filtered through an ashless filter paper in to a standard flask. The residue was dried at 1000°C in a
platinum crucible, cooled and weighed \((w_2 \text{ g})\). Hydrofluoric acid \((5 \text{ mL, 40\%})\) was added and evaporated to dryness on a sand bath. This process was done for five or six times for each sample. All the silicon is removed in the form of \(\text{H}_2\text{SiF}_6\) \([3]\). The residue was then ignited to \(1000^\circ\text{C} (w_3 \text{ g})\). The percentage of silica \((\text{SiO}_2)\) was calculated by using the equation,

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

Potassium peroxodisulphate was added to this residue and heated until a clear melt was obtained. This melt was dissolved in water and was combined with the filtrate in the standard flask. The sodium, aluminium and transition metal ions in this solution were determined by ICP analysis. The unit cell formula of the zeolite was calculated from the Si/Al ratio \([4]\).

2.4.2. CHN analysis

Microanalyses for C, H and N in the zeolite samples were done on a Carto Erba Analyzer Model 1108 at Central Drug Research Institute, Lucknow

2.5. PHYSICO-CHEMICAL METHODS

2.5.1. Magnetic susceptibility measurements

Magnetic susceptibility measurements were done at room temperature on a simple Gouy-type magnetic balance. The Gouy tube was standardised using \(\text{Co[Hg(SCN)]_4}\) as the standard \([5]\).

2.5.2. Surface Area Analysis

Surface area of the samples was measured by multipoint BET method using a Micromeritics Gemini 2360 surface area analyzer. Nitrogen gas was used as the adsorbate.
2.5.3. Infrared Spectra

Infrared spectra of the ligands and encapsulated complexes in the region 4600 cm$^{-1}$ – 400 cm$^{-1}$ were taken by the KBr pellet technique using Schimadzu 8000 Fourier Transform Infrared Spectrophotometer.

2.5.4. Diffuse reflectance spectra

The diffuse reflectance spectra were recorded at room temperature between 200-2000 nm against MgO as standard. In order to make these reflectance data more meaningful and to remove the effect of scattering, a Kubelka-Munk analysis [6,7] was performed on the reflectance data. The Kubelka-Munk equation is,

$$F(R) = (1-R)^2/2R = k/s \text{ where,}$$

$R$ is the diffuse reflectance of the sample compared to a non-absorbing standard such as MgO, $k$ is the molar absorption coefficient and $s$ is the scattering coefficient of the sample. In the case of $s$ remaining constant with wavelength, e.g. in weakly absorbing materials, $F(R)$, the emission factor or Kubelka-Munk (KM) factor, is directly proportional to the molar absorbance coefficient.

2.5.5. EPR Spectroscopy

The X-band EPR spectra of some of the zeolite encapsulated complexes were recorded at liquid nitrogen temperature using a Varian E-109 X/Q band spectrophotometer. The $g$ values were estimated relative to the tetracyanoethylene (TCNE, $g = 2.0027$). The density of the unpaired electrons at the central copper ion can be calculated using the equation,

$$\alpha_{Cu}^2 = (A/P) + (g - 2) + 3/7 (g - 2) + 0.04,$$

where $1-\alpha_0^2$ measures the covalency associated with the binding of the metal ions to the ligand and $P = 0.036 \text{ cm}^{-1}$.
2.5.6. **X-ray diffraction studies**

The powder XRD patterns of the Y-zeolite and the zeolite encapsulated metal complexes were recorded using ‘Rigaka D-Max C’ X-ray diffractometer. The measurements were carried out with a stationary X-ray source of Ni filtered Cu Kα radiation ($\lambda_0 = 1.5404$). The detector that is movable scans the intensity of the diffracted radiation as a function of the angle 2θ between the incident and the diffracted beams.

2.5.7. **Scanning electron microscopy**

Scanning electron microscopy of a representative zeolite complex after and before soxhlet extraction was performed on a Leica Steroscan-440 microscope. The secondary electron probe is used for the analysis. Before exposing to the electron beam it was made conducting by coating with gold.

2.5.8. **TG Analysis**

Thermogravimetric analyses were done on a Shimadzu TGA–50 at a heating rate of $10^0$ C/min in the temperature range 30-800$^0$C in inert atmosphere.

2.6. **CATALYTIC STUDIES**

The detailed procedure regarding the catalytic activity studies is presented in Chapters VII and VIII. The following instruments were used for the screening studies.
2.6.1. Gas Chromatography

The progress of the reaction was monitored by checking the product formation by GLC using a Chemito 8510 GC coupled with PC using 2m long, 3mm ID, 4mm OD stainless steel column packed with SE30, 5% mesh size 60 to 80 with FID detector. A pure sample of the epoxide was used to determine yields by comparison of the peak height and area. The optical purity of the product was checked with chiral capillary column (chiralridex GTA). The analyses were done at Central Salt and Marine Chemicals Research Institute, Bhavnagar, Gujarat.

2.6.2. Polarimeter

The optical rotation of the epoxides was measured using a polarimeter (Atago, Japan.)
REFERENCES


