Chapter II

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Chapter II

MATERIALS AND METHODS

2.1. INTRODUCTION

This chapter deals with the details regarding the reagents used for synthesis. It also describes the methods employed for the synthesis of ligands, metal exchanged zeolite and zeolite-encapsulated complexes. The details of the various analytical and physico-chemical methods used for the characterization of the synthesized complexes and the methods used to study the catalytic activities of the different complexes under study are also presented in this chapter.

2.2. REAGENTS

O-phenylenediamine (Loba Chemie), p-phenylenediamine (Loba Chemie), dimethylglyoxime (E.Merck), salicylaldehyde (E.Merck), ethylene glycol (Aldrich), semicarbazide hydrochloride (Loba Chemie), anthranilic acid (E.Merck), 4-aminobenzoic acid (E.Merck), methanol, pyridine-3-carboxaldehyde (E.Merck) and pyridine-2-carboxaldehyde (E.Merck) were used as starting materials for the preparation of ligands. The metal salt used is RuCl₃.3H₂O (Loba Chemie).

All reagents used were of analytical grade unless otherwise specified. O-phenylenediamine and p-phenylenediamine were purified by the following method¹. The diamine was dissolved in water to which activated charcoal was added. The resultant solution was boiled, filtered and allowed to cool. The crystallised diamine was dried and kept in a desiccator. The solvents used were either 99% pure or purified by standard procedures².

The support used is zeolite Y with a Si/Al ratio of 2.6 and surface area of 650 m²/g obtained from Zeolyst International, Netherlands.
2.3. SYNTHESIS OF LIGANDS

2.3.1. Synthesis of salicylaldehyde semicarbazone (SSC)

To an aqueous solution of semicarbazide hydrochloride (1 g, 0.008 mole), sodium acetate (1.5 g, 0.01 mole) and salicylaldehyde (0.5 g, 0.004 mole) were added slowly with constant stirring. Then the mixture was refluxed for about two hours on a water bath. The product obtained was filtered, washed with ethanol and recrystallised from 1-propanol.

2.3.2. Synthesis of N,N'-bis(salicylaldimine)-o-phenylenediamine (SOD)

The o-phenylenediamine (1.08 g, 0.01 mole) dissolved in very little amount of benzene was added dropwise to the salicylaldehyde solution (2.91 cm³, 0.02 mole) in benzene using a dropping funnel with constant stirring. The yellow solid obtained was separated by filtration and washed using ether. The ligand thus obtained was recrystallised twice from methanol and stored in vacuum in a desiccator.

2.3.3. Synthesis of N,N'-bis(salicylaldimine)-p-phenylenediamine (SPD)

The p-phenylenediamine was recrystallised twice from hot water. To an ethanolic solution of p-phenylenediamine (1.08 g, 0.01 mole), salicylaldehyde (2.91 cm³, 0.02 mole) was added and the resultant solution was refluxed on a water bath for about 3 hours. The bright orange solid obtained by this technique was recrystallised twice from methanol and kept dry over anhydrous calcium chloride in a desiccator.

2.3.4. Purification of anthranilic acid (AA)

Anthranilic acid was purified by dissolving very small portions in methanol and allowing them to form crystals. The crystals thus obtained were again recrystallised using the same solvent and stored over anhydrous calcium chloride.

2.3.5. Purification of 4-aminobenzoic acid (ABA)

Similar procedure was employed for obtaining pure 4-aminobenzoic acid crystals. The solid crystals obtained after recrystallization from methanol were placed in a desiccator over anhydrous calcium chloride.
2.3.6. Purification of dimethylglyoxime (DMG)

The purification of dimethylglyoxime was done by recrystallising them from methanol. The pure crystals of DMG obtained were dried over anhydrous calcium chloride.

2.3.7. Synthesis of N,N'-bis(3-pyridylidene)-1,2-phenylenediamine (PCO)

The starting materials required for the synthesis of this ligand are pyridine-3-carboxaldehyde and o-phenylenediamine. The diamine purchased as such cannot be used for this preparation. It can be used only after recrystallisation as described earlier. Recrystallised o-phenylenediamine (1.08 g, 0.01 mole) was refluxed with ethanolic solution of pyridine-3-carboxaldehyde (2.14 g, 0.02 mole) for about five hours. The reaction mixture was then filtered to get yellow crystals of the ligand. It was washed several times with benzene, recrystallised from ethanol and dried in vacuum over anhydrous calcium chloride in a desiccator.

2.3.8. Synthesis of N,N'-bis(3-pyridylidene)-1,4-phenylenediamine (PCP)

An ethanolic solution of pyridine-3-carboxaldehyde (2.14 g, 0.02 mole) and p-phenylenediamine (1.08 g, 0.01 mole) were allowed to reflux on a water bath for five hours to get the product. The yellow solid formed was filtered, washed several times with benzene and recrystallised from ethanol. Then it was dried in vacuum over anhydrous calcium chloride.

2.3.9. Synthesis of N,N'-bis(2-pyridylidene)-1,2-phenylenediamine (CPO)

Pyridine-2-carboxaldehyde (2.14 g, 0.02 mole) in ethanol was taken in a roundbottom flask. Recrystallised o-phenylenediamine (1.08 g, 0.01 mole) was added to this with stirring. The reaction mixture was boiled under reflux on a water bath for five hours. The product formed was obtained by filtration. Yellow crystals of CPO were washed with benzene, recrystallised twice from ethanol and dried in vacuum over anhydrous calcium chloride.
13.10. Synthesis of \( \text{N,N'-bis(2-pyridylidene)-1,4-phenylenediamine (CPP)} \)

The ligand \( \text{N,N'-bis(2-pyridylidene)-1,4-phenylenediamine (CPP)} \) was synthesized by a procedure similar to that of CPO. The mixture of recrystallized \( p \)-phenylenediamine (1.08 g, 0.01 mole) and pyridine-2-carboxaldehyde (2.14 g, 0.02 mole) in ethanol was refluxed on a water bath for five hours. The crystals separated were collected, washed with benzene and recrystallised from ethanol to get the pure ligand.

24. SUPPORTS USED

The zeolite-\( Y \) used for encapsulation was modified by the following techniques.

24.1. Preparation of sodium exchanged zeolite (NaY)

The zeolite-\( Y \) obtained was modified using the standard ion exchange procedure which is based on the method suggested by Edward \textit{et al.} \(^4\). Zeolite-\( Y \) (5 g) was mixed with a solution of NaCl (0.1 M, 500 ml) and stirred for 24 hours at room temperature to remove any extra ions present by converting them into Na\(^+\) ions. The solution was then filtered to get sodium-exchanged form of the zeolite, which was made chloride free by washing with distilled water till the filtrate becomes free of chloride ions. The NaY thus formed was dried at 100°C for two hours.

24.2. Preparation of metal exchanged zeolite (RuY)

The sodium ions in NaY were replaced by transition metal ions by stirring sodium-exchanged zeolite (5 g) with metal chloride solution (0.001 M) at 90°C for 24 hours. It should be noted that low concentration of metal salt solution was used since there are chances for dealumination at higher concentrations\(^5\). The slurry obtained after the stipulated time was filtered and washed with distilled water several times to make it free from anions. It was then dried in a Muffle furnace at 450°C for four hours\(^6\).

24.3. Preparation of zeolite encapsulated metal complexes

Transition metal cations exchanged into zeolite-\( Y \) are capable of forming well-defined complexes with certain ligands within the large cavities of the zeolite.
The three-dimensional pore structure of zeolites offer the possibility for the preparation of complexes inside the zeolite which are otherwise unstable in solution. This trapping is usually described as making a ‘ship-in-a-bottle’ complex. The zeolites with the aid of their unique ligating and solvating properties stabilize the transition metal complexes. The stabilization can be achieved by anchoring of the complexes to the zeolite lattice by coordination to framework oxygens. The encapsulated metal complexes were prepared using the flexible ligand method where flexible ligand molecules enter the supercages of the zeolite and react with the metal ions already present in the cage. This method generally involves two kinds of encapsulation.

2.4.3.1. Encapsulation by heating in a sealed ampule

This method involves the mixing of the metal exchanged zeolite (2 g) with excess of the ligand and heating the mixture in a closed glass ampule at an optimum temperature in a Muffle furnace for a definite period of time. During this process, the ligand molecules diffuse into the metal exchanged zeolite uniformly and hence complex formation occurs. The advantage is that the large size of the complex prevents its diffusion out of the zeolite structure. The complex formed was soxhlet extracted with suitable solvents to remove unreacted ligands and surface species. The process of soxhlet extraction was continued till the extracting solvent became colourless. The uncomplexed metal ions in the zeolite were removed by back exchange with NaCl solution (0.01 M, 250 ml) for 24 hours. It was then filtered, washed with distilled water to make it free of chloride ions and finally dried at 100°C for two hours. The prepared complex was stored in vacuum over anhydrous calcium chloride.

2.4.3.2. Encapsulation by refluxing the metal exchanged zeolite with the ligand

The metal exchanged zeolite MY (5 g) was added to a solution of the ligand in a suitable solvent and this mixture was refluxed for 24 hours on a water bath. As heating progresses, the ligand molecules enter the zeolite pores and undergo complexation with the metal ions already present there.

The encapsulated complex was purified by soxhlet extraction with suitable solvents for the removal of the surface species. It was then stirred with sodium chloride
solution (0.01 M, 250 ml) to remove any uncomplexed metal ions present in the zeolite. Then it was filtered, made free of chloride ions by washing with distilled water. The zeolite-encapsulated complex thus obtained was stored in vacuum over anhydrous calcium chloride after drying at 100°C for two hours. Further details with regard to the synthesis of encapsulated complexes are given in the respective chapters.

2.5. REAGENTS FOR CATALYTIC ACTIVITY STUDIES

Phenol (Merck), cyclohexanol (Merck), hydrogen peroxide (30% aqueous solution, E.Merck) and tert-butyl hydroperoxide (Merck, 70%) were used for catalytic studies. The solvents used for these studies were either of 99% purity or purified by known laboratory procedures. The experimental setup and the results of these catalytic studies are presented in the relevant chapters.

2.6. CHARACTERIZATION METHODS

The synthesis of the transition metal complexes inside the zeolite pores pose many important questions regarding their stability, retention of the zeolite framework, extent of encapsulation etc. In order to get a correct picture of the distribution of the metal complex within the zeolite framework and a clear understanding of the extent to which encapsulation has taken place, various analytical and physico-chemical techniques have been employed. The details of these techniques are presented in this chapter.

2.6.1. Elemental analysis

2.6.1.1. CHN analysis

Microanalysis for carbon, hydrogen and nitrogen in the synthesized ligands, neat complexes and encapsulated complexes were done on an Elementar model Vario EL III at SAIF, Sophisticated Test and Instrumentation Centre, Kochi. These results give an idea about the composition of the ligands and complexes and provide a method to determine the presence of uncomplexed metal ions in the lattice structure.
2.6.1.2. Analysis of Si, Al, Na and transition metal ion in the zeolite sample

A small amount of the zeolite sample was accurately weighed (w) and taken in a beaker. About 40ml of conc. H₂SO₄ was added and heated strongly. It was then cooled, diluted with water (200 ml) and filtered using an ashless filter paper. The filtrate was collected in a standard flask. The residue was heated in a platinum crucible, cooled and weighed (w₁). Hydrofluoric acid was then added in drops and heated strongly to dryness to remove silica as H₂SiF₆. This process was repeated three to four times. The remaining solid was then ignited to 800°C for about 1 hour, cooled and weighed (w₂). The amount of silica present in the sample can be calculated using the equation:

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

The residue in the crucible was treated with potassium persulphate and fused till a clear melt was obtained. It was dissolved in water and combined with the earlier filtrate collected in the standard flask. The metals present in this solution were determined by ICP-AES method. The Si to Al ratio provides the unit cell formula and the ion exchange capacity of the zeolite. The comparison of the ratio of the encapsulated complexes with that of the pure zeolite shows the retention of the zeolite framework after encapsulation.

2.6.2. Surface area and pore volume analysis

The surface areas of the synthesized complexes were measured to ensure whether encapsulation of metal complexes had occurred and the knowledge of surface area values provide important applications in catalytic studies. The surface areas of the samples were determined by the multipoint BET method₁⁰ of nitrogen adsorption at liquid nitrogen temperature using ‘Micromeritics Gemini 2360 surface area analyzer’. This method involves the measurement of the amount of gas adsorbed by the respective samples. Initially a very small amount of the sample is accurately weighed and taken in a clean dry sample tube. This was heated to about 473 K and kept at this temperature for about 3 hours in an atmosphere of nitrogen gas. The volatile impurities on the surface of the catalyst were completely removed by the heat treatment. Then the sample was allowed to cool to room temperature and again the sample tube containing the
complex was weighed. The sample was kept fixed in the instrument and cooled to very low temperature of about 77 K using liquid nitrogen. The adsorption of nitrogen on the surface of the sample lowers the pressure inside the chamber and equilibrium is established between the adsorbed gas and the free gas phase. The BET equation used for calculating the surface area is

\[
P / V (P_0 - P) = \frac{1}{V_m C} + \frac{(C-1) P}{V_m C P_0} \text{ where}
\]

- \( P \) = volume of the gas adsorbed at relative pressure \( P/P_0 \)
- \( V \) = volume of the gas in the monolayer
- \( V_m \) = saturation vapour pressure of the adsorbate
- \( P_0 \) = BET constant which is related to the heat of adsorption

The plot of the left side of the BET equation against \( P/P_0 \) gives a straight line with slope \((C-1) / V_m C\) and intercept \(1 / V_m C\). The volume of gas in the monolayer, \( V_m \), can be obtained from these values and hence the number of moles of nitrogen adsorbed \( (X_m) \) can be calculated. BET surface area is calculated using the equation,

\[
S_{\text{BET}} = X_m N A_m 10^{-20} \text{ where } N = \text{Avogadro number and } A_m = \text{cross sectional area of the adsorbate molecule.}
\]

The equation used for calculating the total pore volume of the sample is \( V_{\text{tot}} = V.D \) where \( D = \text{density conversion factor.} \)

2.6.3. X-ray diffraction analysis

The X-ray diffraction patterns of the parent zeolite, ion exchanged zeolite and encapsulated complexes were recorded to know their crystalline nature. The comparisons of these diffraction patterns enable us to tell whether any changes occur in the internal crystalline structure of the zeolite upon encapsulation. The X-ray diffractometer used to study the sample is Bruker AXS D8 advance diffractometer. The apparatus consists of a stationary X-ray source, Ni filtered radiation with wavelength 1.5404 Å and a movable detector to scan the intensity of the diffracted radiation as a function of the angle 2θ between the incident and the diffracted beam.
2.6.4. Thermogravimetric analysis

Thermogravimetric analysis is an effective tool to study the nature of decomposition of the metal complexes. In this technique, the sample under consideration is heated at a controlled rate in an atmosphere of nitrogen and the weight loss of the substance is recorded as a function of temperature. The major advantage of this method is that it can directly give an idea about the thermal stability of a material. The thermograms obtained are characteristic for a given sample due to the unique sequence of physico-chemical reactions occurring over definite temperature ranges, which in turn depends upon the structure of the molecule. The changes in weight occur as a result of the rupture or formation of various physical and chemical bonds at elevated temperatures. This may lead to the evolution of volatile products or the formation of heavier reaction products. TG analyses were carried out on a Perkin Elmer, Diamond TG/DSC at a heating rate of 10°C per minute in an atmosphere of nitrogen.

2.6.5. SEM analysis

Scanning electron microscopy analysis of the zeolite encapsulated complexes before and after soxhlet extraction was done using JEOL-JSM-840A SEM. It reveals the presence of materials adsorbed on the surface of the support and the morphological changes associated with encapsulation. A narrow beam of electrons from a tungsten filament is passed through the sample. In order to protect the zeolite sample from surface charging and thermal damage due to collision with electron beam, a thin film of gold is coated over them. The amount of back-scattered or secondary radiation is noted as a function of the primary beam. The major advantage of this method is its ability to give a picture of the effectiveness of soxhlet extraction in removing the substances adsorbed on the surface.

2.6.6 Infrared spectra

The IR spectra provide valuable information regarding the structure of the complex and the nature of the functional groups present. Hence it can be used as an effective tool to confirm the formation of the complexes within the zeolite pores and to
detect the coordination of ligands to the transition metals. Infrared spectra of the ligands, simple complexes and the metal encapsulated complexes in the region 4000-400 cm\(^{-1}\) were recorded using Shimadzu 8000 Fourier Transform Infrared Spectrophotometer. Each zeolite encapsulated complex exhibits a characteristic IR pattern\(^{13}\) and these vibrations are observed in the region 1250-400 cm\(^{-1}\). The shift of characteristic bands on chelation is sometimes masked by the well-defined strong bands of zeolite.

2.6.7. Electronic spectra

The diffuse reflectance spectra were recorded at room temperature in the range 250-850 nm using Ocean Optics, Inc.SD 2000, Fiber Optic Spectrometer with a charged coupled device (CCD) detector. Sodium exchanged zeolite, NaY is used as the blank for zeolite samples. The spectra were computer processed and plotted as percentage reflectance versus wavelength. To get the spectra in the absorbance mode, one has to apply Kubelka-Munk equation, which is as follows.

\[
\log \left( \frac{(1 - r_a)^2}{2r_a} \right) = \log k - \log S
\]

Here \( r_a = R_a\) (sample) / \( R_a\) (standard)

\( R_a \) (sample) is the diffuse reflectance of the sample and \( R_a \) (standard) is taken as 1. \( K \) is the absorption coefficient and \( S \) is the scattering coefficient. The Kubelka-Munk factor, \( F(R) = (1 - r_a)^2/2r_a = K/S \). The plot of \((1-r_a)^2/2r_a\) as a function of wavelength gives the absorption curve.

2.6.8. EPR spectra

The EPR spectra of the powdered zeolite encapsulated complexes in DMF were recorded at liquid nitrogen temperature and the standard used was tetracyanoethylene (TCNE) with \( g \) value of free electron = 2.0027. The EPR spectra of transition metal complexes contain a wealth of information about their electronic structures. The degeneracy of the d orbitals and the presence of the unpaired electrons give rise to orbital contributions as a result of which anisotropic \( g \) values are obtained.
2.7. CATALYTIC STUDIES

2.7.1. Gas Chromatography

The analysis of the reactants and products of the different catalytic reactions was conducted using a Chemito 8510 Gas Chromatograph. The various components in the reaction mixture were separated using an SE-30 column. The peaks appearing on the recorder are characteristic of the different components and the peak area is found to be proportional to the amount of the component present in the mixture.
References


