Chapter-2 Experimental
2.1 INTRODUCTION

A Schiff base ligand, which was formally reported by Hugo Schiff in 1864, is an azomethine group containing compounds with the general formulae RHC=N–R’, where R and R’ are alkyl, aryl, cycloalkyl or heterocyclic groups. The Schiff base ligands are generally synthesized by the simple condensation of carbonyl compounds and the primary amines at suitable reaction condition in an appropriate solvent. The presence of lone pair electrons in sp² hybridized orbital of azomethine nitrogen imparts an outstanding chelating ability of Schiff base ligand, particularly when one or more donor atoms are present next to the azomethine group.

These active binding sites of the Schiff base ligand can easily coordinate with the various transition metal ions and can form active coordination complexes which can be used as a homogeneous catalyst for the various catalytic transformations due to its attractive chemical and physical properties. Consequently, most of the chemical industries utilize chemical products which deal with catalysts directly or indirectly during their manufacturing, thus making the catalysis field indispensable for the needs of modern society.

In this context, heterogenization of homogeneous catalyst seeks utmost attention as it confines the leaching of toxic metal ions in the products, easily recyclable, highly stable, can operate at severe conditions and can be reused over and over again. Nowadays, numbers of solid supports such as polymers, various types of silica, multi-wall carbon nanotube (MWCNTs), zeolite-Y, metal-organic frameworks (MOFs), and magnetic supports are being used for the purpose of heterogenization of homogeneous metal complexes.

Out of these inclusive options, zeolite-Y is found to be superlative supports and incisive choice for the metal complex encapsulations. Once an active metal complex formed inside the ordered supercages of zeolite-Y, it impedes the diffusion of metal complexes from the supercages, which minimize the possibility of toxic metal ion leaching into the final products.

In view of the above facts and consideration, in the present research work, the corresponding zeolite-Y encapsulated complexes (heterogeneous catalysts) are synthesized, well-characterized, and scrutinized as heterogeneous catalyst along
with the homogeneous Co(II), Cu(II), Fe(II), Mn(II), VO(IV), Ni(II), Fe(III), and Ru(III) complexes of H₂hacen, H₂chacen, H₂saliden, and H₂nsaldien ligands to understand the shielding effect of zeolite-Y over the active metal complexes, and to compare the activity and selectivity of the complexes for various catalytic transformations.

2.2 MATERIALS

All chemicals such as 2-hydroxyacetophenone, 5-chloro-2-hydroxyacetophenone, 2-hydroxybenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde, ethylene diamine, diethylene triamine, methanol, acetone, chloroform, CCl₄, ethanol, DMF, DMSO, acetonitrile, 1,2-Dichloroethane, n-hexane, dioxane, VOSO₄·5H₂O, FeSO₄·7H₂O, CuSO₄·5H₂O, CoSO₄·7H₂O, NiSO₄·6H₂O Mn(CH₃COO)₂·4H₂O, RuCl₃·3H₂O, Fe(NO₃)₃·9H₂O, 70% t-butylhydroperoxide (TBHP), 30% H₂O₂, cyclohexene, styrene, benzene, R-(+)-limonene, α-pinene, phenol, benzyl alcohol, cyclohexane and cyclooctane were purchased from Sigma Aldrich, Rankem (India), Otto Chemie and Hi-media with the maximum purity available and used as received unless otherwise specified.

The sodium form of zeolite-Y (Si/Al = 5.62) was procured from Hi-media, India. Generally, the pores of hydrophilic zeolites are filled by physically and chemisorbed water molecules which may reduce the possibility of complexes encapsulation into the supercages of zeolite-Y. In view of the above, pure zeolite-Y was dehydrated overnight at 150 °C prior to the modification processes such as ion exchange and metal complex encapsulation.³⁴

2.3 SYNTHESIS SECTION

2.3.1 Synthesis of Schiff base ligands

2.3.1.1 Synthesis of tetradeutate binegative ligands (H₂hacen and H₂chacen)

A dropwise addition of the methanolic solution of ethane-1,2-diamine (13 mmol, 0.844 ml) into a separately prepared methanolic solution (30 ml) of o-hydroxyacetophenone (26 mmol, 3.85 g) and/or 5-chloro-2-hydroxyacetophenone (26 mmol, 4.50 g) leads to the formation of ligands H₂hacen and H₂chacen, respectively. The progress of the reaction was tested by thin layer chromatography (TLC) using methanol : chloroform (6:4) solvent system. Once the reaction was completed (3 hrs, 60 °C), the product was filtered, thoroughly washed with methanol and then dried for 4 hrs. The purified product, H₂hacen and H₂chacen (Figure 2.1)
were crystallized with chloroform, dioxane and acetone. The purity and the structure of the both Schiff base ligands were inveterate by the spectroscopic techniques such as CHN analysis, FTIR, $^1$H NMR, $^{13}$C NMR and UV-Vis spectroscopy (Section 3.2).

![Figure 2.1](image)

**Figure 2.1** Synthesis route of tetradeionate binegative ligands H$_2$hacen and H$_2$chacen.

### 2.3.1.2 Synthesis of pentadentate binegative ligands (H$_2$saldien and H$_2$nsaldien)

2-hydroxybenzaldehyde and/or 2-hydroxy-5-nitrobenzaldehyde of two molar ratios were dissolved in methanol in a two-neck round bottom flask and refluxed for 15 minutes. Subsequently, one molar ratio of diethylene triamine was added dropwise and refluxed again for 1 h at 70 °C. The movement of the reaction was verified by using TLC with the methanol : chloroform (6:4) solvent system. Once the reaction was completed, the excess of methanol was evaporated and an oily reddish product was obtained in the case of H$_2$saldien ligand. In case of H$_2$nsaldien ligand, a red crystalline solid product was filtered and washed with methanol and dried in air. The purity and structure of H$_2$saldien and H$_2$nsaldien (Figure 2.2) were confirmed using FTIR, CHN analysis, $^1$H NMR, $^{13}$C NMR and UV-Vis spectroscopic techniques (Section 3.2).
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**Figure 2.2** Synthesis pathway of pentadentate binegative ligands H$_2$saldien and H$_2$nsaldien.

### 2.3.2 Synthesis of neat transition metal complexes (Homogeneous catalysts)

#### 2.3.2.1 Synthesis of neat transition metal [Cu(II), Co(II), Mn(II), Ni(II), Fe(II), and VO(IV)] complexes bearing H$_2$hacen and H$_2$chacen ligands

**a) Synthesis of neat metal complexes of Cu(II) and Co(II)**

A dropwise addition of the aqueous metal salt (1.3 mmol CoSO$_4$·7H$_2$O and/or CuSO$_4$·5H$_2$O) solution to a 25 ml of an ethanolic H$_2$hacen and/or H$_2$chacen (2.6 mmol) solution leads to the formation of neat metal complexes instantly (Figure 2.3 and 2.4). The subsequent mixture was heated at 80 °C in a water bath for 4 hrs. After cooling, the solid product was isolated by vacuum filtration and dried under vacuum for overnight at 60 °C.

**b) Synthesis of neat metal complexes of Ni(II)**

The aqueous solution of NiSO$_4$·6H$_2$O (1.3 mmol) was added to a 25 ml of the methanolic solution of the H$_2$hacen and/or H$_2$chacen (1.3 mmol). The resulting reaction mixture (pH was adjusted for maximum complexation) was heated with stirring at 60 °C on a water bath for 4 hrs (Figure 2.3 and 2.4). After cooling, the solid product was isolated by vacuum filtration and dried under vacuum for overnight at 60 °C.

**c) Synthesis of neat metal complexes of Mn(II)**

A methanolic solution of Mn(CH$_3$COO)$_2$·4H$_2$O (1.3 mmol) was added to the methanolic solution of H$_2$hacen and/or H$_2$chacen (1.3 mmol) under stirring.
conditions. After addition, the pH of the reaction mixture was adjusted at 5-6 and then refluxed for 3 hrs (Figure 2.3 and 2.4). The solid product was obtained after the evaporation of solvent; subsequently, it was crystallized with chloroform, methanol, and acetone.
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Figure 2.4 Synthesis pathway of Co(II), Cu(II), Fe(II), Mn(II), Ni(II) and VO(II) complexes of ligand H,chacen.
d) *Synthesis of neat metal complexes of Fe(II) and VO(IV)*

Initially, 1.13 mmol of H$_2$hacen and/or H$_2$chacen was dissolved in 15 ml of acetone in round bottom flask, and then the aqueous metal salt solution of VOSO$_4 \cdot 5$H$_2$O and/or FeSO$_4 \cdot 7$H$_2$O (1.13 mmol) was added dropwise into it. The pH of the resulting solution was adjusted to 5–6 by dropwise addition of CH$_3$COONa solution in the reaction media. The resultant reaction medium was stirred and refluxed for 4 hrs (Figure 2.3 and 2.4). After cooling, the solid product was separated by filtration and dried under vacuum for overnight at 60 °C.

2.3.2.2 *Synthesis of neat transition metal [Fe(III) and Ru(III)] complexes of H$_2$saldien and H$_2$nsaldien ligands*

a) *Synthesis of neat metal complexes of Fe(III) and Ru(III)*

As shown in figure 2.5, the neat metal complexes of Fe(III) and Ru(III) were synthesized by the addition of a methanolic metal salt solution (1.25 mmol of RuCl$_3 \cdot 3$H$_2$O and/or Fe(NO$_3$)$_3 \cdot 9$H$_2$O) to the well stirred methanolic solution of the H$_2$saldien and/or H$_2$nsaldien (1.25 mmol) ligands. The resulting reaction medium was refluxed with continuous stirring on a water bath for 4 hrs. The obtained solid product was filtered, washed with methanol, recrystallize with chloroform, and then finally dried under vacuum at 60 °C.

2.3.3 *Synthesis of transition metal exchanged zeolite-Y (Heterogeneous catalysts)*

2.3.3.1 *Synthesis metal exchanged M(II/IV)-Y [Co(II), Co(II), Fe(II), Mn(II), Ni(II) and VO(IV)]*

Various transition metal-exchanged zeolite-Y were synthesized by the well-known conventional ion-exchange method. As an extremely concentrate (1 M) metal salt solution may cause dealumination in the zeolite-Y framework, a lower concentrate metal salt aqueous solution (3 mmol of VOSO$_4 \cdot 5$H$_2$O, FeSO$_4 \cdot 7$H$_2$O, CuSO$_4 \cdot 5$H$_2$O, CoSO$_4 \cdot 7$H$_2$O, NiSO$_4 \cdot 6$H$_2$O and Mn(CH$_3$COO)$_2 \cdot 4$H$_2$O in 500 ml deionized water) having 4-4.5 pH was refluxed at 90 °C for 24 hrs with 5.0 g of pure zeolite-Y (Figure 2.6). The resultant slurry was filtered and washed with deionized water to eradicate any free metal ion (each filtrate was tested by AAS) on the exterior surface of the zeolite-Y and then dried overnight at 120 °C.
Figure 2.5: Synthesis pathway of Fe(III) and Ru(III) complexes bearing H-saldien and H-psaldien ligand.
Figure 2.6 Synthesis pathway of metal exchanged zeolite-Y and zeolite-Y encapsulated complexes of Co(II), Co(II), Fe(II), Mn(II), Ni(II) and VO(IV) of $H_2$hacen and/or $H_3$hacen ligands
2.3.3.2 Synthesis metal exchanged M(III)-Y [M=Fe(III) and Ru(III)]

A mixture of 6 g of the zeolite-Y and 1 mmol of RuCl$_3$·3H$_2$O (0.242 g) and/or Fe(NO$_3$)$_3$·9H$_2$O (0.403 g) were taken in 500 ml of deionized water and then stirred under reflux at 90 °C for 16 hrs (Figure 2.7). The pH of the reaction medium was adjusted within 4.0–4.5 using buffer tablets in order to avert the formation of respective metal hydroxides. The slurry was then filtered, washed with deionized water to take out the excess of metal ions (inveterate by AAS), chlorides, and/or nitrate ions, and finally dried overnight in an oven at 100–120 °C.

2.3.4 Synthesis of zeolite-Y encapsulated transition metal complexes (Heterogeneous catalysts)

As mention in chapter 1 section 1.3.4.1, zeolite-Y encapsulated transition complexes were synthesized by the ‘flexible ligand’ method. A stoichiometric excess amount (about 6 mmol) of the H$_2$hacen and/or H$_2$chacen, which can diffuse through the supercages of zeolite-Y, was refluxed with 1 g of pre-metal exchanged zeolite-Y (Co(II)-Y, Co(II)-Y, Fe(II)-Y, Mn(II)-Y, Ni(II)-Y and VO(IV)-Y) in chloroform (30 ml) for 16 hrs (Figure 2.6), whereas in the case of Ru(III) and Fe(III) encapsulated complex synthesis (Figure 2.7), a 1 g of activated Ru(III)-Y and/or Fe(III)-Y were refluxed for 16 hrs with methanolic solution of H$_2$saldien and/or H$_2$nsaldien (3 mmol). The change in the color of solid mass after reaction gives preliminary clue about the formation of complexes inside the supercages of zeolite-Y. After completion of the reaction, the slurry was filtrated, washed frequently with deionized water, and then pensively stirred for 6 hrs in an aqueous solution of 0.01 M NaCl to consent the exchange of uncomplexed transition metal ions by Na$^+$ ions. The resultant slurry was again washed with deionized water until the filtrate was free from chloride ions and dried overnight at 140 °C.

Furthermore, to remove the unreacted excess ligands and the complexes formed on the surface of the zeolite-Y, the resultant slurry were further purified by Soxhlet extractor using various solvents such as methanol, acetonitrile, chloroform, and DMF until a colorless filtrate was obtained in each case. Finally, the products were dried under vacuum and kept in a muffle furnace overnight at 140–150 °C to obtain anhydrous zeolite-Y encapsulated transition metal complexes.

Figure 2.7 Synthesis pathway of metal exchanged zeolite-Y (Fe(III)-Y and Ru(III)-Y) and zeolite-Y encapsulated complexes of Fe(III) and Ru(III) bearing H$_2$saldien and/or H$_3$nsaldien ligand.
2.4 PHYSICO-CHEMICAL TECHNIQUES

The various physicochemical methods have been employed to characterize the structure of Schiff base ligand, neat transition metal complexes, transition metal exchanged zeolite-Y, and zeolite-Y encapsulated transition metal complexes. A brief account of these methods in the present research work is discussed as below:

2.4.1 Elemental analysis (CHN Analyzer)

The microanalysis for carbon, hydrogen, and nitrogen in the synthesized Schiff base ligands, neat transition metal complexes, and their respective zeolite-Y encapsulated transition metal complexes were carried out using Perkin Elmer, USA 2400-II CHN Elemental analyzer at Central Salt and Marine Chemical Research Institute (CSMCRRI), Bhavnagar, Gujarat.

2.4.2 Elemental analysis (ICP-OES)

The quantitative analysis of Si, Al, Na and the transition metal ions of neat transition metal complexes, transition metal exchanged zeolite-Y, and zeolite-Y encapsulated transition metal complexes was carried out by inductive coupled plasma optical emission spectrometry (ICP-OES) using a model PerkinElmer Optima 2000DV at Central Salt and Marine Chemical Research Institute (CSMCRRI), Bhavnagar, Gujarat. The sample solution for analysis of zeolite-Y based materials (10 mg sample was taken) was prepared using 25 ml of 1% of HF solution. With help of ICP-OES analysis, we were able to find out the % loading of transition metal ion in zeolite-Y framework upon modification processes such as ion exchange and metal complex encapsulation.

2.4.3 BET Surface area and pore volume analysis

Brunauer-Emmett-Teller (BET) analysis provides detailed specific surface area evaluation of zeolite-Y based porous materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. The technique includes external surface area and pore volume evaluations to determine the total specific surface area in m²/g. The pure zeolite-Y porous material, which is used as a host material for the guest metal complex in the present research work, can adsorb more quantity of nitrogen gas due to their high surface areas of several hundred m² g⁻¹. However, due to the loading of large transition
metal complexes into the supercages of zeolite-Y, the nitrogen adsorption capacity of these materials decreases hypothetically and results into a lowering of the surface areas and the pore volume of modified zeolite-Y materials.

In the present work, the BET surface area analysis of zeolite-Y base materials was carried out using Micromeritics, ASAP2010 surface area analyzer at Central Salt and Marine Chemical Research Institute (CSMCRI), Bhavnagar, Gujarat and Laxmi Analytical Laboratories, Mumbai to confirm whether the complex has encapsulated or not into the supercages of zeolite-Y. Prior to the BET measurements, all the zeolite-Y based materials were de-gasified at 110 °C for 2 hrs to remove any adsorbed gasses.

2.4.4 Powder X-ray diffraction studies (XRD)

Powder X-ray diffraction (XRD) is an analytical technique principally used for powder or crystalline materials to get the information of unit cell dimensions of materials. The powder XRD of zeolite-Y and modified zeolite-Y materials was carried out using Bruker AXS D8 advance X-ray powder diffractometer with a CuKα (λ=1.54058) target and movable detector, which scans the intensity of diffracted radiation within the range of 5–70° as a function of the angle 2θ between the incident and diffracted beams, at Department of Metallurgical and Materials Engineering, The M. S. University of Baroda, Gujarat.

In the present research work, the powder XRD was employed for zeolite-Y base materials such as transition metal exchanged zeolite-Y and zeolite-Y encapsulated complexes to check whether the transition metal exchange and/or metal complex encapsulation does impact on crystallinity and morphology of pure zeolite-Y or not.

2.4.5 Scanning electron microscope (SEM)

SEM analysis is appropriate for obtaining highly magnified real-space images from a highly irregular structure. The formation of metal complexes is basically targeted inside the supercages of zeolite-Y; however, the possibility of some uncoordinated ligands and the surface metal complex on the peripheral surface of zeolite-Y encapsulated metal complexes cannot be excluded. The presence of such redundant particles and the effective removal of such particles (by soxhlet extraction) from the external surface zeolite-Y was confirmed by SEM image taken before and
after the soxhlet extraction of materials by SEM instrument (model-JSM-5610LV), JEOL at Central Salt and Marine Chemical Research Institute (CSMCR), Bhavnagar.

2.4.6 Fourier transform infrared spectroscopy (FTIR)

FTIR of Schiff base ligands, neat metal complexes, and zeolite-Y based materials was recorded using IRPrestige-21, Shimadzu FTIR spectrometer at Department of Chemistry, M. K. Bhavnagar University, Gujarat.

In the present research work, this technique was mainly used to follow coordination of Schiff base ligands with transition metal ions to identify various functional groups, and to confirm the complex encapsulation into the supercages of zeolite-Y without disturbing the integrity of zeolite-Y framework.

2.4.7 Electronic spectroscopy (UV-Vis)

Electronic absorption spectra of Schiff base ligands, neat metal complexes, and zeolite-Y based materials (metal exchanged and encapsulated complexes) were carried by UV-1800, Shimadzu UV-Vis spectrometer using quartz cell of 1 cm³ optical path at Department of Chemistry, M. K. Bhavnagar University, Gujarat. Electronic absorption spectra of zeolite-Y encapsulated complexes and metal exchanged zeolite-Y were recorded in solution which has been prepared according to the method reported by P. Lainé et al (10 mg sample + 200 μL of 10% HF + 50 ml distilled water). However, the electronic spectra of Schiff base ligands, and neat metal complexes were mainly recorded in methanol as a solvent.

2.4.8 Thermogravimetric analysis (TGA)

TGA is a method of thermal analysis in which changes in physical and chemical properties of materials or compounds are measured as a function of increasing temperature with the constant heating rate. The TG analysis of Schiff base ligands, neat metal complexes, and zeolite-Y based materials was carried out at an air atmosphere in the temperature range 30–700 °C using Shimadzu TGA-50 Instrument at Department of chemistry, The M. S university of Baroda, Gujarat.

In the present research work, this technique was employed to understand the decomposition pattern (stability) of Schiff base ligands and their respective neat metal complexes, whereas, decomposition stage in zeolite-Y based materials due to loss of physically and chemisorbed water, and the loaded metal complexes, if present, (at high temperature) was measured with the help of TG analysis.
2.4.9 Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (¹H- & ¹³C-NMR) spectra of Schiff base ligands were recorded using CDCl₃ (¹³C-NMR) and MEOD (¹H-NMR) as a solvent and TMS as an internal standard on a model Varian-Gemini (200 MHz) instrument at Central Salt and Marine Chemical Research Institute (CSMCRI), Bhavnagar. An aim of using this technique for Schiff base ligands was to determine the exact structure of Schiff base ligands.

2.4.10 Molar conductivity

According to the Warner’s theory, the neat transition metal complexes can behave as an electrolyte in an appropriate solvent if it possesses ionizable counter anions (primary valency) outside the coordination sphere of the complexes. In the present research work, to find out whether the synthesized neat transition metal complexes have electrolytic nature or not, the molar conductivity of each neat metal complexes were measured in DMSO as solvent using Metrohm 712 Conductometer at Department of Chemistry, M. K. Bhavnagar University, Gujarat.

2.4.11 Magnetic susceptibility

The magnetic properties of the neat metal complexes were measured with a magnetic susceptibility balance of models Johnson Matthey and Sherwood at Department of Physics, M. K. Bhavnagar University, Gujarat.

2.4.12 Melting point apparatus

The melting point of Schiff base ligand and neat metal complexes was determined with Griffin Melting Point apparatus and were uncorrected at Department of Chemistry, M. K. Bhavnagar University, Gujarat.

2.4.13 Gas chromatography (GC) and Gas Chromatograph with Mass Spectrometer (GC-MS)

The catalytic oxidation of organic substrates by utilizing synthesized homo- and heterogeneous catalysts was undertaken and the progress of the catalytic reaction was checked quantitatively and qualitatively by GC and/or GC-MS as a function of time by withdrawing small aliquots after certain time intervals. Catalytic reaction products were quantitatively evaluated by using gas chromatograph (GC) Agilent 7890 fitted with FI detector and HP-5 phenylmethylsilicon capillary column.
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(30 m x 330 pm x 0.25 mm) at Patel Ana Lab, Chhani Jakat Naka, Baroda. Moreover, possible catalytic reaction products were identified using GC-MS (Shimadzu, QP-2012) having a BP-5 capillary column (30m × 0.25 mm × 0.25 m) 95% silicoxane surface and FID detector at Laxmi Analytical Laboratories, Mumbai and SICART-Charutar Vidya Mandal (CVM), Vallabh Vidyanagar.

2.4.14 Atomic absorption spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is a spectroanalytical method for the quantitative determination of chemical elements using the absorption of optical radiation by free atoms in the gaseous state. In the present research work, the mixture of catalytic crude products after catalytic reaction was filtered for recycling the heterogeneous zeolite-Y based catalyst and subsequently, the filtrate was checked by AAS of model PerkinElmer 4100-1319 to confirm whether the leaching of transition metal ions from the heterogeneous catalysts occur or not.

2.4.15 Thin layer chromatography (TLC)

TLC was used to track the movement of the reaction and the purity of the Schiff base ligands using methanol : chloroform (6 : 4) as a mix solvent system. TLC of Schiff base ligands was performed on silica gel (Merck, India) using mixed solvent (methanol + chloroform, 6 : 4) system.

2.4.16 Soxhlet extractor

After the synthesis of the zeolite-Y encapsulated transition metal complexes, the uncoordinated ligands and the exterior metal complexes must be removed effectively to avoid the leaching of metal complexes and ligands during the catalytic activity. Consequently, each zeolite-Y encapsulated transition metal complexes was extensively purified by the soxhlet extractor (ASGI glassware) using various solvents such as methanol, acetonitrile, chloroform, and DMF before their catalytic study.

2.3.17 Oil bath for catalytic study

The catalytic activity of synthesized homo- and heterogeneous catalyst was scrutinized over oxidation reaction and these catalytic reactions were carried out using DBK Digital Multi Magnetic Stirrer at Department of Chemistry, M. K. Bhavnagar University, Gujarat.
REFERENCES

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