

Chapter 2:

**Experimental and Theoretical Methods and
Characterization Techniques**

This chapter deals with the details of the materials and experimental methodologies, which have used to synthesize M(II) Schiff-base complexes in free-state as well as in encapsulated states, their characterization and catalytic applications. To characterize these systems, several techniques are employed, such as energy dispersive X-ray analysis (EDX), atomic absorption spectroscopy (AAS), X-ray photoelectron spectroscopy (XPS), Powder X-ray diffraction (XRD), BET, thermo gravimetric analysis (TGA), scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectroscopy, Solid and solution phase UV-Visible spectroscopy and magnetic susceptibility measurement (SQUID). Catalytic studies of these hybrid systems are performed with the help of gas chromatography (GC). Furthermore, theoretical study is also performed to have better understanding about the electronic structure of the metal complexes both in ‘free’ as well as encapsulated states.

2.1 MATERIALS

The following chemicals summarized in Table 2.1 are used to pursue the current thesis work.

Table 2.1. List of the chemicals used in current thesis along with the name of their suppliers.

S.No.	Chemicals	Name of Supplier
1	Parent zeolite-NaY	Sigma-Aldrich, India
2	Nickel acetate	S.D. Fine, India
3	Palladium acetate	TCI chemicals, India
4	Copper acetate	S.D. Fine, India
5	Cobalt acetate	S.D. Fine, India
6	o-phenylenediamine	S.D. Fine, India
7	m-phenylenediamine	Sigma-Aldrich, India
8	Salicylaldehyde	Merck
9	5-Hydroxy-salicylaldehyde	Sigma-Aldrich, India
10	5-Bromo- salicylaldehyde	Alfa-aecer
11	5-Methyl-salicylaldehyde	Sigma-Aldrich, India
12	5 -Methoxy-salicylaldehyde	Sigma-Aldrich, India

13	5-Nitro-salicylaldehyde	Sigma-Aldrich, India
14	Sodium chloride	Molychem
15	Silver nitrate	Spectrochem
16	Ethanol	S.D. Fine, India
17	Methanol	S.D. Fine, India
18	Acetone	S.D. Fine, India
19	Diethyl ether	S.D. Fine, India
20	Acetonitrile	S.D. Fine, India
21	N, N-Dimethylformamide	S.D. Fine, India
22	Styrene	Alfa-aecer
23	Hydrogen peroxide	Merck
24	Sodium carbonate	RANKEM
25	Styrene oxide	Alfa-aecer
26	Bromobenzene	Alfa-aecer
27	Rhodamine B	SDFCL
28	Barium Sulphate	Wako
29	Potassium bromide	SDFCL

2.2 EXPERIMENTAL METHODS

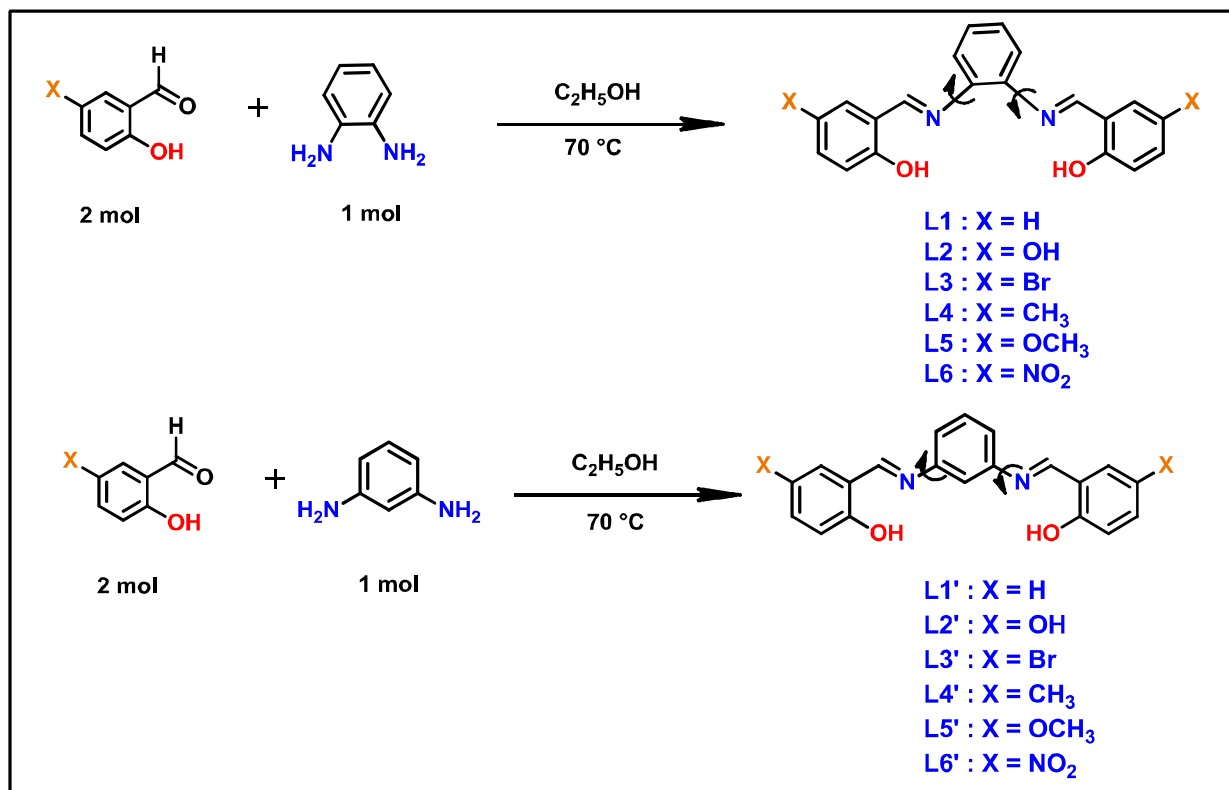
2.2.1 Synthesis of Schiff-base ligands (L1, L2, L3, L4, L5, L6)¹:

The Schiff-base ligands are prepared by the following literature report. 10 mmol of 1,2-phenylenediamine and 20 mmol of salicylaldehyde or its derivatives are refluxed at 70 °C for 4 h in ethanol. At the end of the reaction, the product is filtered out, washed thoroughly with ethanol and finally air-dried (shown in Scheme 2.1).

2.2.2 Synthesis of Schiff-base ligands (L1', L2', L3', L4', L5', L6')²:

In a round bottom flask, 10 mmol of 1,3-Phenylenediamine, 20 mmol of salicylaldehyde or its derivatives in ethanol are mixed with constant stirring at 70 °C for 4 h. After the end of the reaction, the yellow solid

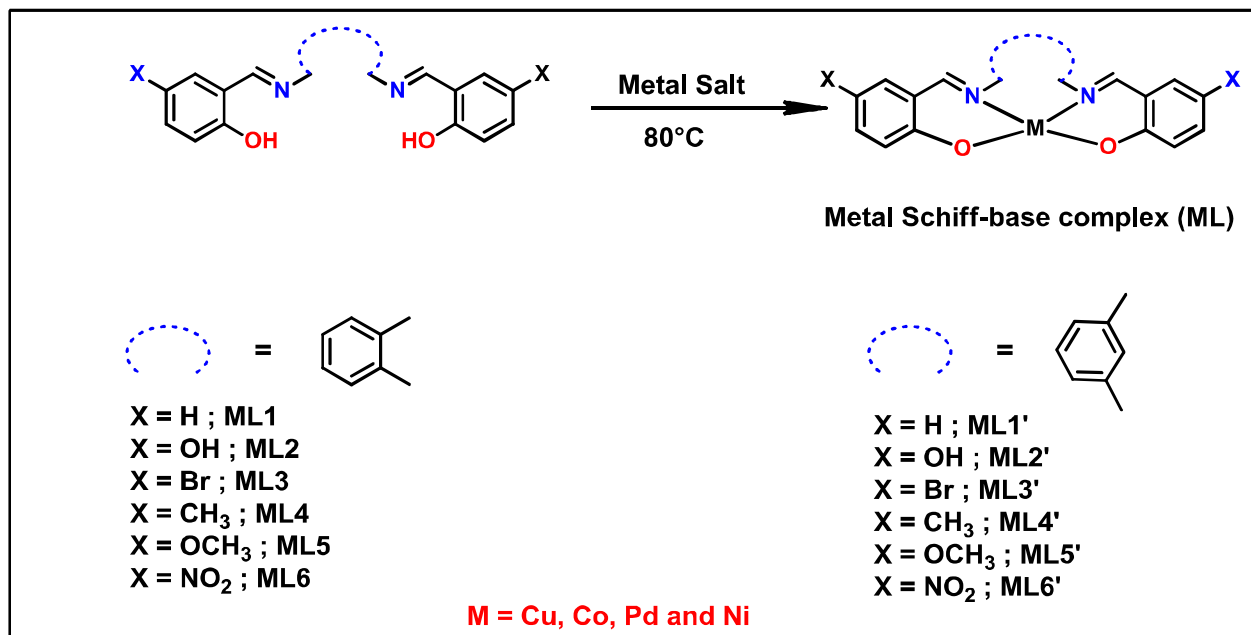
product is vacuum filtered, washed with ethanol and finally dried at room temperature (shown in Scheme 2.1). The purity and structure of the compound is analyzed by recording its melting point, FT-IR and UV-Vis spectroscopies.



Scheme 2.1: Synthesis of Schiff base Ligand L1, L2, L3, L4, L5, L6, L1', L2', L3', L4', L5' and L6'.

2.2.3 Synthesis of Metal (Cu, Co, Pd and Ni) Schiff-base complexes²:

To synthesize the metal Schiff base complex, an ethanolic solution of the ligand is heated at 80°C for 30 minutes and metal salt is added in a 1:1 ligand to metal molar proportion. The reaction mixture is refluxed for 3 h. To synthesize ML₂' Schiff-base complex, N, N-dimethylformamide (DMF) is used as solvent. The solid metal Schiff base complex is washed with ethanol and finally dried. All the metal complexes are synthesized following same procedure (presented in Scheme 2.2).



Scheme 2.2 : Synthesis of metal Schiff base Complexes.

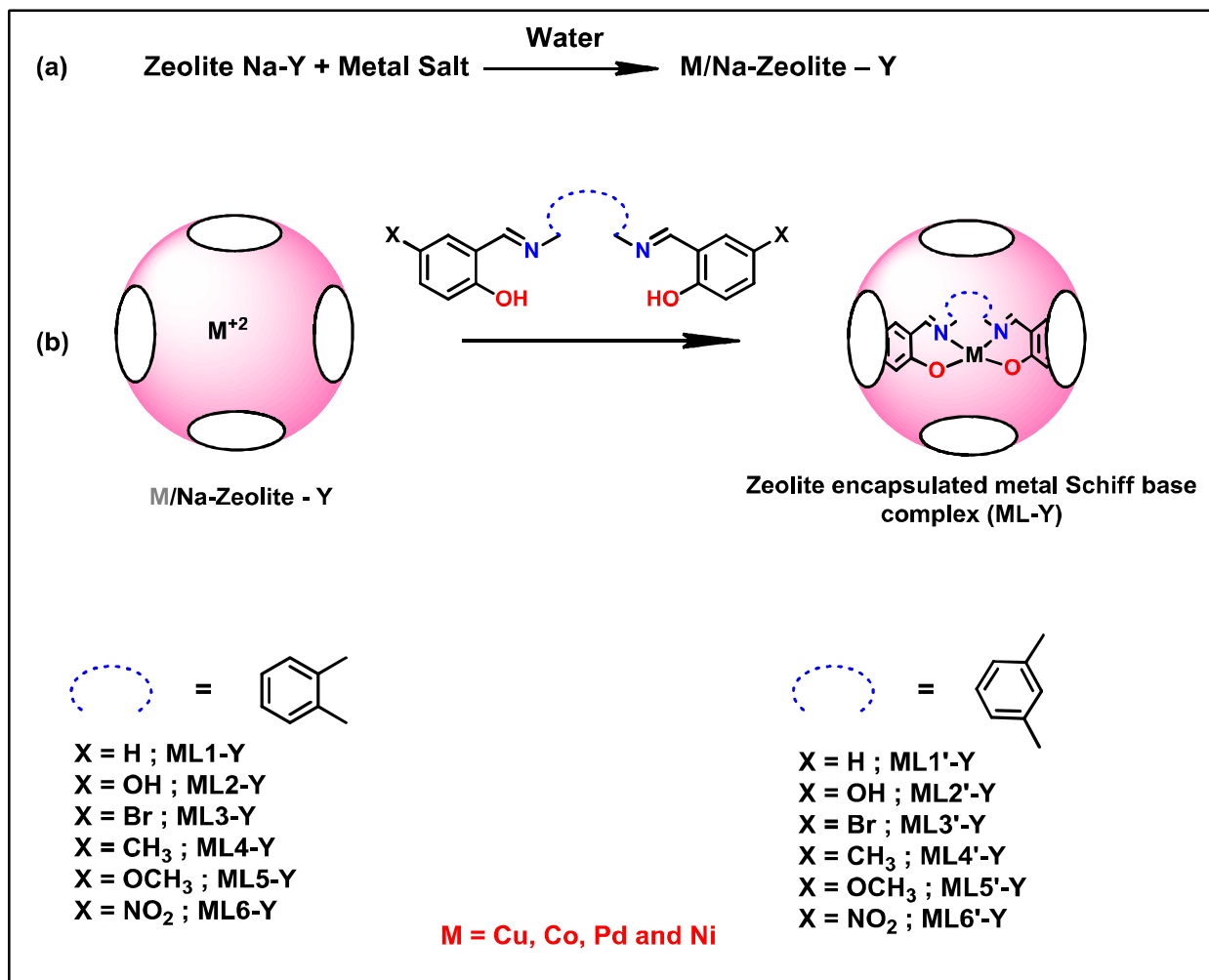
2.2.4 Preparation of M(II) exchanged zeolite-Y³:

Parent zeolite-NaY (10 g) is allowed to react with 0.01 M metal salt [$\text{Cu}(\text{CH}_3\text{COO})_2 = 0.181\text{g}$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = 0.177\text{g}$, $\text{Pd}(\text{CH}_3\text{COO})_2 = 0.224\text{g}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = 0.258\text{g}$] in 100 mL of distilled water to acquire the required loading level of metal ions and stirred at room temperature for 24 h. The slurry is filtered, washed repeatedly with water, and then desiccated for 12 h at 150 °C (presented in Scheme 2.3).

2.2.5 Preparation of encapsulated M(II)–Schiff base complexes in zeolite Y^{4,5}:

The M(II) exchanged zeolite-Y is treated with a stoichiometric excess of respective Schiff base ligand. Being a flexible ligand, it diffuses through the channels of the host when the reaction mixture is refluxed for 24 h at 150-200°C under constant stirring and reacts with the metal ions present in the supercage. The color of solid reaction mass changes from yellowish to dark brown. The reaction mass is then recovered and dried at room temperature. The resultant product is further purified by Soxhlet extraction maintaining the sequence of solvents as acetone, methanol, and finally with diethyl ether to remove unreacted ligand and metal complex adsorbed on the surface of the host. The obtained product is then dried in muffle furnace at 150°C for 12 h. The product is allowed to react with 0.01M NaCl solution to remove the unreacted metal ions, finally followed by filtration and washed with distilled water thoroughly until the

filtrate is negative for chloride ion test. Finally, zeolite encapsulated metal Schiff-base complexes (represented as EPdL1-Y, EPdL2-Y and EPdL3-Y) are obtained as dark brown powders (given in Scheme 2.3).

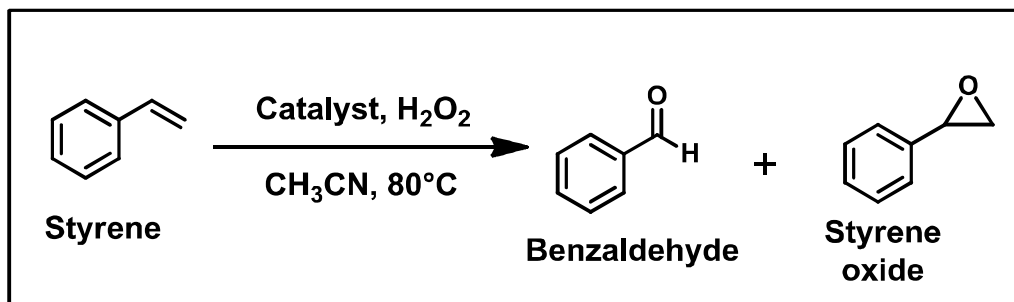


Scheme 2.3 : (a) Synthesis of metal exchanged zeolite-Y and (b) synthesis of zeolite encapsulated metal Schiff base complexes via flexible ligand synthesis method.

2.2.6 Oxidation of styrene:

To investigate the catalytic activity of the encapsulated complexes, styrene oxidation transformation catalyzed by copper Schiff-base complexes in free and encapsulated states are explored by using H₂O₂ as an oxidant in the aerobic condition. The optimum conditions for epoxidation reaction are as follows: (Styrene: 1.56 g, 15 mmol), (H₂O₂: 3.40 g, 30 mmol), acetonitrile 15 ml, temperature 80 °C, and catalyst (0.05 g for encapsulated complexes and 0.0045 g for neat complexes). Once the reaction is finished, the

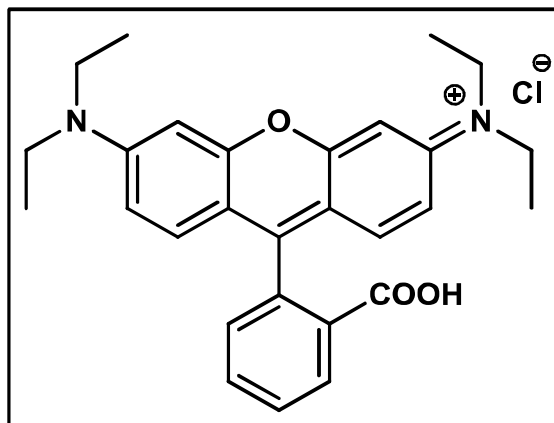
products are identified and quantified with the help of Gas Chromatography by using the internal standard method (given in Scheme 2.4).



Scheme 2.4: Schematic representation for the oxidation of styrene.

2.2.7 Degradation of rhodamine B:

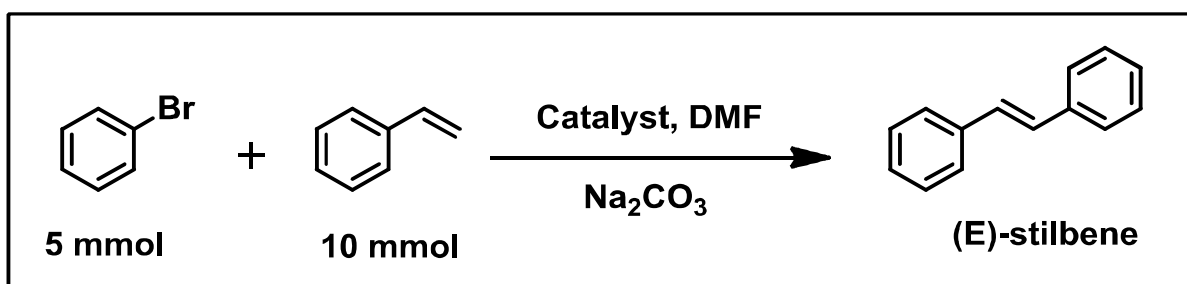
0.1197 g of Rhodamine-B dye is added to a 250 mL milli-Q deionized water in a volumetric flask, to prepare a 1 mmol stock solution of Rhodamine B dye (given in Scheme 2.5). For catalytic reaction, 1 mL of stock solution was further added to a 50 mL volumetric flask having milli-Q water, to get a 20 μ M solution of Rh-B dye. This solution of Rhodamine-B dye (50 mL) taken in a beaker, free-state or encapsulated Co(II) Schiff-base complex is added as catalyst and H₂O₂ is used as oxidant. Reaction mixture is kept on a magnetic stirrer and irradiated in presence of UV light (12 Watts, 254 nm). A series of runs are performed to figure out the optimum amount of metal complex catalyst and the oxidant. 0.0036 mmol of metal complex and 0.88 mmol of H₂O₂ are finalised as optimum amounts of catalyst and oxidant respectively. The degradation of dye has been monitored by using UV-Vis spectrophotometer at different time intervals within the range of 200-800 nm. The aliquot samples of the reaction mixture is collected at certain time intervals and spectral changes are analyzed at the wavelength of 554 nm (λ_{max} of rhodamine B dye). The percentage of the degradation has been calculated by using Lambert-Beers law.



Scheme 2.5: Schematic representation for the structure of Rhodamine-B dye.

2.2.8 Heck coupling reaction:

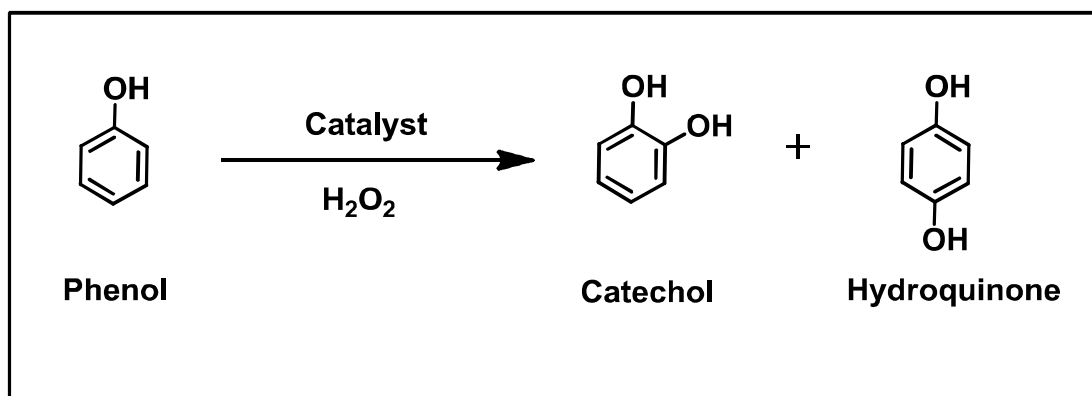
To carry out the Heck coupling reaction, 0.70 mmol% of catalyst, 10ml DMF as a solvent, 5 mmol of bromobenzene, 10 mmol of styrene and 1.06 g Na_2CO_3 as a base are added and then the whole reaction mixture is refluxed for 20 h at 140 °C under constant stirring. The reaction is monitored by collecting a small amount of the reaction mixture after 1, 4, 8, 12, and 20 h of reaction time and reaction mixture is analyzed by Gas chromatography (GC). After the completion of the reaction, the catalyst is extracted by filtration and washed with solvents and the supernatant solution of the reaction mixture is collected after centrifugation. The reaction mixture is then analyzed by FID-GC using n-heptane as the internal standard. For the recycling experiments, the solid catalyst is separated by centrifugation from the reaction mixture, washed thoroughly with the organic solvents (DMF and DCM) and water and then again has been utilized in a new catalytic cycle under the same reaction conditions (given in Scheme 2.6).



Scheme 2.6: Schematic representation of the Heck coupling reaction.

2.2.9 Oxidation of phenol:

To carry out the catalytic hydroxylation of phenol 0.05 g of catalyst, 2 ml of acetonitrile as a solvent, 6.16 mmol of phenol, and 2.54 ml of 30% H₂O₂ as an oxidant are added and refluxed with constant stirring for 6 h at 80°C (given in Scheme 2.7). The progress of reaction is monitored by Gas chromatography (GC). At the end of the reaction, the solid catalyst is extracted by filtration and washed with solvents and the supernatant solution of the reaction mixture is analyzed by Gas chromatography after centrifugation.



Scheme 2.7: Schematic representation for the oxidation of phenol.

2.3 CHARACTERIZATION TECHNIQUES

The following instrumental techniques used for the detailed characterization and catalytic studies of the metal complexes in both free-state as well as encapsulated state.

2.3.1 Powder X-ray diffraction (XRD)

Powder X-ray diffraction is a technique used for structural elucidation of the powdered or micro crystalline samples. In this technique, X-rays are generated in X-ray tube, where highly accelerated electrons from cathode collide with the anode metal. These X-rays are filtered to produce monochromatic radiation, collimated to concentrate and directed towards the sample.



Figure 2.1: Photograph of the powder X-ray diffractometer (RIGAKU MiniFlex II).

XRD technique is based on the constructive interference of the incident monochromatic X-rays and sample. The constructive conclusions about crystal structure are produced by the interaction between the sample and the monochromatic X-rays, if they satisfy Bragg's equation.

$$\text{Bragg's equation} = 2d \sin \theta = n\lambda$$

Where n is a positive integer and known as order of diffraction, λ represents the wavelength of incident X-rays, d represents the spacing between the two successive lattice planes and θ is the angle between incident beam / reflected beam and the crystallographic reflecting plane i.e., glancing angle

In current work, the X-ray diffraction patterns have been recorded by a powder X-ray diffractometer (RIGAKU MINIFLEX II) using Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) within the scan range of $2\theta = 8\text{--}50^\circ$ and with the scanning rate of $2^\circ/\text{min}$. The XRD patterns of parent zeolite -NaY, metal-exchanged zeolite Y

and zeolite encapsulated M(II) Schiff-base complexes have been recorded. Comparative powder XRD patterns of zeolite encapsulated metal complex and pure zeolite Y are significant enough to obtain information about the crystallinity of host zeolite framework.^{6, 7}

2.3.2 Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX)

SEM (scanning electron microscope) and EDX/ EDS (energy dispersive X-ray spectroscopy) are the integral parts of fundamental analytical technique used in present study. . The analytical technique SEM is also equipped with an EDX system. In this technique, a high-energy beam of electrons or beam of X-rays is focused at the surface of the solid samples. The signals originated due to interactions of incident beam and sample exhibit the information related to the surface morphology, elemental composition and crystalline structure of the samples. SEM is an efficient technique where analysis can be performed at specific selected points on the sample and it is very proficient approach to get information qualitatively or semi-quantitatively about the chemical compositions by using EDX/EDS analysis, crystalline structure and crystal orientations by using EBSD (Electron Backscatter Diffraction) analysis. In the current thesis work, SEM-EDX analysis has been carried out by using a Zeiss EVO 40 instrument with an accelerated voltage of 5–20 kV and samples are coated with gold coating. SEM-EDX analysis for pure zeolite Y and zeolite encapsulated M(II) Schiff-base complexes have been performed to know the surface morphology and elemental analysis of these systems.



Figure 2.2: Photograph of Scanning Electron Microscope (Zeiss EVO 40).

2.3.3 BET surface area analysis

Brunauer-Emmett-Teller (BET) analysis offers the measurement of specific surface area by the multilayer adsorption of nitrogen gas and it is measured as a function of relative pressure with the help of a fully automated analyzer. To determine total specific surface area, external area and pore area are evaluated by using this technique. This helps in the studying of surface porosity and particle size of the materials.

In present study, nitrogen sorption isotherms have been recorded on a Quantachrome instruments with the help of a volumetric adsorption setup at $-196\text{ }^{\circ}\text{C}$. For the parent zeolite-Y and encapsulated systems, the Brunauer-Emmett-Teller (BET) surface area and pore volume have been calculated. Current study obtains type I isotherm from BET analysis hence indicates the microporous nature of materials.^{8,9} The presence of metal Schiff-base complexes within the supercages of zeolite-Y is well supported by the decline of the pore volume and surface area of parent zeolite-Y upon encapsulation process.



Figure 2.3: Photograph of the surface area analyzer (Quantachrome instrument-Autosorb iQ3).

2.3.4 Thermal analysis

In thermogravimetric analysis (TGA) mass change in a sample is measured as a function of temperature or time. Here, a controlled temperature program is subjected to the sample. TGA is based on the fact that the sample is weighed continuously while being heated to the elevated temperatures and changes in the mass of a sample are studied. Not all thermal changes bring a change in mass of sample such as melting, crystallization etc. but some thermal changes such as desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition etc. bring a drastic change in mass of sample.

In present study, to know the thermal stability of the free-state as well as encapsulated systems, thermogravimetric (TGA) analysis in nitrogen atmosphere from 25 to 800° C have been performed on a TGA-50, SHIMADZU apparatus and TGA 4000 PerkinElmer with a heating rate of 10 °C min⁻¹.



Figure 2.4: Photograph of the thermogravimetric analysis (TGA) instruments - TGA 4000 PerkinElmer and TGA-50, SHIMADZU apparatus.

In the present work, for the thermal study of some Pd(II) Schiff-base complexes derivative thermogravimetry (DTG) and differential thermal analysis (DTA) are performed by using simultaneous DTA-TGA thermal analyzer device (Shimadzu DTG-60H). DTG is a type of thermal analysis which deals with the rate of weight changes upon heating and it is plotted against temperature. DTG simplify the thermogram peaks which occur close together because it provides difference thermogravimetry ratio of measurement of weight loss at heating or cooling.



Figure 2.5: Photograph of the simultaneous thermogravimetric and differential thermal analyzer (SHIMADZU DTG-60H).

2.3.5 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy provides the information about the samples in infrared region of the electromagnetic radiation to obtain an infrared spectrum of absorption or emission of a sample. Photon energies (1 to 15 kcal/mole) associated to the IR though not enough to excite the electrons, however, they induce vibrational excitation in the covalently bonded atoms and groups. According to gross selection rule of IR spectroscopy, an ‘IR active’ vibrational mode must be associated with changes in the electric dipole moment.

In this thesis, FT-IR measurements have been carried out for the ligands, M(II) complexes, parent zeolite-Y and zeolite encapsulated systems by using an ABB FTIR and SHIMADZU IRAffinity-1S spectrometer in the range of $450\text{--}4000\text{ cm}^{-1}$ with a DRIFT accessory. This spectroscopic technique is mainly useful to get the information about the functional groups and their chemical linkages. Furthermore, this technique

is also helpful to know the integrity of host framework i.e., zeolite in this case, during the encapsulation process.



Figure 2.6. Photograph of the Fourier Transform Infrared spectrometer - ABB FTIR and SHIMADZU IRAffinity-1S.

2.3.6 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy is a well-known technique which is used to study of surface chemistry of the samples. This technique can quantify the empirical formula, elemental analysis, chemical and electronic states of the constituent's elements of the sample of interest in attenuation depth of 20 Å. XPS spectra are acquired by irradiating a material surface with a beam of monoenergetic soft X-rays and energy analyzing the electrons emitted by generally using Mg K α (1253.6 eV) or Al K α (1486.6 eV) X-rays and at the same time, by measuring kinetic energy and number of electrons emitted from the surface of material being analyzed.

In present study, X-ray photoelectron spectroscopic measurement (XPS) is carried out on a commercial Omicron EA 125 spectrometer with an Mg K α X-ray source (1253.6 eV). Samples are kept in a vacuum oven overnight before XPS analysis done and used in form of pellets after neutralization. High-resolution XPS spectra for elements are deconvoluted using the Gaussian and Lorentzian statistical analysis by Origin-9 software. XPS analysis of free-state metal complexes and zeolite encapsulated systems are

carried out and all elements (except hydrogen) present in samples are recognized by identifying their corresponding binding energies.



Figure 2.7: Photograph of the X-ray photoelectron spectrophotometer (Omicron EA 125).

2.3.7 UV-Visible/Diffuse Reflectance Spectroscopy(UV-Vis/DRS)

Electronic spectroscopy or UV-Vis spectroscopy deals with the interactions of ultraviolet and visible part of the electromagnetic radiation with the sample and induces electronic transitions by promotion of the electrons from their ground state to a higher energy excited state. The wavelength of ultraviolet region falls in the range between 190-380 nm and the visible region falls between 380-750 nm. Many compounds as well as metal complexes can be characterized with the help of electronic spectroscopy.

In present work, UV-Visible spectra are recorded in solution as well as solid states of the samples with the help of Shimadzu Spectrophotometer with model UV-2450. The diffuse reflectance spectra are recorded by using a Shimadzu UV- 2450 spectrophotometer with a diffuse reflectance attachment, which is outfitted with an integrating sphere of 60 mm inner diameter. The spectra are often recorded in the

absorbance mode in the range of 190 nm to 800 nm by using BaSO₄ as reference material. Some of the solution UV-Vis spectra are recorded by using JASCO V-650 spectrophotometer. Both the instruments cover the wavelength range 190-900 nm, with two different lamps, tungsten (W-lamp) lamp covers 900 to 350 nm range and a deuterium (D₂-lamp) has the range of 350-190 nm region. The light sources Si-photodiodes are used as the light detectors.



Figure 2.8: Photograph of the UV-Vis spectrophotometers - Shimadzu with model UV-2450 and JASCO with model V-650.

2.3.8 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is a spectroscopic technique which is used for the quantitative determination of constituent elements of a sample. This technique is based on the absorption of optical radiation by free atoms in the gaseous state produced in an atomizer and is a useful technique in analytical chemistry for determining the concentration of a particular element in a sample. In the present study Shimadzu AA-7000 spectrophotometer is used to determine the copper metal content in the zeolite encapsulated copper systems.

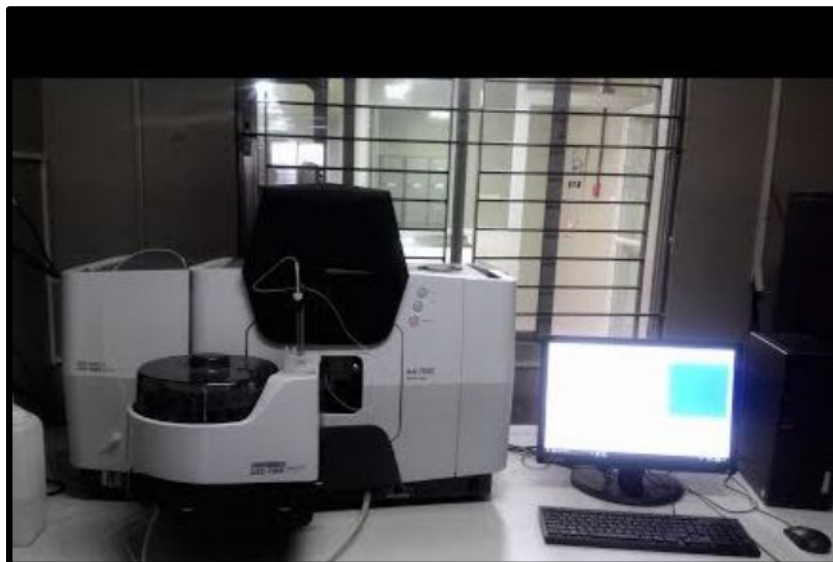


Figure 2.9: Photograph of atomic absorption spectrophotometer (Shimadzu AA-7000).

2.3.9 Superconducting quantum interference device (SQUID)

SQUID magnetometer is used for the measurement of magnetic properties of the samples. This technique is capable to determine the indirect magnetic moment of a material. In this work, temperature dependent magnetic studies of free-state and encapsulated state of the nickel complexes have been performed by using SQUID magnetometer Quantum Design MPMS XL Ever Cool and FC measurement is carried out in the field strength of 1000 Oe in the temperature range of 5K to 300K.



Figure 2.10: Photograph of SQUID magnetometer Quantum Design MPMS XL Ever Cool.

Calculation for the Molar Magnetic Susceptibility (χ_m)

$$\text{Magnetic Susceptibility } (\chi) = \frac{\text{Magnetisation (emu)}}{\text{Magnetic field (Oe)}}$$

$$\text{Molar Magnetic Susceptibility } (\chi_m) = \frac{\text{Magnetic Susceptibility } (\chi)}{\text{Moles of metal centers}}$$

Calculation of Magnetic Moment (BM)

$$\text{Curie constant } (C) = \chi_m \times T$$

$$\mu = 2.82 * \sqrt{\chi_m} \times \sqrt{T}$$

2.3.10 Gas Chromatography (GC)

Gas chromatography (GC) is well-established chromatographic technique which is used for the identification, separation and quantification of the compounds that can be vaporized without decomposition. Gas chromatography consists carrier gas (usually an inert gas such

as helium, nitrogen) as a mobile phase and stationary phase is a very thin layer of an inert liquid or polymer on an inert solid support such as beads of silica packed into a long thin tube and known as column. Principle of GC is similar to column chromatography such as HPLC and TLC etc. Compounds having greater affinity for the mobile phase reach quickly to the detector at the end of the column and substances having higher affinity for the stationary phase move slowly through the column. Thus, the substances of the mixture to be analyzed interact differently with the stationary phase and mobile phase and subsequently move along the column and are separated according to their respective retention times.

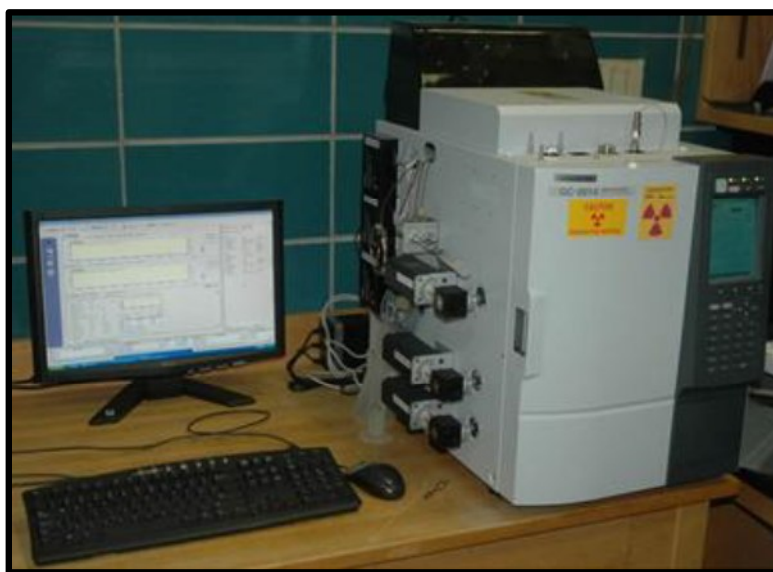


Figure 2.11: Photograph of gas chromatography (GC Shimadzu-2014).

2.3.11 Theoretical Methods

The electronic structure calculations based on Density Functional Theory (DFT) is used to study and analyse the structural and optical properties of the palladium complexes in free-state and zeolite encapsulated states. All results presented here are obtained using GAUSSIAN 09 suite of *ab initio* quantum chemistry programs.¹⁰ The structural optimizations used the hybrid B3PW91^{11, 12} exchange and correlation functional with the double-zeta 6-31G** basis set for all atoms except Palladium (Pd) for which LanL2DZ basis-set along with effective core potential was used. Vibrational frequencies for all complexes were calculated to ascertain the stable structures with no symmetry constraints imposed.

In the studies involving encapsulation of Pd complexes within zeolite pore, only a part of zeolite-Y supercage has been modelled only a portion of zeolite-Y supercage and all the unsatisfied valencies of silicon atoms are terminated by hydrogen atoms. During the study of encapsulated complexes, the experimental structure of the zeolite supercage is taken without changes, and not relaxed, however the positions of the terminal hydrogen atoms are optimized. In these cases, the structure of complex inside the zeolite pore is optimized keeping zeolite structure fixed and lowest energy state is obtained. Both the singlet triplet states of the neat as well as encapsulated forms of the Pd-complexes, and the optical spectra are calculated using time dependent density functional (TD-DFT) methods by taking basis set as B3PW91/6-31++G** for all atoms and Lan2DZ basis-set and ECP for Pd atom on B3PW91/6-31G** optimized structures. In case of triplet, encapsulated complexes the optical spectra are calculated without the zeolite supercage, *i.e.* after removing the encapsulated triplet Pd-complex and keeping the geometry fixed. The optical spectra is better understood in terms of the molecular orbitals of the Pd-complexes in free or encapsulated states, thus the electron density plots for frontier molecular orbitals, of the complexes in both singlet and triplet states are shown in the Supporting Information. The molecular orbitals are defined with respect to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as HOMO-n (H-n) and LUMO+n (L+n). Triplet to triplet transitions are only considered for the triplet complexes, though pure d-d transitions are hard to identify due to strongly hybridized nature of the metal d-orbitals with ligand p orbitals.

2.4 REFERENCES

1. H.-C. Zhang, W.-S. Huang and L. Pu, *J. Org. Chem.*, 2001, **66**, 481-487.
2. A. P. Andrade, L. M. Arantes, J. Y. Kadooca, R. L. Carvalho, A. de Fatima and A. A. Sabino, *ChemistrySelect*, 2016, **1**, 886-890.
3. M. Salavati-Niasari, *Chem. Lett.*, 2005, **34**, 1444-1445.
4. Y. Yang, H. Ding, S. Hao, Y. Zhang and Q. Kan, *Appl. Organomet. Chem.*, 2011, **25**, 262-269.
5. K. K. Bania, D. Bharali, B. Viswanathan and R. C. Deka, *Inorg. Chem.*, 2012, **51**, 1657-1674.
6. R. H. Jarman, *Zeolites*, 1985, **5**, 213-216.
7. K. K. Bania and R. C. Deka, *J. Phys. Chem. C*, 2013, **117**, 11663-11678.
8. A. N. Parikh, A. Navrotsky, Q. Li, C. K. Yee, M. L. Amweg and A. Corma, *Microporous Mesoporous Mater.*, 2004, **76**, 17-22.
9. H. S. Abbo and S. J. Titinchi, *Top. Catal.*, 2010, **53**, 1401-1410.
10. M. J. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. Petersson, *Inc.: Wallingford, CT*, 2009.
11. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
12. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>