I. Introduction

Catalysis is an area of prime importance in the frontier area of chemistry. Recent years have witnessed a great deal of interest in the research of different types of supported transition metal complexes \(^1-^4\). The interest in the design and synthesis of novel transition metal complexes lies in their biological and catalytic activity in many reactions \(^5,^6\). In accordance with growing environmental concerns and the demand for more efficient and cheaper processes, the use of heterogeneous transition metal complexes to catalyze organic reactions have received widespread attention in recent years \(^7-^9\). Thus there is a continuing interest for the design and synthesis of new compounds that can function as catalysts in reactions of industrial significance and modification of the properties of already synthesized molecules. All chemical reactions involving catalysis are associated with changes in the oxidation state and coordination environment of the central metal ion and ligand field environment.

Recent years have witnessed a great deal of interest in the study of heterogeneous catalytic systems due to their importance as catalysts for many reactions. Heterogenised homogeneous catalysts possess the advantages of both homogeneous and heterogeneous systems. They offer several advantages such as the simplification of the reaction procedures, easy separation of products, recyclability of expensive catalysts, possibility to design continuous flow processes, good control of morphology of polymers and high polymer bulk density \(^10,^11\). It is possible to improve the properties of neat complexes such as selectivity, thermal stability, recyclability, ease of catalyst separation etc. by immobilizing them on various supports. Immobilized catalysts couple the high activity of a homogeneous system and good workability of an heterogeneous system.

The term heterogenisation refers to the process of immobilization of homogeneous transition metal complexes by anchoring them to an inert polymer or inorganic support. This type of bonding to a solid surface stabilizes the complex and generates catalytically active centers \(^12\). The supported complexes possess higher selectivity and greater catalytic activity than
their homogeneous analogues. Immobilized catalysts couple the high activity of a homogeneous system and good workability of a heterogeneous system.

The use of zeolite-encapsulated transition metal complexes to catalyze organic reactions has gained considerable attention in recent years on account of their fascinating properties. Zeolites are porous metal oxides, typically aluminoilicates, which contain extensive cavities and well-defined channel structures with, pore diameters in the 3-12Å range. The zeolite pores act as reaction centers for binding and catalysis of molecules. The well-defined cages and channels of the zeolite serve as a sort of reaction flask with suitable molecular dimension for the encapsulation of metal complexes.

Homogeneous catalysts immobilized in the cage system of zeolite-Y are expected to be stabilized against aggregation or bimolecular deactivation. Furthermore, the zeolite cage system may favor unique selectivity of a catalytic reaction due to changed complex geometries, transition-state modifications and diffusional selectivity for the substrate molecules. The combined effects of the shape selectivity of zeolites and high dispersive power of metal ions of transition metal exchanged zeolites are of great interest in catalytic studies.

2. Synthesis of ligands

Schiff base ligands were synthesized using reflux method.

(a) Synthesis of N, N’–bis(salicylaldimine)-o-phenylenediamine

The o-phenylenediamine dissolved in very little benzene was added dropwise to the salicylaldehyde solution in benzene using a dropping funnel with constant stirring. The yellow solid obtained was separated by filtration, washed with ether and recrystallized from methanol.

(b) Synthesis of N, N’–bis(salicylaldimine)-p-phenylenediamine

The p-phenylenediamine was recrystallized twice from hot water. To an ethanolic solution of p-phenylenediamine, salicylaldehyde was added and the resultant solution was refluxed on a water bath for about 3 hours. The bright orange solid obtained was recrystallized twice from methanol.

(c) Synthesis of salicylaldehyde semicarbazone
To an aqueous solution of semicarbazide hydrochloride, sodium acetate and salicylaldehyde were added slowly with constant stirring. Then the mixture was refluxed on a water bath for about 3 hours. The product obtained was filtered, washed with ethanol and recrystallized from 1-propanol.

3. Preparation of simple transition metal complexes

The metal complexes of the synthesized ligands were prepared by refluxing them on a water bath with the corresponding metal chloride in a suitable solvent.

4. Preparation of supported transition metal complexes

(a) Synthesis of zeolite encapsulated ruthenium complexes of salicylaldehyde semicarbazone

The zeolite encapsulated ruthenium complex of the Schiff base was prepared from the ruthenium-exchanged zeolite using the flexible ligand method. The ligand salicylaldehyde semicarbazone was mixed thoroughly with the ruthenium-exchanged zeolite RuY in the ligand to metal ratio 1:1. Then the above mixture is heated at 200°C for 6 hours in a sealed glass ampoule to form the encapsulated complex. The unreacted ligand and surface species present are removed by soxhlet extraction of the material first with methanol and then with chloroform. The uncomplexed metal ions in the zeolite and ionisable portions of the ligand were removed by ion exchange with NaCl solution (0.01M, 500 ml) for 24 hours. It was filtered, washed free of chloride ions and finally dried at 100°C for two hours.

(b) Synthesis of zeolite encapsulated ruthenium complexes of N,N’-bis(salicylaldimine)-o-phenylene diamine and N,N’-bis(salicylaldimine)-p-phenylene diamine

The encapsulation of ruthenium complexes of salicylidene-o-phenylenediammine and salicylidene-p-phenylenediamine were also achieved by flexible ligand method\textsuperscript{15-17}. The metal exchanged zeolite RuY (5g) was added to the ligand SOD dissolved in methanol (50 ml). The mixture was refluxed on a water bath for about 12 hours. The product formed was then filtered and soxhlet extracted with methanol and dichloromethane. The complex of p-phenylenediamine was also prepared according to the similar procedure.
5. Characterization methods

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.

(a) Elemental 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. 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.

(ii) 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 method of nitrogen adsorption at liquid nitrogen temperature using ‘Micromeritics Gemini 2360 surface area analyzer’.

(iii) 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 structure. 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.

(iv) Thermo gravimetric analysis

Thermo gravimetric analysis is an effective tool to study the nature of decomposition of the metal complexes. 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. TG analyses
were carried out on a Perkin Elmer, Diamond TG / DTA at a heating rate of 10°C per minute in an atmosphere of nitrogen.

(v) 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 complexes and the morphological changes associated with encapsulation.

(vi) Infra red 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.

(vi) 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.

6. Catalytic studies

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.