Chapter 1
Introduction
1.1 INTRODUCTION

Catalysis is a branch of science that quickens the rate of chemical transformations. In general, commercial starting materials are converted into valuable complex molecules with the help of various types of catalysts for the resourceful applications. These transformations offer a range of intermediate products that can be used directly or indirectly in the production of various additives, perfumes, pharmaceuticals, plasticizers, coating materials, drugs, commodity chemicals, and catalytic converter used in vehicles and industrial exhaust.\(^1\) The crucial role of a catalyst is to get down the activation energy of chemical transformation (Figure 1.1) and mold the manufacture of predesigned molecules more energy efficient and the economical feasible along with minimizing the unwanted by-products.

![Figure 1.1](image)

**Figure 1.1** Contrast of activation energy between catalyzed and uncatalyzed reaction.

Due to these qualities, most of the chemical industry employs more than 80 percent of chemical products, which come into the contact with catalysts during their synthetic process hence, making the catalysis field essential for the needs of modern society. Moreover, a recent prompt development of catalysis makes it a renowned branch of science cutting through various disciplines such as chemistry, engineering, biology, physics, and mathematics.\(^9\)
The excess of chemical production will only be environmentally sustainable if imperative chemical products are synthesized in specific, environmentally benign, and the economic way by lessening the formation of by-products or pollutants. These can only be accomplished by using various types of homo or heterogeneous catalytic system (Figure 1.2).  

**Figure 1.2** Significance of catalysis in the various fields.

### 1.2 TYPES OF CATALYSTS

A catalyst can be categorized in many ways, such as on the basis of its surrounding whether it is in liquid or gas phase and on the basis of the type of structure from atoms of large structures such as zeolite, MOFs, and enzymes. Mainly catalysts can be divided into six types: photocatalysts, biocatalysts, nanocatalysts electrocatalysts, homogeneous and heterogeneous catalysts (Figure 1.2).
1.2.1 Photocatalysts:

A material that functions as a catalyst when exposed to the light is called photocatalyst. There are number of materials that show photocatalytic capability: however, titanium dioxide is found to be potent candidate so far. In 1970’s, Dr. Fujishima found that titanium metal could break water molecule into oxygen and hydrogen gas when exposed to light.\(^\text{12}\) Thereafter, by restructuring titanium dioxide particles in nano-scale, a number of new physical and chemical properties were discovered. Right from this opening research, utilization of photocatalyst titanium dioxide has amplified in the breakdown of numerous organic substances such as oil grime and hydrocarbons from car exhaust and industrial smog, the volatile organic compounds found in various building materials and furniture, and organic growth such as fungus and mildew.\(^\text{13-15}\)

However, various utilities and potentials of the photocatalyst, still it faces some limitations such as low reaction rate, low efficiency, low specificity, and low stability which make it inappropriate catalysts for the commercial uses.

1.2.2 Biocatalysts:

Natural substances that speed up chemical reactions are called biocatalyst. The natural substances can be one or more enzymes, cells, and non-protein-based biomolecules. Biocatalysts can be either homogeneous if soluble in water or heterogeneous if bonded to membranes and insoluble in water. The most significant benefit of a biocatalyst is its higher stereoselectivity, regioselectivity, and chemoselectivity.\(^\text{16}\) Such high selectivity is very necessary for the synthesis of chemicals as it may offer numerous benefits such as shortened or no use of protecting groups, reduced side reactions, easier separation, and less environmental problems.

Other eye-catching benefits like high catalytic proficiency and mild operational conditions are vivacious in commercial applications.\(^\text{16, 17}\) However, the characteristics of limited operating regions, substrate or product inhibition, reactions in aqueous solutions and high cost have often been considered as the most solemn downsides of biocatalysts.\(^\text{17}\) Nowadays, the high operating budget of biocatalysts can be abridged by immobilization of an active biocatalyst onto solid supports like functionalized cellulose, glass, ceramics, metallic oxides, and membranes.\(^\text{18, 19}\)
1.2.3 Nanocatalysts:

A substances or materials with a catalytic activity that has at least one nanoscale dimension, either externally or in terms of internal structures are often coined as nanocatalysts. Nanoparticles of aluminium, iron, titanium dioxide, clays, and silica have been used as catalysts since last many years. In an era of nanotechnology where size of every object is going to be smaller and smaller with their heightened properties; catalysts of nano size are also used in several chemical transformations and found to be advantageous for human being.

Moreover, due to heterogeneous nature of these nanocatalysts, it can be easily recovered and reused several times which indirectly lowers the operating budget for the transformation of organic substrates.

1.2.4 Electrocatalysts:

In view of electrochemistry, precisely in fuel cell engineering, various metal-containing catalysts are used to improve the rates of the half reactions that include the fuel cell. Electrocatalysts are a specific form of catalysts that function at electrode surfaces or may be the electrode surface itself. Electrocatalysts can either be heterogeneous such as platinum surface and nanoparticles, or homogeneous like coordination complexes. The electrocatalysts promote a transfer of electrons between the electrode and reactants, and/or enable an intermediate chemical transformation illuminated by an overall half-reaction.

Conventionally, Pt or Pt-based electrocatalysts are used, but the main shortcomings like intolerance to methanol, high price, and instability in the fuel-cell environment have greatly obstructed these energy storage devices in finding reasonable roles in real life. Moreover, these types of electrocatalysts can be used in the fuel cell for splitting of water mostly and not for the commercial organic transformation.

1.2.5 Homogeneous catalysts:

A catalyst is said to be homogeneous if the entire catalytic system, including components, catalyst, and reactants are in the same phase, more frequently in the liquid phase. Homogeneous catalysts are the simple molecules or ions such as HF, H₂SO₄, metal complexes, organometallic complexes, macrocyclic compounds, and large enzyme molecules. The homogeneous neat metal complexes are often most
active and selective due to presence of easy accessible active site in it; however, apart from disadvantages of trouble in separation and recycling of this catalyst, the contamination of toxic metal due to homogeneous complex degradation in the product is a solemn matter especially for the synthesis of biologically active intermediates and products.

1.2.6 Heterogeneous catalysts:

Currently, it is almost difficult to envisage the world without the utilization of heterogeneous catalysis and still needs this field to propagate for sustainable development. Homogeneous catalysts refer to the catalytic medium including each reactant in the different phase from catalyst phase. Usually, homogeneous catalysts are being used for the various chemical transformations due to their high selectivity and activity towards the anticipated product. But the practical utilization of these catalysts is rather provoking due to its difficulty in the separation and retrieval of catalyst from the reaction medium.

On the other hand, the uses of heterogeneous catalysts which are fairly easy to operate under unembellished conditions, highly stable, usually prepared at comparatively low budgets, and can be simply isolated from the products without tedious experimental work have gained considerable attention over the last few decades. 46-48

Generally, the heterogeneous catalysts are synthesized by heterogenization of active homogeneous organometallic catalysts/coordination complexes and expensive metals supported into or onto various solid supports, like silica, polymers, zeolites, multi-wall carbon nanotubes (MWNTs), and metal organic framework (MOFs). An overview, merits, and demerits of well-known heterogenization methods are described as below.

1.3 TYPES OF WELL-KNOWN HETEROGENIZATION METHODS

1.3.1 Metal complexes or active metal supported on silica

For the heterogenization, various types of silica fulfil many of the essential benchmarks as an appropriate solid supports for immobilization of metal complexes and/or transition metals like Pd, Rh, and Pt on it. Pore diameters in most of such materials are in the range between two and few tens of nanometers allowing bulky catalytically active species onto the support. 49-51 Most of mesoporous materials are
hexagonal (MCM-41, SBA-15, FSM-16) or cubic (MCM-48, KIT-6, SBA-16) in the symmetry. The pore size of hexagonal MCM-41, SBA-15, cubic MCM-48, and KIT-6 is in the range 1.5 – 10, 3.6 – 30, 1.6 – 4.2, and 8 – 10 nm, respectively. In terms of porosity, the materials having disordered structures but uniform pore sizes (HMS, TUD-1), mesoporous solids with (SBA-2, SBA-12) or without (SBA-15, MCM-48) large cages, and materials having micropores in the walls of the mesopores (SBA-15, KIT-6) are also astute choice for heterogenization. Moreover, dealuminated zeolitic materials (ITQ-2, ITQ-6) known as two-dimensional zeolites are also can be used as solid supports.

Because of its easiness and flexibility, such solid supports have been extensively used for the immobilization of metal complexes or transition metals. Earlier, in 1974, Čapka et al. synthesized supported metal (Rh, Pt, and Pd) catalysts by treatment of silica with 3-(dimethylamino)propyltriethoxysilane and other anchoring groups. Later, Sharf et al. synthesized Na$_2$[PdCl$_4$] supported on conventional silica gel by using H$_2$N(CH$_2$)$_n$Si(OEt)$_3$ (n = 1, 3) as an anchoring group.

In recent years, heterogenization of coordination complexes on silica has become an interesting area of research. Several immobilization strategies have been widely applied for creating active sites on the support surface. In general method, surface modification of silica can be done by reaction of various derivatives of 3-aminopropyltrialkoxysilane and/or 3- (dimethylamino)propyltriethoxysilane with the surface hydroxyl group of silica. The resultant amino-functionalized silica is treated with various aldehyde or ketone to produce Schiff base ligand covalently bonded to silica, which can easily form silica immobilized metal complexes when reacted with transition metal salt solution.

Koner et al., in 2007, has effectively reported Cu(II) complex derived from salicylaldehyde and (3-aminopropyl)triethoxysilane (APTES) anchored on MCM-41. The resulting catalyst is highly active for epoxidation of olefins using TBHP as an oxidant. Recently, in 2013, Titinchi et al. has immobilized Cr(III) complexes of Schiff base ligand derived from salicylaldehyde and 3-aminopropyltriethoxysilane on silica gel by two synthetic pathways (Figure 1.3).
Figure 1.3 Synthetic routes of Cr(III) complexes supported on silica gel.

The promising properties such as accessibility, stability, low prize, recyclability, and variability of active silica immobilized metal complexes is appeared to be one of auspicious heterogenization method; however, silica is hydrothermally unstable at high reaction temperatures.

Moreover, the possibility of metal complex leaching from the catalyst cannot be entirely excluded here because the complexes are formed on the exterior surface of silica and not loaded into the nanopores of the silica which can restrict the leaching of active metal complexes.
1.3.2 Polymer-supported metal complexes

In 1963, Merrifield has established the concept of solid phase peptide synthesis, after that solid polymer supports was used expensively in other areas of chemistry like in immobilization of enzymes, biomolecules, and homogenous metal complexes. At the present time, polystyrene is commonly used as solid supports for the synthesis of metal complexes anchored onto the polymer. This method has been developed as an auspicious strategy for combining the edge of both homogeneous and heterogeneous catalysts. Polymer-supported metal complexes are normally synthesized by the interaction of functionalized polymer ligand with the transition metal ions. In the first step; the functionalized polymeric ligand is synthesized either by polymerization of the monomer containing coordinating sites or achieved by multistep reaction between a polymer and various functional groups having a coordinating ability. In the second step, the functionalized polymeric ligand is reacted with appropriate transition metal salt solution which ultimately forms metal complex onto the surface of the polymer.

Recently, in 2012, S.M. Islam et al. have reported recyclable polymer anchored copper(II) catalyst for the oxidation reaction of olefins and alcohols with tert-butylhydroperoxide in an aqueous medium. They have synthesized polymer supported copper(II) complex by the complexation of copper salts with polymer anchored ligand (Figure 1.4). In the beginning of synthesis, amino polystyrene is reacted with di-bromo ethane under refluxing condition using \( \text{K}_2\text{CO}_3 \) as a base and results into functionalized polymer, which is further reacted with \( \text{o-aminophenol} \) and yield a corresponding polymer supported ligand. At the end, a solution of copper chloride was added to polymer supported ligand which results into dark brown polymer anchored copper(II) complex. Moreover, numerous methods are reported for the synthesis of polymer-supported metal complexes. One of the general synthetic route for the synthesis of polymer-supported metal complexes is displayed in figure 1.4.

The polymer-supported metal complexes are highly stable, robust, highly efficient can be recycled several times, and can be operated at low cost; however, use of this kind of catalysts for particular catalytic reactions involving free radicals as an intermediates that can leads further annoying polymerization hence, use of polymers as a solid support is bit inappropriate for the heterogenization.
Figure 1.4 Synthetic route of polymer anchored copper(II) complex.

1.3.3 Multi-wall carbon nanotube-supported metal complexes

Multi-wall carbon nanotube (MWCNTs), an allotrope of carbon with cylindrical nano structure formed by multiple rolled layers of carbon nanotubes (CNTs), have been fabricated with length-to-diameter ratio of up to 132,000,000:1 considerably larger than any other materials. In order to enhance the catalytic activity of nanocatalysts, active nano-carbon materials (CNTs, MWCNTs, and SWCNTs) are frequently used as solid support for the heterogenization of homogeneous catalysts. Out of that, multi-wall carbon nanotubes (MWCNTs) are found mesmerizing solid support due to their special characteristics, including large chemical surface area, high electronic conductivity, and commercial availability.

In view of the above, a lot of MWCNTs anchored Pd or Pt nanoparticles have been reported and it revealed that the interaction between MWCNTs and the nanoparticles (transition metals) can augment catalytic performance of supported catalyst. However, there are still rare reports about immobilization of metal complexes onto well-defined facets of MWCNTs and their catalytic performance over various organic transformation.

Very recently, Rayati et al. have described the synthesis of manganese (III) porphyrin complexes onto the multi-wall carbon nanotube (MWCNTs) for oxidation of alkenes and alkanes with urea-hydrogen peroxide (Figure 1.5). This type of heterogeneous catalyst can be easily prepared by single-step esterification of MWCNT-COOH (contain –COOH group) with metalloporphyrins (contain –OH
Studies on transition metal complexes encapsulated in the supercages of zeolite-Y: Synthesis, characterization and catalytic aspects

Ph. D thesis of Haresh D. Nakum

...group) in the presence of 2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate (TBTU), and N,N'-diisopropylamine (DIPEA).

Figure 1.5 Representative synthetic pathway of multi-wall carbon nanotube (MWCNs) supported metalloporphyrins complexes.

The MWCNTs are satisfying each parameter that is necessary for any solid support to become an astute choice for heterogenization but its lower thermal stability, and possibility of metal complex leaching from the external surface of MWCNs show the way to the researcher to find out more apposite solid support which falls into the criteria of ideal solid support.

1.3.4 Zeolite-Y encapsulated metal complexes

Zeolites are the inorganic crystalline aluminosilicates with the general formula \( M^{n+} \frac{x}{n} [(AlO_2)_x(SiO_2)_y] \cdot zH_2O \), (where \( M \) stands for the exchangeable cation of valency \( n \), \( z \) stands for the number of water molecules) characterized by a regular structure of channels and supercages of molecular dimensions. Basically, zeolite...
framework is made up of central Si or Al atom encircled by four oxygen atoms, that is to say [SiO$_4$]$^4-$ or [AlO$_4$]$^5-$. These tetrahedrons are bonded each other through the oxygen atoms to form channels and supercages of distinct shapes and sizes with no two aluminium atoms can share the same oxygen atom (Figure 1.6 a and b). The negative charge of [AlO$_4$]$^5-$ unit is usually balanced by alkali or alkaline earth metal cations. These cations can be exchanged by conventional ion-exchange methods.

According to the IUPAC classification, the porous materials are mainly divided on the basis of their pore dimensions; microporous (<20 Å), mesoporous (20-500 Å) and macroporous (>500 Å) materials.$^{117}$ The significant features of the microporous zeolites are the geometry of the nanopores present in it. In this view, zeolites can be categorized as uni-, bi-, and tri-dimensional zeolites if the channel system is organized along one, two, or the three Cartesian axes, respectively. Due to open pore system present in tri-dimensional zeolites; its diffusion coefficient is normally larger than those of uni-dimensional zeolites. Moreover, such well-defined nanopores of tri-dimensional zeolites can act as nanoreactors whose activity and selectivity is frequently heightened by introducing the guest molecules into it.

To date, more than 200 types of various zeolites have been reported in the Atlas of zeolite framework types, as issued by the International Zeolite Association (IZA).$^{118,119}$ They have been classified on the basis of small, medium, large, and extra-large pore structures depending on whether the number of oxygen atoms is 8, 10, 12 or more than 12 atoms, correspondingly.$^{120,121}$ Due to this open pores, zeolites can permit the diffusion of molecules from external to the internal site of the zeolite particles.

**Figure 1.6** (a) Detail of a zeolite structure built up from corner-sharing tetrahedral units, (b) Structure of Zeolite Framework, (c) Framework of Zeolite-Y (Faujasite).
The well-known zeolites such as ZSM-5 (MFI), mordenite (MOR), zeolite A (LTA), zeolite Y (Faujasite), and zeolite L (LTL) are frequently used in the various fields like adsorption, separation, catalysis, microelectronics, metal diagnosis, and in ion-exchange method for domestic and commercial water purification and softening.

Out of these, zeolite-Y (Figure 1.6 c) which belongs to the Faujasite (FAU) family and have a three-dimensional framework built up by α-cages linked by hexagonal prisms, is an astute choice for the heterogenization of homogeneous catalyst.\textsuperscript{122-133} The large cages (β-cages) thus possess an internal diameter of ca. 13 Å and are accessible and interconnected through four windows (12-membered rings) with a diameter of ca. 7.4 Å.\textsuperscript{134, 135} These nanopores can lodge large molecules such as transition metal complexes, whose size is too big to cross the window.

The encapsulation of large metal complexes in the nanopores starts from smaller precursors like transition metal ions that can diffuse through supercages via ion-exchange process and then it react with Schiff base ligand and form large metal complex inside the supercages of zeolite-Y. Now, this encapsulated complex is too large to diffuse out from the supercages of zeolite-Y, and thus can be used as a true heterogeneous catalyst for various organic transformations. Upon encapsulation in the supercages of zeolite-Y, the activity, selectivity, and stability of metal complexes is enhanced due to the reduction in dimerization of complex molecules in supercages.\textsuperscript{136-140} The area of transition metal complexes encapsulated in the supercages of zeolite-Y was formerly established by Lunsford’s and Ben Taarit’s groups,\textsuperscript{122, 123} developed by Meyer et.al,\textsuperscript{124} subsequently, research in this area was boosted\textsuperscript{125-128} and till remained as a leading area of catalysis.\textsuperscript{129-133}

1.3.4.1 Methods of complex encapsulation in zeolite-Y

Generally, there are three well-established methods for encapsulated metal complexes in zeolite-Y. These are as explained below:

\textit{a) Zeolite synthesis method (ZS):} In this method, transition metal complexes that are stable under the condition of zeolite synthesis are added to the synthesis mixture. After the synthesis of host zeolite-Y over the guest, metal complexes are too large to diffuse out from the supercages of zeolite-Y. During this synthesis method, strong chelating ligands replace the weak field ligands such as H\textsubscript{2}O, OH\textsuperscript{−} or oxide which are surrounded to the metal ion of metal exchanged zeolite-Y.
b) Template synthesis method (TS): In this method, pre-synthesized metal complex that acts as a structure directing agent (template) is reacted with the reaction medium which is synthesizing zeolite-Y and encapsulating the complexes in the supercages of zeolite-Y, simultaneously. A major drawback of this method is that one cannot synthesize encapsulated complexes if the metal complex to be used as the templating agent is not stable enough at the high pH and temperatures, which are primary reaction parameters for zeolite synthesis.

c) Flexible ligand method (FL): In this method, the excess of ligand easily reacts with the anticipated metal ions which have been previously exchanged in the zeolite-Y and form a stable metal complex inside the supercages of zeolite-Y provided that the size of ligand is smaller than the diameter of zeolitic channels and it can diffuse freely through the channels. Furthermore, once the ligand has inserted in the supercages of zeolite-Y and formed a complex with the previously exchanged transition metal ions, the complex is incapable to abscond from the zeolite supercages due to its much larger size than zeolite pore diameter.

Flexible ligand synthesis for Iron-phthalocyanine encapsulated in zeolite-Y was reported by Kimura et al.\textsuperscript{141} They concluded slight distortion in the geometry of complexes upon encapsulation from the original planar structure under the impact of zeolite-Y framework.

Zeolite-Y encapsulated ruthenium (III) complexes of Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde and 1,2-phenylenediamine, 2-aminophenol, or 2-aminobenzimidazole (RuYqpd, RuYqap and RuYqab, respectively) and the Schiff bases derived from salicylaldehyde and 1,2-phenylenediamine, 2-aminophenol, or 2-aminobenzimidazole (RuYsalpd, RuYsalap and RuYsalab, respectively) have been prepared and characterized by Mohammed Yusuff et al.\textsuperscript{142} The integrity of encapsulation was confirmed by spectroscopic studies as well as chemical and thermal analysis.

Recently, K. K. Bania et al.\textsuperscript{132} have reported the zeolite-Y encapsulated metal picolinato complexes as a catalyst for oxidation of phenol under microwave irradiation. The encapsulated complexes was synthesized by flexible ligand method in which previously transition metal exchanged zeolite M(II)-Y, (where M= Cu, Ni, Co) is refluxed for 48 h at 90 °C with an excess of picolinato ligand (Figure 1.7). The spectroscopic and theoretical studies of this encapsulated complexes revealed that
the walls of the zeolite-Y framework impart space constrain to the metal complexes, which modifies their structural, electronic, and catalytic behavior. Under microwave irradiation and in the presence of hydrogen peroxide these metal complexes facilitate the selective oxidation of phenol to catechol with moderate to good yield.

Figure 1.7 Synthesis of zeolite-Y encapsulated metal (Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$) picolinato complexes by Flexible ligand method.

The necessity of inexpensive and environment-benign catalysts has prejudiced the modern research in favor of heterogeneous catalysts because they can be operated under severe conditions, highly stable, usually prepared at comparatively low budgets, and can be simply isolated from the products without tedious experimental work.

In the case of zeolite-Y encapsulated complexes, the guest complex is loaded in the restrictive pores of zeolite-Y matrix by retaining all the properties of their homogeneous counterpart. Furthermore, the possibility of metal complex leaching from the nanopores of zeolite-Y during the catalytic study is left out here, which is usually observed in the case of complex immobilized on the external surface of other solid supports like silica, clay, polymer, MWCNs, and magnetic supports.

In addition to silica, polymers, MWCNs, and zeolites, other types of supports can be used for anchoring of metal complexes including metal-organic frameworks, and magnetic supports. However, said solids can have such drawbacks as relatively low stability (metal-organic frameworks), and lack of structural variability (magnetic nanoparticles). Therefore, due to favorable properties (accessibility, stability, recyclability, variability, no leaching possibility and generally low prize), zeolite-Y is seemed to be one of the most promising materials for applications as solid supports.
From above survey\textsuperscript{122-142} and facts, we enthused to synthesize zeolite-Y encapsulated transition metal complexes (along with neat complexes) derived from various Schiff base ligands using FL method. These nanohybrid materials have been characterized by various physico-chemical and spectroscopic techniques such as ICP-OES, Fourier transform infrared spectroscopy (FTIR), \textsuperscript{1}H and \textsuperscript{13}C NMR, elemental analyzes, and UV-Vis spectral studies, Brunauer, Emmett and Teller (BET), Thermogravimetric analysis (TGA), Scanning electron microscope (SEM), X-ray diffraction (XRD), conductivity, magnetic susceptibilities as well as atomic absorption spectroscopy (AAS).

1.4 AIM AND OBJECTIVES

Looking to the important of the present topic and literature survey, we will focus on synthesis, characterization and catalytic activity of zeolite–Y encapsulated transition metal complexes as heterogeneous catalysts over oxidation of cyclohexene, styrene, and benzene. Our goal is to not only describe the current status of our knowledge of such materials but also to highlight and discuss the opportunities and outlooks, new areas of application, from environment protection to cost–effective view, etc.

To achieve the above goal, the objectives of the present research work are given below:

3. To study the catalytic activity of such homo- and heterogeneous metal complexes over the oxidation of cyclohexene, styrene, and benzene.
REFERENCES

Studies on transition metal complexes encapsulated in the supercages of zeolite-Y: Synthesis, characterization and catalytic aspects

Studies on transition metal complexes encapsulated in the supercages of zeolite-Y: Synthesis, characterization and catalytic aspects

Studies on transition metal complexes encapsulated in the supercages of zeolite-Y: Synthesis, characterization and catalytic aspects

Studies on transition metal complexes encapsulated in the supercages of zeolite-Y: Synthesis, characterization and catalytic aspects