CHAPTER 1
INTRODUCTION
1.1. INTRODUCTION

There is an ever-growing need to develop and apply industrial chemical processes that are cleaner, greener and cheaper for lasting and sustainable development. Catalysis in general and heterogeneous catalysis in particular plays a key role in developing such chemical processes with high efficiency and selectivity leading to improved process economics, better product quality and reduced pollution. The new generation solid catalysts are also aimed at developing chemical processes where cheaper and renewable raw materials can be used with minimum, if at all, side products. Global trade of catalysts (Fig. 1.1) is currently being estimated at about 10 billion US Dollar, where applications in the area of environmental clean-up, fuels and chemicals sector constitute around 40 %, 32 % and 28 %, respectively.

![Pie chart showing distribution of global catalyst trade expenditure](image)

**Fig. 1.1:** Global trade expenditure for application of catalysts
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While most of the petroleum and petrochemical technologies use various catalysts, the fine-chemical and pharmaceutical sectors have also started increasingly using catalytic processes replacing conventional and often polluting chemical routes. In fact, the use of catalysts in general and solid recyclable catalysts in particular has been synonym of green chemical processes for producing variety of useful materials needed for modern living.

It is worth recalling that the solid catalysts have been at the fulcrum of the phenomenal progress of chemical industrial processes during last century. The discovery of highly active and selective microporous zeolite materials and their catalytic applications in refining and petrochemical sector spearheaded the economic development in the area of transport fuels and bulk chemical sectors. This could be achieved not only by replacing the liquid mineral acids with solid zeolite catalysts but also getting improved selectivity towards desired products. In fact, the molecular dimensions of zeolites make it possible to design and fine-tune the pore architecture to suit a particular product due to their high product shape selectivity. It is no wonder that because of their precise pore dimensions, zeolites are also called as molecular sieves, as they can literally sieve the organic molecules depending upon their shape and size or bulkiness. However, this unique molecular sieving property of zeolites and related materials also became their most critical limitation, as these materials could be effectively used only for the organic transformations involving smaller molecules of the dimensions in the range 0.5 to 0.75 nm. However, quite a few fine chemicals and drug intermediates require larger pore size to be accommodated.
1.1.1. General Background of Catalysis and Catalysts

The Greek meaning of *Catalysis* is to *break down*. A catalyst facilitates a chemical reaction by lowering the activation energy of the reaction pathway.\(^1\) This is shown in Fig. 1.2 for a condensation reaction between substrate molecule A and B. The product C is formed from a transition state structure C’ and C’’ in case of the non-catalyzed and catalyzed reaction paths, respectively. Catalyst increases the reaction rate and therefore the efficiency of the overall chemical process by lowering the activation energy \((E_a'' \ll E_a')\).

*Fig. 1.2:* Energy scheme for catalyzed and uncatalyzed reactions between two substrates.
In other words catalyst can be defined as "a substance, which increases the rate at which a chemical reaction approaches towards equilibrium, without itself becoming permanently involved in the reaction." A catalyst can therefore only accelerate the rate of reaction, which is already thermodynamically feasible. Besides being responsible for a higher activity, catalyst also directs a reaction that influences the selectivity of a chemical process. Most of the bulk and fine chemicals are increasingly produced with the aid of catalysts.

1.1.2. Classification of Catalysis

Generally catalysis is divided in following types depending on the catalyst materials i) Heterogeneous Catalysis ii) Homogeneous Catalysis iii) Phase Transfer Catalysis iv) Bio-Catalysis. Scheme 1.1 gives an overview on classification of catalysis.

1.1.2.1. Heterogeneous catalysis

When reaction system is differentiated with two or more phases then it is called as Heterogeneous Catalysis. In this type mainly the catalyst is in solid phase and products and / or reactants are generally in gas, vapor or liquid phases. This area has been exploited by researcher, due to the high selectivity, easy separation and reusability of catalyst by simple procedure. On the basis of these advantages heterogeneous catalysis has became the basis of industrial and environmental chemistry during last century.

1.1.2.2. Homogeneous catalysis

The name itself explains the term homogeneous, as in this the catalyst, reactant and product are in one phase. The homogeneous catalysts are more reactive in general mainly due to the absence of phase boundaries, diffusion limitation and physisorption phenomenon.
1.1.2.3. **Phase Transfer Catalysis**

The phase transfer catalyst methodology involves a substrate (which is soluble in the organic layer) and an anionic reagent (often a nucleophile), which is dissolved in the aqueous layer. The substrate and the anion are then brought together by a catalyst, which transports the anion into the organic phase where reaction can take place with the substrate at the interphase.

1.1.2.4. **Bio-catalysis**

This involves catalyst in the form of enzyme, whole cell etc. These are considered as ideal catalyst, as they can be operated in aqueous medium at or below room temperature and atmospheric pressure and with nearly 100 % selectivity. These catalysts were used for various reactions such as oxidation, reduction, etc\(^1\).

**Scheme 1.1:** Classification of catalysis
1.2. Selectivity in Heterogeneous Catalysis

The selectivity in chemical transformations is broadly classified as

- Regioselectivity
- Chemoselectivity
- Stereo / Enantioselectivity
- Atom Economy

It has been stated by B. M. Trust\textsuperscript{5} that if heterogeneous catalysis has to make any significant impact in the area of fine and specialty chemical sector, it has to climb the selectivity ladder, as depicted in Fig. 1.3.

Fig. 1.3: Selectivity ladder
1.2.1. Regioselectivity

Shape selectivity is a consequence of geometric restrictions on (i) access of reactants to the zeolite framework, (ii) diffusion controlled ingress of the reactant(s) and/or egress of the product(s), and (iii) formation of restricted transition states. These geometric restrictions result in following shape selectivities, as proposed by Csicsery.\(^6\)

1.2.1.1. Reactant Shape Selectivity

Reactant shape selectivity takes place when one component in a mixture of the reactants is small enough to diffuse through the catalyst pores leaving aside the bulkier reactant. For example, preferential cracking of n-heptane (relative rate of 1.00) over dimethylhexane (relative rate of 0.09) is the best illustration of reactant selectivity for cracking of a straight chain versus branched C\(_7\) (Fig. 1.4 A).

1.2.1.2. Product Shape Selectivity

Product shape selectivity occurs when certain product formed within the pores is too bulky to diffuse out and hence it is either converted to less bulky molecules (e.g. by equilibrium reaction) or eventually deactivate the catalyst by blocking the pores (Fig. 1.4 B). For example, the preferential production in modified pentasil zeolites of \(p\)-xylene over the ortho and meta isomers due to pore diameter restrictions illustrate the product shape selectivity of the zeolite.

1.2.1.3. Restricted Transition State Shape Selectivity (RTSSS)

Restricted transition state shape selectivity occurs when the space available in the pores of the zeolite strongly inhibits or prevents the formation of bulkier reaction intermediate or transition species that does not favor the corresponding product. For example, in the \(m\)-xylene disproportionation, \(1.2.4\) trimethyl benzene (pseudocumene) is
preferentially formed due to less bulkier transition state needed for its formation vis-à-vis 1,3,5 trimethyl benzene (mesitylene) as depicted in Fig. 1.4 C.

![Diagram](image)

**Fig. 1.4:** Different shape selectivities observed in microporous solid catalysts$^6$

### 1.2.2. Chemoselectivity

In several chemical transformations involving molecules having either more than one functional groups in the same molecule or same functional moieties in different chemical environments in the same molecule, chemists need to manipulate only one functional moiety without altering the other. This requires protecting / deprotecting chemical steps, particularly in the area of fine / specialty chemicals and pharma
intermediates, causing multiple step organic transformation resulting in huge utilization of solvent and tedious down-stream processing. New generation heterogeneous solid catalysts have shown great promise in chemoselective oxidation and hydrogenation reactions involving reactants with more than one functional moiety. In epoxidation reactions, titanium silicate analogue of MFI (zeolite ZSM-5) structure, popularly known as TS-1, exhibits very high chemo-selectivity in the oxidation of allylic alcohols towards epoxidation without significantly oxidizing the alcohol group to aldehyde. Similarly, in hydroxyl assisted chemoselective epoxidation of geraniol, TS-1 selectively epoxidizes only that C=C bond, which is in the vicinity of hydroxyl group without oxidizing the other C=C and −OH groups.

Similarly, in hydrogenation of unsaturated aldehydes, Ru-Binap catalyst show some preference (ca. 75 %) towards the hydrogenation of "=C=O" group to corresponding unsaturated alcohol, the remaining being saturated aldehyde.

1.2.3. Asymmetric Heterogeneous Catalysis (Stereo - and Enantioselectivity)

Asymmetric organic transformations are of significant importance particularly for specialty and pharma-intermediate chemicals. Generally, for such asymmetric reactions homogeneous catalysts are used, where very high enantiomeric excess (ee) up to ca. 99+ could be achieved. However, the down stream processing becomes tedious and energy intensive due to catalysts separation followed by elaborate work-up procedures. Consequently, significant efforts are being devoted to develop enantioselective heterogeneous catalytic systems. However, there has been limited success in this very important area using heterogeneous catalytic systems mainly due to relatively lower ‘ee’
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Selectivity in heterogeneous catalysis

exhibited by solid catalysts. Since the separation of enantiomers is rather difficult and costly, the \( \text{ee} \) should be around 98 or more for any practical industrial application. Recently, chiral Ru-SB-SDPEN-MCM-41/MCM-48 catalysts (SB: (S)-BINAP that is S,S-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl and SDPEN: (S,S)-1,2-Diphenylethlene diamine) has been reported as heterogeneous catalyst for asymmetric transfer hydrogenation of prochiral ketones with very high conversions (99%) and enantioselectivity \( \text{ee} = 95-99\% \). The conversion and \( \text{ee} \) obtained over solid catalyst are comparable to that obtained over same metal complex under homogeneous conditions.\

1.2.4. Atom Economy

The concept of atom economy where, no atom is wasted in the formation of undesired co-products, asks chemists to consider how many reactant atoms end up in the desired product of a chemical synthesis and, moreover, how many contribute to the formation of waste products.

Efficient synthetic methods required to assemble complex molecular arrays include reactions that are both selective (chemo-, regio-, diastereo-, and enantio-) and economical in terms of atom count (maximum number of atoms of reactants appearing in the products) as the prime focal point because it defines the overall length of a sequence of reactions that constitutes a synthetic strategy. Transition metal-catalyzed methods that are both selective and economical for formation of desire product, and are of great interest for chemical industry, represent an important starting point for this long-term goal. A key goal must be synthetic efficiency in transforming readily available starting materials to the final target.
The atom economy of the reaction is therefore calculated by the empirical formula as below:

\[
\text{% Atom Economy} = \left(\frac{\text{no. of atoms in desired product}}{\text{no. of atoms used in reactant}}\right) \times 100
\]

By definition, all addition reactions like alkylation of aromatics by olefins, disproportionation of aromatics, such as toluene, ethylbenzene, etc., hydrogenation of carbonyl compounds are potentially 100 % atom economic. On the other hand substitution reactions can never achieve 100 % atom economy.

1.3. GREEN CATALYSIS USING SOLID CATALYST SYSTEMS

The need on developing environmentally clean and sustainable chemical processes can hardly be overemphasized. Although, all the material wealth and comforts the mankind is enjoying today are mainly due to tremendous contribution by the chemical industry, ironically the same chemical industry is held responsible, and quite rightly so, for the present status of pathetic environmental conditions mainly caused by environmentally detrimental industries in as diversified areas as energy (CO₂ emission), dyes, leather, bulk and fine chemicals and pharmaceuticals (use of solvents, less efficient multi step chemical transformations) etc. Anastas has laid down 12 point guidelines for green chemistry needed to be followed by practicing chemists and chemical technologists.\(^{(1)}\) Some most relevant guidelines for developing environmentally benign green chemical process, among others, are:

(i) Use of catalysts

(ii) Use of water to avoid co-solvents
(iii) Use of water as reaction medium

(iv) To achieve sight selectivity and atom efficiency etc.

Fine chemical sector constitute an important class of chemicals bridging the bulk chemical and pharmaceutical sectors. This implies a broad spectrum of production scale where relatively larger-scale production (as high as up to 10,000 TPA) of chemicals as well as kg-scale synthesis of chemicals for pharmaceuticals. It means that there are quite different driving forces, and the different approaches needed to be considered for this sector. For example, while larger scale fine chemical area is mainly driven by the cost, whereas in pharma-intermediate chemical area the purity and high selectivity (regio-, chemo- and stereo-selectivity) are more important issues. However, for the chemicals falling in the range of intermediate production capacity both the cost and the high purity and selectivity are quite important parameters. Compared to petro- and bulk-chemical sectors, the fine or specialty chemical sector poses different problems as well as offers distinct opportunities.

1.3.1. Catalytic Organic Transformations in Aqueous Medium

The greater understanding of chemistry has dramatically altered the way in which people live. Chemistry has been responsible for revolution of medicine, transportation, communication, construction etc., leading to evidently better living standards. However, the development of the modern chemical industry has not been without cost. Waste emanating from chemical manufacturing has, and continues to have, a negative impact on both human health and the environment. The response of the chemical industry to
environmental legislation has been one of waste treatment after the event rather than prevention at source. Therefore, environmental and economic pressures are forcing chemical manufacturers to reassess their operations. The concept of sustainable products and processes has been popularized under the Green Chemistry banner and represents the fastest growing area of chemistry today. The Green Chemistry Program was established in the US in 1991, following the passage of the Pollution Prevention Act the year previous.11 Broadly defined, Green Chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. To help chemists in their efforts towards practicing green chemistry, Anastas and Warner have compiled The twelve principles of Green Chemistry.10

One of the major problems encountered in liquid phase heterogeneous catalytic systems, using either homogeneous catalyst and two immiscible liquids (liquid-liquid, LL) where catalyst is soluble in at least one liquid phase or heterogeneous catalyst along with two immiscible liquid phases, (solid-liquid-liquid, SLL), is mutually immiscible reagent and substrate due to phase boundaries. If the reaction occurs at liquid-liquid phase boundary, rapid stirring may help in facilitating the reaction. However, most commonly an organic co-solvent is used to remove phase boundaries and thereby facilitating the reaction. But, the use of organic solvents poses major problems in downstream processing. Further, the use of organic solvents causes environmental concerns also and thereby against the principles of green chemistry. Hence, the organic transformations under either solvent-free conditions or in the presence of water as reaction medium are attracting increasing attention. However, from the practical point of view the green chemical processes should also favorably compete economically with
enhanced yield of desired product and reduce the cost of downstream work-up and product recovery.

1.4. MESOPOROUS SOLIDS AS SUPPORT

Microporous and mesoporous materials can be used as support for the heterogenization of homogeneous catalyst. The main limitation of microporous material is the pore size constrain of \textit{ca.} 0.75 nm, which limits the use of microporous materials in the organic reaction where the size of reactant molecule exceeds than 0.75 nm in diameter. Hence there is always an interest for the synthesis of mesoporous material. Researchers at Mobil Corporation synthesized M41S\textsuperscript{12} type of mesoporous materials having very high surface area, well defined mesopore and large pore size (2 - 10 nm). These materials were aimed to overcome the constrain of catalytic transformation of bulkier organic materials. These M41S materials are further classified into three types depending on their structures: MCM-41 (hexagonal), MCM-48 (cubic) and MCM-50 (lamellar) respectively. The use of M41S materials is briefly reviewed in this study.

The concept of heterogenization provides the prospective for extending the benefits of heterogeneous catalysis to homogeneous systems. These benefits include easier separation of catalyst and reaction products leading to shorter work up time, high selectivity, improved process efficiency, the potential for reactivation and reuse of the supported catalyst comprising of expensive ligands. However, the prime requirement of the heterogenization approach is to maintain the stability of the heterogenized complex, so that it does not decompose or leach out from the solid matrix into the liquid phase during the course of reaction, and at the same time shows high activity and selectivity.
Chapter 1 Mesoporous Solid as Support

The utilization of mesoporous materials for the anchoring of metal complexes is widely exploited by surface modification\textsuperscript{13}. The ordered hexagonal MCM-41 and cubic MCM-48 material possesses narrow and controlled pore size distribution and large pore openings, which has stimulated fundamental research in inclusion of metal\textsuperscript{14}, metal oxide\textsuperscript{15}, nanoclusters\textsuperscript{16} and metal complexes\textsuperscript{17} inside the mesoporous channels.

1.4.1. Mechanisms for the Formation of Mesoporous Materials

A number of models have been proposed in order to explain the mechanism of formation of mesoporous materials by various synthesis routes. All these models are based on the presence and the role of surfactants in solution to guide the formation of inorganic mesostructures. In solution, surfactants having two parts within the same molecule (hydrophilic head group and long chain hydrophobic tail group) will aggregate and self-organize in such a way as to minimize contact between the incompatible ends. The type of interaction between the surfactant and the inorganic precursor under different synthesis conditions needs careful attention and is a subject of much discussion.

1.4.1.1. Liquid Crystal Templating (LCT) Mechanism

In order to explain the synthesis mechanism, Mobil researchers proposed a liquid crystal templating (LCT) mechanism, based on the similarity between liquid crystalline surfactant assemblies (i.e. lyotropic phases) and M41S. The mesostructure formation depends on the hydrocarbon chain length of the surfactant tail group,\textsuperscript{18} the effect of variation of the surfactant concentration and the additional organic swelling agents. The lowest concentration at which surfactant molecules aggregate to form spherical isotropic
micelles is called critical micelle concentration (CMC₁). Further increase in the surfactant concentration initiates aggregation of spherical into cylindrical or rod-like micelles (CMC₂). There are three main liquid crystalline phases with hexagonal, cubic and lamellar structures. The hexagonal phase is the result of hexagonal packing of cylindrical micelles, the lamellar phase corresponds to the formation of surfactant bilayers and the cubic phase may be regarded as a bicontinuous structure. Two mechanistic pathways were postulated for the formation of M41S type materials:

(A) The structure is defined by the organization of surfactant molecules into lyotropic liquid crystal (LC) phase, which serves as template for the formation of the MCM-41 structure. The first step of the synthesis is the formation of a micellar rod around the surfactant micelle, which will produce a hexagonal array of rods, followed by incorporation of an inorganic array around the rod-like structures in the second step (Scheme 1.2).

(B) Highly sensitive liquid crystal structures formed in surfactant solutions may also interact with the silicate species directly which results in the ordering of the subsequent silicate-enclatherated surfactant micelles to form MCM-41 structure.

So, the negatively charged inorganic components preferentially interacted with the positively charged ammonium head groups of the surfactants and condensed into a solid. However, it was clearly shown¹⁹ that pathway A (Scheme 1.2) did not take place because the surfactant concentrations used were far below the critical micelle concentration (CMC₂) required for hexagonal LC formation.
Scheme 1.2: Liquid crystal templating mechanism proposed for the formation of MCM-41: (A) liquid crystal phase initiated and (B) silicate anion initiated.

1.4.1.2. Silicate Rod Assembly

Davis and co-workers,\textsuperscript{27} by carrying out \textit{in situ} \textsuperscript{14}N NMR spectroscopy, concluded that the liquid crystalline phase is not present in the synthesis medium during the formation of MCM-41, and consequently, this phase cannot be the structure-directing agent for the synthesis of the mesoporous materials (Scheme 1.3)
Scheme 1.3: Silicate rod assembly proposed for the formation of MCM-41: (1) and (2) involve the random ordering of rod-like micelles and interaction with silicate species; (3) represents the spontaneous packing of the rods and (4) is the remaining condensation of silicate species upon final heating of the organic/inorganic composites.

1.4.1.3. Charge Density Matching and Folding Sheets

Both the 'charge density matching' and 'folding sheets' mechanistic models are based on the transformation of lamellar phase to hexagonal one. The 'charge density matching' model proposed by Monnier et al.\textsuperscript{21} and Stucky et al.\textsuperscript{22} suggested that the condensation of initially formed silicate species by the electrostatic attraction between the anionic silicates and the cationic surfactant head groups, reduces the charge density and therefore, curvature was introduced into the layers to maintain the charge density balance with the
surfactant head groups, which transformed the lamellar mesostructure into the hexagonal one (Scheme 1.4A).

Similarly, Inagaki et al.\textsuperscript{21} proposed the 'folding sheets mechanism' and suggested that the incorporation of surfactants by ion-exchange of interlayer Na\textsuperscript{+} ions into the highly flexible sodium silicate sheets of kanemite resulted in folding of the silicate sheets around the surfactants which ultimately condensed into a hexagonal mesostructure (FSM-16) similar to MCM-41 (Scheme 1.4B).

**Scheme 1.4:** Mechanism proposed for the transformation of surfactant-silicate system from lamellar to hexagonal mesophases. (A) hexagonal mesophase obtained by charge density matching and (B) folding of kanemite silicate sheets around intercalated surfactant molecules formed the hexagonal mesostructure.
1.4.1.4. Silicatropic Liquid Crystals

Firouzi and co-workers\textsuperscript{24} showed that the properties and structure of a particular system were not determined by the long-range ordered organic arrays, but by the dynamic interplay among ion-pair inorganic and organic species. The silicate anions ion-exchanged with the surfactant halide counter ions formed the ‘silicatropic liquid crystal’ (SLC) phase (Scheme 1.5), which exhibited very similar behavior to that of typical lyotropic systems and finally condensed irreversibly into MCM-41. The various stages of synthesis were monitored by means of small angle neutron scattering (SANS).

\textbf{Scheme 1.5:} The model (cooperative organization) for the formation of silicatropic liquid crystal phase/silicate-surfactant mesophases. (A) represents the organic and inorganic precursor solutions, (B) represents the preliminary interaction of the two precursor solutions after mixing and (C) represents the multidentate interaction of the oligomeric silicate units with the surfactant molecules.
1.4.1.5. Generalized Liquid Crystal Templating Mechanism

1.4.1.5.1. Electrostatic Interaction

A generalized mechanism for the formation of mesostructured materials based on the specific type of electrostatic interaction between given inorganic precursor I and surfactant head group S (similar to that of Scheme 1.5) was proposed by Huo and coworkers.\textsuperscript{25} In this way, cationic quaternary ammonium surfactants ($S'$) were used for the structuring of anionic inorganic silicate species (I), which could be categorized as the ST pathway. On the other hand, anionic surfactants (S) are employed for structuring cationic inorganic species (I') (ST mesostructures). Organic-inorganic combinations with identically charged partners are also possible, but then the formation of the mesostructure is mediated by the counter-charged ions, which must be present in stoichiometric amounts ($S'X^-$ (X$^-$ is a counter anion) and $S'MI$ (M$^+$ is a metal cation) mesostructures).

1.4.1.5.2. Hydrogen Bonding Interaction

Neutral amine template surfactants ($S''$) and hydroxylated TEOS (I$''$) have been used by Taney and Pinnavaia\textsuperscript{26} to prepare hexagonal mesoporous silicas (HMS) that have thicker pore walls, high thermal stability and smaller crystallite size, but have higher amounts of interparticle mesoporosity and lower degree of long-range ordering of pores than MCM-41 materials. At high concentrations, the non-ionic head groups (N$''$) of polyethylene oxide\textsuperscript{27} and ethylene glycol hexadeeyl ether\textsuperscript{28} can also act as structure directors like the amine head group ($S''$).
1.4.1.5.3. Covalent Interactions

In a different synthetic approach, Ying and co-workers have successfully synthesized hexagonally packed mesoporous metal oxide materials completely stable to surfactant removal through a ligand-assisted templating (LAT) mechanism. The surfactants were pre-treated with the metal alkoxides precursor in the absence of water to form metal-ligated surfactants by nitrogen-metal bond formation between the surfactant head group and the metal alkoxide precursor. The control of mesostructure phase was found possible by adjustment of the metal/surfactant ratio. The existence of covalent interaction is concluded by NMR spectroscopic studies.

1.4.2. Immobilization of Metals/Metal Complexes in Mesoporous Silicates

Either in-situ or post-synthesis immobilization of metals and organometallic complexes, on the surface of mesoporous silicates allows the preparation of multifunctional molecular sieves with desired catalytic properties. Mesoporosity and very high surface area of mesoporous materials have been largely used for the immobilization of different metals as well as bulky organometallic complexes. The processes for metal immobilization include wet impregnation, vapor deposition, treatment with (NH$_4$)$_2$MF$_6$ (M = Si$^4$, Ti$^4$, etc.), metal alkoxides and ion exchange with metal salts, etc.

The immobilization of metal complex is mostly done by ion exchange followed by the complexation with ligand and also by direct incorporation of the metal complex in the mesoporous hexagonal channels of MCM-41.
1.4.3. Covalently Anchored Organofunctionalised Mesoporous Silicates

The advantages of inorganic-organic hybrid materials raised from the fact that inorganic components can provide mechanical, thermal or structural stability, while the organic moieties are more readily modified for specific applications in selective catalysis, separation or sensing.\textsuperscript{38} The presence of large amount of silanol groups [(-O-):SiOH] in MCM-41 and HMS materials attracted the researchers primarily for anchoring the organic functional groups using the concept of organic functionalization in silica gel and then those organic functional groups or ligands were used for anchoring different types of metal complexes with or without modification of the parent functional groups.

![Scheme 1.6: In-situ direct synthetic methods for synthesis of organofunctionalised mesoporous silicates by co-condensation [Source: Ref.\textsuperscript{34}]]

1.4.3.1. In-situ Direct Synthetic Methods

Organically functionalised mesoporous silica was prepared conveniently at room temperature\textsuperscript{39} or at higher temperature\textsuperscript{41} by the co-condensation of tetraalkoxysilane (Si(OR)\textsubscript{4}) and organosiloxanes (R\textsuperscript{1}−Si(OR)\textsubscript{3}) in the presence of surfactant (template) and auxiliary chemicals. Thus, a variety of inorganic-organic hybrid materials, where the organic functional groups are attached covalently with the silica surface of MCM-41 through Si-C bonds, are very important for their various potential applications. An acidic
solvent extraction technique is generally used to remove the surfactant from the product to yield an organo-functionalized ordered porous silica material.

1.4.3.2. Post Synthetic Methods

Organofunctionalised groups were also introduced to the pore surface of mesoporous silica as the terminal group for organic monolayer by post synthesis modification. The treatment of mesoporous silica with organosiloxane precursors produces hybrid inorganic-organic materials by hydrolysis and finally condensation of organosiloxane groups.\textsuperscript{42} Although, the organic functional groups have been introduced into mesoporous silica in both ways, \textit{in situ} and post synthetic methods, organometallic complexes attached covalently to the pore surface are introduced only by post synthesis modifications.\textsuperscript{12,43}

![Diagram](image)

**Scheme 1.7:** Post Synthesis method for functionalization of mesoporous silicates

[Source: Ref.\textsuperscript{50}]
1.5. PHYSICOCHEMICAL CHARACTERIZATION OF CATALYST:

There are numerous techniques available for the characterization of organo-inorganic hybrid mesoporous materials. Each technique is unique by itself and provides important information for understanding different structural features of a particular material. Along with powder X-ray diffraction technique, following characterization tools are used

1. Spectroscopic techniques:
   (a) Ultraviolet-visible spectroscopy (UV-Vis)
   (b) Fourier transform infrared spectroscopy (FTIR)
   (c) X-ray photoelectron spectroscopy (XPS)
   (d) Atomic absorption spectroscopy (AAS)

2. Microscopic techniques:
   (a) Scanning electron microscopy (SEM)
   (b) Transmission electron microscopy (TEM)

3. Volumetric techniques:
   (a) Surface area and porosity measurement by nitrogen adsorption (BET method)

1.5.1. X-ray Diffraction

Powder X-ray diffraction is the most important and commonly used tool to identify and measure the uniqueness of structure, phase purity, degree of crystallinity and unit cell parameters of crystallite materials. This technique is mostly used as primary tool, which support the structural features obtained from other spectroscopic and
microscopic techniques. X-ray diffraction is one of the nondestructive technique and don't require elaborative work for the sample preparation.

The X-ray diffraction patterns were obtained by measurement of the angles at which an X-ray beam is diffracted by the sample. Bragg's equation relate the distance between two hkl planes (d) and the angle of diffraction (2θ) as \( n\lambda = 2d\sin\theta \), where \( \lambda \) = wavelength of X-ray, \( n \) = an integer known as the order of reflection (\( h, k \) and \( l \) represent Miller indices of the respective planes).\(^{45}\) The unit cell parameter \( (a_0) \) of a cubic lattice can be determined by the equation: \( a_0 = d_{hkl} \sqrt{h^2 + k^2 + l^2} \), where \( d \) = distance between two consecutive parallel planes having Miller indices \( h, k \) and \( l \).

1.5.2. UV-Vis Spectroscopy

UV-Vis spectroscopy deals with the study of electronic transition between orbital or bands of atoms, ions or molecule in gaseous, liquid and solid state.\(^{46}\) Change in coordination sphere at metal atom or ion effect on the optical properties and can be characterized by UV-Vis spectroscopy. The position of "metal-to-ligand charge transfer" \((M \rightarrow L)\) band depends on the ligand field symmetry surrounding the metal center and the electronic transitions from ligand-to-metal.

1.5.3. Fourier Transfer Infrared Spectroscopy

This type of spectroscopy deals with the vibration of chemical bonds in a molecule at various frequencies depending on the elements and types of bonds. After absorbing electromagnetic radiation the frequency of vibration of a bond increases leading to transition corresponds to the infrared region \((4000-400 \text{ cm}^{-1})\) of the
electromagnetic spectrum. The term Fourier transform (FT) refers to a recent development in the manner in which the data are collected and converted from an interference pattern to an infrared absorption spectrum, that is like a molecular "fingerprint".47

1.5.4. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is widely used for probing the electronic structure of atoms, molecules and condensed matter. When an X-ray photon of energy $h\nu$ is incident on a solid matter, then kinetic energy ($E_k$) and the binding energy ($E_b$) of the ejected photoelectrons can be related as: $E_k = h\nu - E_b$

This kinetic energy distribution of the photoelectrons is fabricated by a series of discrete bands, which symbolizes for the electronic structure of the sample.48 The core level binding energies of all the elements (other than H and He) in all different oxidation states are unique, which provides instant detection of the chemical composition of the sample after a full range scan.49 However, to account for the multiplet splitting and satellites accompanying the photoemission peaks, the photoelectron spectra should be interpreted in terms of many-electron states of the final ionized state of the sample, rather than the occupied one-electron states of the neutral species.50

1.5.5. Atomic Absorption Spectroscopy

The principle of atomic absorption spectroscopy is based on the energy absorbed during the transitions between electronic energy levels of an atom. When some sort of energy is provided to an atom in ground state by a source such as a flame (temperature
ranging from 2100 - 2800 °C), outer shell electrons are promoted to a higher energy excited state. The radiation absorbed as a result of this, transition between electronic levels can be used for quantitative analysis of metals and metalloids present in solid matrices, which have to be dissolved in appropriate solvent before analysis. The basis of quantitative measurement of radiation intensity is the assumption that radiation absorbed is proportional to atomic concentration. Analogy of relative intensity values for reference standards is used to determine elemental concentration.\textsuperscript{51}

1.5.6. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is one of the most widely used techniques for the morphological characterization of mesoporous and microporous materials. The resolution of SEM approaches a few nanometers, and the instrument can operate at magnifications that are easily adjusted from 10 to over 300,000.

A scanning electron microscope can generate an electron beam scanning back and forth over a solid sample. The interaction between the beam and the sample produces different types of signals providing detailed information about the surface structure and morphology of the sample. When an electron from the beam encounters a nucleus in the sample, the resultant Coulombic attraction leads to a deflection in the electron path, known as Rutherford elastic scattering. A fraction of these electrons will be completely backscattered, reemerging from the incident surface of the sample. Since the scattering angle depends on the atomic number of the nucleus, the primary electrons arriving at a given detector position can be used to produce images containing topological and compositional information.\textsuperscript{52} The high-energy incident electrons can also interact with
the loosely bound conduction band electrons in the sample. However, the amount of energy given to these secondary electrons as a result of the interactions is small and so they have a very limited range in the sample. Hence, only these secondary electrons that are produced within a very short distance from the surface are able to escape from the sample. As a result, high-resolution topographical images can be obtained in this detection mode.\textsuperscript{53}

1.5.7. Transmission Electron Microscopy

Transmission electron microscopy (TEM) is used for high resolution imaging of thin films of a solid sample for microstructural and compositional analysis. The technique involves: (i) irradiation of a very thin sample by a high-energy electron beam, which is diffracted by the lattices of crystalline or semicrystalline material and propagated along different directions. (ii) Imaging and angular distribution analysis of the forward-scattered electrons (unlike SEM where backscattered electrons are detected) and (iii) energy analysis of the emitted X-rays.\textsuperscript{54} The topographic information obtained by TEM in the vicinity of atomic resolution can be utilized for structural characterization and identification of various phases of mesoporous materials, viz., hexagonal, cubic or lamellar.\textsuperscript{55} TEM also provides real space image on the atomic distribution in the bulk and surface of a nano crystal.\textsuperscript{56}

1.5.8. Porosity Measurements by N\textsubscript{2} Adsorption

Despite of some theoretical limitations, the Brunauer-Emmett-Teller (BET) method continues to be the most widely used method for the evaluation of surface area.
pore volume and pore size distribution of porous solids from N\textsubscript{2} physisorption isotherm data. The BET equation can be represented as follows:

\[
\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_0},
\]

where \(v\) = volume of N\textsubscript{2} adsorbed by the sample under pressure \(p\), \(p_0\) = saturated vapor pressure at the same temperature, \(v_m\) = volume of N\textsubscript{2} adsorbed when the surface is covered with a unimolecular layer and \(c\) = constant for a given adsorbate.\textsuperscript{57} The equation suggests that the plot of \(\frac{p}{v(p_0 - p)}\) versus \(\frac{p}{p_0}\) should be linear, and from the intercept \(\frac{1}{v_m c}\) and slope \(\frac{c - 1}{v_m c}\), the values of \(v_m\) and \(c\) can be determined as follows:

\[
v_m = (\text{slope} + \text{intercept})^{-1}.
\]

Thus the specific surface area \((S)\) of a sample can be determined as follows:

\[
S = \frac{N_A v_m A}{22414 m}, \text{ where } N_A = \text{Avogadro number, } m = \text{amount of solid adsorbent, } A = \text{cross-section of the gas molecules (16.2 Å}^2\text{ for N}_2), \text{ and } S \text{ is expressed in cm}^2 \text{ g}^{-1}\text{ unit.}
\]

Several computational procedures are available for the derivation of pore size distribution of mesoporous samples from physisorption isotherms. Most popular among them is the Barrett-Joyner-Halenda (BJH) model, which is based on speculative emptying of the pores by a stepwise reduction of \(p/p_0\), and allowance being made for the contraction of the multilayer in those pores already emptied by the condensate.\textsuperscript{58} The mesopore size distribution is usually expressed as a plot of \(\Delta V_p/\Delta r_p\) versus \(r_p\), where \(V_p\) = mesopore volume, and \(r_p\) = pore radius. It is assumed that the mesopore volume is completely filled at high \(p/p_0\).
1.6. CATALYTIC APPLICATION AND PROSPECTS

Catalytic hydrogenation and transfer hydrogenation of carbonyl and nitro compounds are among important synthetic reactions in view of not only academic interest but also industrial significance. The reduction of organic compounds is a key step in the synthesis of several industrially important chemicals. Conventionally, the reduction has been carried out using stoichiometric amounts of reducing agents such as sodium borohydride, lithium aluminum hydride, hydrazine hydrate, etc.\cite{59} The major disadvantages of these conventional reduction processes are: (a) use of stoichiometric amounts of reducing agents posing serious waste disposal problems due to generation of large quantities of undesired inorganic salts, (b) difficulties in the separation of products from the reaction mixture and its effect on reducing the product yield, (c) non-reusability of reagents and (d) corrosion problems (e.g. in case of iron-acid reagents). Replacement of conventional reduction methods by the catalytic hydrogenation is perhaps one of the most significant achievements of modern catalysis. Table 1.1 summarizes a few important examples of industrially relevant catalytic hydrogenation processes.
<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Product</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2,4-Dinitrotoluene</td>
<td>Pd Al2O3</td>
<td>Toluenediamine</td>
<td>Intermediate for TDH (fine chemicals)</td>
<td>60</td>
</tr>
<tr>
<td>2.</td>
<td>Chloronitrobenzenes</td>
<td>PtS-C</td>
<td>Chloroanilines</td>
<td>Pharmaceuticals &amp; dyes</td>
<td>61</td>
</tr>
<tr>
<td>3.</td>
<td>o-Nitroanisole</td>
<td>Pd/C</td>
<td>o-Anisidine</td>
<td>Dyes &amp; fine chemicals</td>
<td>62</td>
</tr>
<tr>
<td>5.</td>
<td>p-Isobuty lacetophenone</td>
<td>Pd C, Ni HY</td>
<td>p-Isobuty lphenyl ethanol</td>
<td>Intermediate for Ibuprofen</td>
<td>64</td>
</tr>
<tr>
<td>6.</td>
<td>Glucose</td>
<td>Raney Ni</td>
<td>Sorbitol</td>
<td>Pharmaceuticals</td>
<td>65</td>
</tr>
<tr>
<td>7.</td>
<td>Adiponitrile</td>
<td>Raney Ni</td>
<td>Hexamethylenediamine</td>
<td>Intermediate for Nylon 66</td>
<td>66</td>
</tr>
<tr>
<td>8.</td>
<td>1,5,9-Cyclocododecatriene</td>
<td>Pd Al2O3</td>
<td>Cycloododecene</td>
<td>Intermediate for 121-laurolactum</td>
<td>67</td>
</tr>
<tr>
<td>9.</td>
<td>Cinnamaldehyde</td>
<td>Pt-Co C or Pt-Ru C</td>
<td>Cinnamyl alcohol</td>
<td>Fine chemicals, perfumery</td>
<td>68</td>
</tr>
<tr>
<td>10.</td>
<td>2,8-Dichloroadenosine</td>
<td>Pd/BaSO4</td>
<td>Adenosin</td>
<td>Pharmaceutical Neuro-regulatory drug</td>
<td>69</td>
</tr>
<tr>
<td>11.</td>
<td>4-Aminoacetylphenol</td>
<td>Pd support</td>
<td>Octopamine</td>
<td>Pharmaceuticals</td>
<td>70</td>
</tr>
<tr>
<td>12.</td>
<td>Soyabin oil</td>
<td>Ni Support</td>
<td>Saturated oil</td>
<td>Fat industry</td>
<td>71</td>
</tr>
<tr>
<td>13.</td>
<td>Phenylacetylene</td>
<td>Pd C, Al2O3</td>
<td>Styrene</td>
<td>Raw material for polystyrene</td>
<td>72</td>
</tr>
<tr>
<td>14.</td>
<td>Acetophenone</td>
<td>Ru Al2O3</td>
<td>1-Phenylethanol</td>
<td>Pharmaceuticals, fragrance</td>
<td>73</td>
</tr>
</tbody>
</table>
1.6.1. Hydrogenation of Carbonyl Compounds

Among all catalytic methods, utilizing molecular hydrogen to reduce olefins, ketones, and imines, has become one of the most efficient methods. The catalytic hydrogenation of aldehydes and ketones is in widespread industrial practice and relatively straightforward. Palladium is usually the preferred metal of choice for aromatic aldehyde and ketone hydrogenation in neutral non-polar solvents such as hexane, DMF, or ethyl acetate in the range of 5 - 100 °C and 1-10 bar of molecular hydrogen pressure. However, Ruthenium can be preferred over other metals because of its lower cost. The rate of hydrogenation depends on the type of metal used, i.e. Rh > Ru > Pt > Ni > Pd > Co. Nickel catalysts are also in widespread use, but require higher pressure and temperature. They are gradually being phased out because of their associated toxicity and their greater handling and disposal difficulties. Ruthenium catalyst employed in hydrogenation reactions in both gas and liquid phase are most often supported or in the form of complex either with nitrogen and/or phosphorous containing ligand. This section will review the catalytic application and prospects of the “transition metal complexes and encapsulation of transition metal complexes in the mesoporous material for hydrogenation reactions using molecular hydrogen.”
1.6.1.1. Hydrogenation of Mono-ketones

The catalytic hydrogenation of organic compounds containing a carbonyl group is important in the synthesis of fine chemicals, pharmaceuticals, dyes and agrochemicals. Reduction of acetophenone using supported metal catalyst, metal complexes and supported metal complexes, nanoparticles is an important reaction. The products formed during the course of hydrogenation such as, phenyl ethanol and cyclohexyl ethanol are of great industrial importance. For example, cyclohexyl ethanol finds application in the manufacture of polyvinylcyclohexane, which is a high-temperature resistant polymer; while phenyl ethanol finds application in the manufacture of perfumery products, fine chemicals and pharmaceutical.

1.6.1.1.1. Hydrogenation of Ketones using Metal Supported Catalyst

Earlier work for the selective synthesis of 1-phenylethanol was based on Raney Ni, Pd, Ru and Pt catalysts. Wismeijer et al.\textsuperscript{76} found that Ru/TiO\textsubscript{2} gives higher selectivity to 1-phenylethanol compared to Ru supported on fumed silica and carbon. These catalysts were activated at 773 K before using for the hydrogenation of acetophenone. The high selectivity was attributed to the metal-support interaction between Ru and TiO\textsubscript{2} at 773 K while with other supports, the metal support interaction doesn’t occur at that temperature. With Ru/TiO\textsubscript{2} catalyst activated at a lower temperature (473 K) the selectivity obtained for 1-phenylethanol was found to be lower. In metal support interaction, metal particles of the catalyst are supported on titanium-oxide generating new stable active sites for selective carbonyl group hydrogenation, which is a possible explanation for the higher selectivity.\textsuperscript{77} Masson et al.\textsuperscript{78} have investigated the influence of
temperature, pressure and the nature of the solvent on the activity and selectivity of Raney Ni catalysts for hydrogenation of acetophenone to 1-phenylethanol. In cyclohexane as the solvent, low temperature and high pressure were found to give 85% selectivity towards the formation of 1-phenylethanol. Lower alcohols as solvents gave higher selectivity to 1-phenylethanol (> 92%), which is explained on the basis of inhibition of ring hydrogenation by polar molecules and attributed to the difference in dielectric constant of the solvent. Masson et al.\textsuperscript{70} investigated kinetics of acetophenone hydrogenation using Cr promoted Raney Ni catalysts in cyclohexane as the solvent. In the presence of Cr, the hydrogenation of the C=O bond is favored with respect to two side reactions: the hydrogenation of aromatic ring and the hydrogenolysis of the C-OH bond. Kluson\textsuperscript{80} investigated the effect of supports, method of preparation and conditions of catalyst activation on hydrogenation of acetophenone using Ru supported catalysts. It was concluded that the catalyst prepared by impregnation technique with ethanol as the impregnating solvent gives better rate and selectivity for 1-phenylethanol. Rocchini et al.\textsuperscript{81} showed that, in the hydrogenation of acetophenone molecules inserted in cyclodextrins with Ir, Rh and Pt supported catalysts ring hydrogenation was minimum. Organic compounds are known to form 1:1 adducts with cyclodextrins, if they possess a suitable hydrophobic group that can fit in its cavity. By the incorporation of acetophenone molecules in cyclodextrins, the phenyl ring of the acetophenone is inserted in the cyclodextrin cavity thus inhibiting its reduction. The adduct will approach the metallic surface from the side of the carbonyl group, thereby giving aromatic alcohol as a product.
Recent developments on hydrogenation of acetophenone reveal that cheaper catalysts like copper based catalysts can be used for the selective synthesis of 1-phenylethanol. Masaya et al.\textsuperscript{82} have used Cu based catalysts for the selective formation of 1-phenylethanol from acetophenone. Rajasekharam et al.\textsuperscript{83} studied the kinetics of hydrogenation of acetophenone using 10 % Ni/HY catalyst with methanol as the solvent over a temperature range of 353-393 K. The effect of hydrogen partial pressure, initial concentration of acetophenone and temperature on the concentration-time profile in a semi-batch slurry reactor was investigated. It was found that, water a side product formed during the reaction had a strong inhibitory effect on hydrogenation activity. Liquid phase hydrogenation of acetophenone using Rh/C catalyst was studied by Bergault et al.\textsuperscript{84} in trickle bed reactor and slurry airlift reactor and the performance of these two reactors were compared in terms of productivity and yield. Bergault et al.\textsuperscript{85} investigated the kinetics of hydrogenation of acetophenone using 3 % Rh/C catalyst with cyclohexane as the solvent.

1.6.1.1.2. Hydrogenation of Ketones by Phosphorous Containing Metal Complexes

Hydrogenation of simple aromatic ketones has also been studied with some phosphorous containing Rh, Ir, and Ru catalysts. Ru(diphosphine)(diamine)Cl\textsubscript{2} system, is the most remarkable catalyst for the hydrogenation of olefins, ketones, imines, aldehydes. The \textit{trans}[RuCl\textsubscript{2}(bisphosphine)-(1,2-diamine)] catalyst, combined with \textit{t}BuOK as the base and 2-propanol as the solvent, is a very effective catalytic system for hydrogenation of a diverse range of simple aromatic ketones.\textsuperscript{86, 87} Various substituted acetophenones and
acetylnaphthalenes are reduced quantitatively using 'BuOK as base and i-PrOH as the solvent.

1.6.1.1.3. Hydrogenation of Ketones by Nitrogen Containing Metal Complexes

In recent years, optically active chelating chiral nitrogen ligands have found various applications in the field of asymmetric catalysis in the form of transition metal complexes. This renaissance partly arises from several distinct advantages presented by nitrogen ligands over other phosphorous ligands. First, they are not so sensitive towards reaction condition as those of phosphine ligands. Second, they can bind through coordinate bond to wide range of transition metal ions. Third and most important advantage is easy availability and low cost of nitrogen containing ligand as compared to other phosphine ligand. The most commonly used nitrogen containing ligands are those that involve the pyridine ring. Three classes of ligands are 2,2'-bipyridine, 1,10-phenanthroline and cinchonidine. Pt-cinchona modified catalytic system is used for the asymmetric hydrogenation of prochiral ketones. Hess et al. studied the effect of cinchona modifier ratio with metal and substrate to achieve the maximum 70 % ee. Some of these reports are summarized in the Table 1.2.

1.6.1.1.4. Hydrogenation of Ketones by Encapsulated Metal Complexes

Several attempts have been made to develop suitable heterogeneous catalysts for the chemoselective hydrogenation of the C=O group in α,β-unsaturated aldehyde. Number of reports are available in literature, where heterogeneous catalysts by
immobilized transition metal complexes on mesoporous silica were used for hydrogenation of carbonyl compounds have been addressed.\textsuperscript{94, 95, 17b}

### Table 1.2: Literature survey for hydrogenation of ketones

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Catalyst</th>
<th>Reaction parameters</th>
<th>Max Yield</th>
<th>Condition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chiral bipyridyl</td>
<td>Acetophenone</td>
<td>TON = 172.</td>
<td>Sub-Rh = 200.</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Transfer</td>
<td>ee = 15 %</td>
<td>83 °C. IPA.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrogenation</td>
<td>KOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ru(diphosphine)(1,2-diamine)</td>
<td>Amino ketones</td>
<td>ee &gt; 99 %</td>
<td>IPA, 8 bar H\textsubscript{2}, 25 °C, Sub:Cat:base = 2000:1:20</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>Ru-(4,4'-</td>
<td>Acetophenone, substituted</td>
<td>ee &gt; 80 %</td>
<td>IPA, 1 mol %</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>BINAP)(chiral diamine)(Cl-)</td>
<td>acetonaphone</td>
<td>selectivity &gt;95</td>
<td>KO' Bu, 50 bar</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ru{N,N'-bis[o-(diphenylphosphino)benzylidene]cycloheptene-1,2-diamin}</td>
<td>Acetophenone</td>
<td>ee 97 % (S), yield 93 %</td>
<td>IPA, 45 °C, 7h.</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Transfer</td>
<td>(S),</td>
<td>Substrate:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrogenation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Rh-P,P'-1,2-phenylenebis{(1R,2S4R,5S)-2,5-dimethyl-7-dimethyl-7-phosphabicyclo[2.2.1]heptane}</td>
<td>Acetophenone</td>
<td>ee 95 %</td>
<td>MeOH, 25 °C, 50 bar, KBr, 24 h, additives = ionic base, halides, neutral base</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>[Rh-(diox)Cl]2 &amp; chiral alkylphenanthroline</td>
<td>Acetophenone</td>
<td>Turn over rate</td>
<td>IPA, 83 °C, KOH, 10 h.</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Transfer</td>
<td>10000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrogenation</td>
<td>cycles hour. ee 65 %</td>
<td>[S] [Rh]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Catalyst</th>
<th>Substrate</th>
<th>Reaction parameters</th>
<th>Condition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Ru-η⁷-arene with (1S,2R)-2-amino-1,2-diphenylethanol</td>
<td>Acetophenone</td>
<td>Transferring hydrogenation</td>
<td>IPA, 35 °C, ionic liquid</td>
<td>102</td>
</tr>
<tr>
<td>8</td>
<td>Ru⁷⁺(η⁷-C₆H₄mes)</td>
<td>Acetophenone</td>
<td>Transfer hydrogenation</td>
<td>HCOONa, 4 h, water, pH ~ 4</td>
<td>103</td>
</tr>
<tr>
<td>9</td>
<td>Cr promoted Raney Nickel</td>
<td>Acetophenone</td>
<td>Hydrogenation</td>
<td>IPA &amp; water, 80 °C, 10 bar, 2 h</td>
<td>104</td>
</tr>
<tr>
<td>10</td>
<td>RuCl₃(η⁷-C₆H₄mes)</td>
<td>Acetophenone</td>
<td>Transfer hydrogenation</td>
<td>IPA, ligand (S)-phenylglycinol, NaOH, 25 °C, 6 h</td>
<td>105</td>
</tr>
<tr>
<td>11</td>
<td>[Ru(acac)₃]-MeC(C112PPh₂)₃</td>
<td>Esters to alcohols, benzyloxyacetate</td>
<td>TOF = 2071</td>
<td>IPA + HBr, 100 °C, 85 bar, 16 h, MeOH, additives</td>
<td>106</td>
</tr>
<tr>
<td>12</td>
<td>Ru-BINOL derived monodonor phosphorous &amp; substituted acetophenone</td>
<td>Acetophenone</td>
<td>ee 90 %</td>
<td>S/C = 3000, IPA, 20 h, 10 bar, 20-22 °C</td>
<td>107</td>
</tr>
<tr>
<td>13</td>
<td>Rh-phen containing norpinanyl substituent</td>
<td>Acetophenone</td>
<td>TON = 510</td>
<td>IPA, 83 °C</td>
<td>108</td>
</tr>
<tr>
<td>14</td>
<td>Ru, Rh, Ir with chiral bis(oxazoline)</td>
<td>Acetophenone</td>
<td>conv. 85 %, ee 50 %</td>
<td>H₂ = 40 bar, THF, 50 °C, 15 h</td>
<td>109</td>
</tr>
</tbody>
</table>
1.6.1.2. Chemoselective Hydrogenation of Unsaturated Ketones

The α,β-unsaturated alcohols are compounds of great commercial importance as they are used as fragrances, in pharmaceutical industries, intermediates in fine chemicals, etc. Chemoselective hydrogenation of unsaturated ketones and aldehydes using catalyst is a demanding task, as thermodynamics favors the C= C hydrogenation over C= O by ca. 35 kJ/Mol. The achieved selectivity level depends both on the electronic and geometric structures of reactants and metal surfaces.

1.6.1.2.1. Chemoselective Hydrogenation of Unsaturated Ketones by Supported Metals

In accordance with the increasing environmental concern the metals anchored on solid supports have been utilized for the chemoselective hydrogenation of unsaturated ketones to corresponding unsaturated alcohols as heterogeneous catalysts. Moline et al. reported gold catalyst supported on various types of iron oxide for the chemoselective hydrogenation of unsaturated ketones to achieve maximum selectivity up to 65 %. Gold supported on zirconia was found to be very active catalyst for the hydrogenation of unsaturated aldehydes. Ir/H-β shows very high chemoselecivity towards the reduction of unsaturated ketones.

1.6.1.2.2. Chemoselective Hydrogenation of Unsaturated Ketones by Phosphorous Containing Metal Complexes

Recently, ruthenium complexes with ether-phosphine and diamine ligands were successfully tested in the catalytic hydrogenation of unsaturated ketones. These reactions have been performed under moderate reaction conditions to achieve maximum
conversion and selectivity ca. > 99 \%[^14]. To increase the reusability of catalyst, Wu et al. has synthesized the diamine(diphosphine)ruthenium(II) complex by sol-gel process and used for effective reduction of unsaturated ketones with very high selectivity[^15]. Phosphine stabilized Copper (I) hydride catalyst was utilized for the chemoselective reduction of ketones in the presence of alkenes and broad range of other functionality, which are typically reactive towards hydrogenation[^16].

1.6.1.2.3. Chemoselective Hydrogenation of Unsaturated Ketones by Nitrogen-Containing Metal Complexes

There are very few reports available on the hydrogenation of unsaturated ketones using nitrogen containing metal complex. Baiker et al. reported the use of molecular hydrogen in the synthesis of unsaturated alcohol using cinchonidine-modified-Pt/alumina catalyst[^17]. Ruthenium bipyridine metal complex was also investigated for the hydrogenation of ketones in presence of unsaturated compound[^18].

1.6.1.3. Chemoselective Hydrogenation of Diketones

Chemoselective hydrogenation of diketones is one of the fascinating areas for research as the hydroxy-ketones have immense demand in pharmaceutical industries[^19]. For example, 1-hydroxy-1-phenylpropane-2-one (particularly R enantiomer) is used as intermediate for the synthesis of ephedrine and pseudo-ephedrine, which are major ingredients for several pharmaceuticals as anti-asthmatics, vaso-constricting agents and nasal decongestants. The literature available on hydrogenation of diketones to diols is voluminous, however it is pertinent to mention that very few reports are available on the
chemoselective hydrogenation of diketone to hydroxy-ketone. Some of these reports are summarized in the Table 1.3.

1.6.1.3.1. Chemoselective Hydrogenation of Diketones by Nitrogen Containing Metal Complexes

It is well reported that modified cinchonidine on Pt/Al₂O₃ has been utilized for chemoselective hydrogenation of diketones. This modified cinchonidine on the metal surface is successfully used for asymmetric hydrogenation of ethyl pyruvate, 2,3-butanedione, 1-phenyl-1,2-propanedione, cyclic imidoketones, etc. Recently Leino et al. observed that the catalyst modified with hydrosilylation of cinchonidine can be used for chemoselective hydrogenation of 1-phenyl-1,2-pentanediene to 1-hydroxy-1-phenyl-2-one with 70 % enantiomeric excess at very low conversion. The main drawback of this modified Pt-cinchonidine catalyst is that it has very low substrate specificity.

1.6.1.3.2. Chemoselective Hydrogenation of Diketones by Encapsulated Metal Complexes

To the best of our knowledge chemoselective hydrogenation of diketones with encapsulated metal complexes has not been reported in literature.
<table>
<thead>
<tr>
<th>No.</th>
<th>Catalyst</th>
<th>Reaction parameters</th>
<th>Max Yield</th>
<th>Condition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cinchona-modified Pt γAl₂O₃</td>
<td>Ethyl pyruvate &amp; 2,3-Butanedione</td>
<td>86% ee &amp; 47%</td>
<td>50 bar H₂, 20°C, 1200 rpm.</td>
<td>121</td>
</tr>
<tr>
<td>2</td>
<td>Cinchona-modified Pt γAl₂O₃</td>
<td>Butane-2,3-dione</td>
<td></td>
<td>20 ml toluene, 107 bar.</td>
<td>122</td>
</tr>
<tr>
<td>3</td>
<td>Cinchona alkaloid modified Pt</td>
<td>1-phenylpropane-1,2-dione</td>
<td>Yield 1-hydroxy-1-phenyl-2-one &gt; 60%</td>
<td>7 bar, 15°C, 1950 rpm.</td>
<td>123</td>
</tr>
<tr>
<td>4</td>
<td>Cinchona-modified Pt γAl₂O₃</td>
<td>(R)-1-L-t-3-hydroxy-4,4-di-Mepyrroldine-2,3-trione</td>
<td></td>
<td>Toluene, 15°C, 70 bar</td>
<td>124</td>
</tr>
<tr>
<td>5</td>
<td>Hydrosilylation of cinchonidine-Pt γAl₂O₃</td>
<td>Ethylpyruvate &amp; 1-phenylpropane-1,2-dione</td>
<td>Yield = 70% ee 70%</td>
<td>Toluene, 15°C, 10 bar</td>
<td>125</td>
</tr>
<tr>
<td>6</td>
<td>Ru(BINAP)</td>
<td>Various 2,4-dione</td>
<td>Yield of mono hydrogenated product 17%</td>
<td>SubCat = 5000, 60°C, 70 bar</td>
<td>126</td>
</tr>
<tr>
<td>7</td>
<td>Ru-atropisomeric diphosphine 2,2'-diphenyl-6,6'-di-Me-biphenyl</td>
<td>Pentane-2,4-dione</td>
<td>Yield of monohydrogenated bar, 50°C.</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>85% (ee 99%) at 24 h.</td>
<td>EtOH, 100 bar, 50°C</td>
<td>127</td>
</tr>
</tbody>
</table>
### Chapter 1

#### Hydrogenation of Di-ketones

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Catalyst</th>
<th>Substrate</th>
<th>Max Yield</th>
<th>Condition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Pt Silica modified by cinchonidine</td>
<td>Butane-2,3-dione</td>
<td>85%</td>
<td>25°C, 10 bar, DCM.</td>
<td>128</td>
</tr>
<tr>
<td>9</td>
<td>Pt Al₂O₃ modified cinchonidine</td>
<td>1-phenyl-1,2-propanedione</td>
<td>41% for (S)-1-hydroxy-1-phenylpropanone, ee 60%</td>
<td>Ethylacetate, 25°C, 5 bar</td>
<td>129</td>
</tr>
<tr>
<td>10</td>
<td>Hydrosilylated cinchonidine on PdAl₂O₃</td>
<td>1-phenyl-1,2-propanedione</td>
<td></td>
<td>Ethylacetate, 25°C, 5 bar</td>
<td>130</td>
</tr>
<tr>
<td>11</td>
<td>Cinchona modified Pt</td>
<td>1-phenyl-1,2-propanedione</td>
<td>88% yield at 31% conv. (ee 57%)</td>
<td>Toluene, acetic acid.</td>
<td>131</td>
</tr>
<tr>
<td>12</td>
<td>Knitted Pt silica fibers modified with cinchonidine</td>
<td>1-phenyl-1,2-propanedione</td>
<td>Max ee 60%</td>
<td>Gas flow 60 cm³ min⁻¹, 5 bars, 25°C.</td>
<td>132</td>
</tr>
</tbody>
</table>

#### 1.6.2. Chemoselective Hydrogenation of Nitro Compounds

The selective synthesis of amines from the hydrogenation of nitro compounds is commonly used to manufacture important intermediates for dyes, urethanes, agro-chemicals and pharmaceuticals. Aniline is mainly used for production of methylene diphenyl diisocyanate (MDI), and also used as additive for rubber process, intermediates, dyes and pigments, pesticides and herbicides. About 85% of global aniline is produced...
by catalytic hydrogenation of nitrobenzene. The hydrogenation of nitrobenzene to produce aniline can be carried out in the gas or liquid phase using supported metal catalysts and organic solvents such as alcohols, acetone, benzene, ethyl acetate, or aqueous acidic solutions.\textsuperscript{133} The use of these solvents has drawbacks owing to their toxicity, flammability, or environmental hazards. In addition, the solvent may play a crucial role in the stabilization of reactive intermediates and have a decisive influence on chemical reactions. Therefore, the choice of solvent is an important and a green solvent like water should be considered for contemporary chemical processes.

The conventional process for reduction of nitro compounds (commonly known as Béchamp process) employed stoichiometric amounts of Fe-acid as the reducing agent producing almost equivalent amount of Fe-FeO sludge as a byproduct.\textsuperscript{114} Apart from the serious waste disposal problems, the Béchamp process also suffered from the difficulties in the separation of desired products from the reaction mass and use of corrosive reagents like acids. The catalytic hydrogenation using supported metal catalysts (gas-liquid-solid multiphase catalytic reactions) has emerged as a cleaner alternative to the conventional Béchamp process with better selectivity and yields.\textsuperscript{135, 136}

Metal nano-clusters have also been used for the hydrogenation of nitro compounds. Carbon nano-tubes are used as support for the deposition of metal nanoparticles. Dai and coworkers, reported use of various metal nano-particles deposited on carbon nano-tubes.\textsuperscript{137} 3 \% Pt on carbon nano-tubes showed very high activity for the nitrobenzene hydrogenation at ambient temperature and at atmospheric pressure.\textsuperscript{138} Xu et al. investigated the Pd-macromolecule supported on copolymer for the hydrogenation of
4-nitro-phenol.\textsuperscript{139} Platinum on carbon was used for the hydrogenation of nitrobenzene halides.\textsuperscript{140,141} The environmentally benign process which involves the supercritical carbon dioxide has also been investigated.\textsuperscript{142} The heterogenized rhodium metal on zinc aluminate spinel has been studied for chemoselective hydrogenation of nitro compounds.\textsuperscript{143} The Pt and Pd clusters supported on ordered mesoporous carbon molecular sieve showed high catalytic activity towards the hydrogenation of nitro compounds.\textsuperscript{144} Deshpande et al. reported the hydrogenation of substituted nitrobenzene using water-soluble iron complex catalyst under heterogeneous reaction conditions.\textsuperscript{145} All these above mentioned efforts indicates the importance of developing environmentally benign methodologies for hydrogenation of carbonyl and nitro compounds using heterogeneous catalytic system.

1.7. SCOPE AND OBJECTIVE OF THE THESIS

The chemoselective hydrogenation of ketones to secondary alcohol, diketones to hydroxyketones (ketol), \(\alpha,\beta\)-unsaturated ketones to \(\alpha,\beta\)-unsaturated alcohols and nitroaryls to amin-aryls is an interesting area of research as it contains other potentially reducible moieties in the same molecule. These unreduced moieties are very much useful for the synthesis of various dye intermediate, pharmaceutical intermediates and in fine chemical synthesis.\textsuperscript{146} The earlier studies reported for hydrogenation reactions gives very less chemoselectivity of product because of formation of co-condense products and reduction of other moieties as byproducts over transition metal catalysts. Among the other transition metals used in hydrogenation reactions Ru has \(4d^{5}5s^{1}\) electronic
configuration and it has widest scope of oxidation states from -2 to +8 and therefore it forms various coordination geometry in each electronic configuration. It has also great potential for the exploitation of novel catalytic reactions and variety of Ru complexes are prepared and used for various reactions.\textsuperscript{147} Therefore, it is very interesting to utilize this complex in hydrogenation. Also the increased environmental concern in recent years demands the replacement of organic solvents (VOCs) by water for environmentally benign catalytic systems and also to use easily separable and recyclable catalyst in the reaction.

Therefore, following work for doctoral degree has been undertaken with above considerations.

Synthesize and characterize Ru-phenanthroline complexes and their utilization in chemoselective hydrogenation of ketones, diketones, $\alpha,\beta$-unsaturated ketones and nitro-aryls.

To synthesize and characterize immobilized Ru-Phenanthroline complex in organo-functionalised MCM-41 and their utilization in chemoselective hydrogenation of ketones, diketones, $\alpha,\beta$-unsaturated ketones and nitro compounds.

To use water as reaction medium for above mentioned hydrogenation reactions and compare the results with those obtained in the process of commonly used other organic solvents (VOCs).
1.8. OUTLINE OF THE THESIS

The thesis will be presented in FIVE chapters, a brief summary of which is given below.

Chapter 1 presents a general introduction about catalysis emphasizing on selectivity, green chemical transformation, use of solid catalyst and various physicochemical aspects of mesoporous molecular sieve materials. The different characteristic properties of these materials, their synthesis parameters and different approaches for surface-functionalization, characterization techniques, and application as supports for immobilization of transition metal complex in different catalytic reactions are discussed in brief. Based on these reviews, the scope and objective of the present work have been outlined.

Chapter 2 presents experimental results on synthesis of Ru-Phen-Cl₃ catalyst and MCM-41 type molecular sieves and their surface modification by reactive organic functional groups through different approaches followed by encapsulation of Ru-Phen-Cl₃ in organo-functionalised MCM-41 material to form solid composite catalyst. The merits and demerits of these approaches by extensive characterization (XRD, UV-Vis, FTIR, XPS, AAS, SEM, TEM, N₂ adsorption and microanalyses) of these parent and organically modified materials are highlighted.

Chapter 3 deals with a homogeneous (Ru-phenanthroline complexes) and heterogeneous catalyst system containing immobilized Ru-phenanthroline complexes in mesoporous support (MCM-41) for chemoselective hydrogenation of ketones, diketone, α, β-unsaturated ketones. Results of hydrogenation of ketones, diketone, α, β-unsaturated ketones under different reaction conditions are discussed in detail. AAS analyses of the
catalysts before and after the reactions and that of the reaction mixtures are highlighted to emphasize the leaching of ruthenium metal for finding out the recyclability of the heterogeneous catalysts.

Chapter 4 focuses on a novel method for hydrogenation of nitro compounds using ruthenium phenanthroline complexes.

Chapter 5 summarizes the results obtained and the basic findings of the present work. The scope for future work is also discussed at the end of this chapter.
1.9. REFERENCES


