

**SYNTHESIS, CHARACTERIZATION AND CATALYTIC  
APPLICATION OF HETEROGENIZED TRANSITION  
METAL COMPLEXES IN SOLID POROUS MATERIAL**

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## **CERTIFICATION OF RESEARCH GUIDE**

Certified that the work incorporated in the thesis entitled: "**Synthesis, characterization and catalytic application of heterogenized transition metal complexes in solid porous material**", submitted by Mr. Amit Deshmukh, for the Degree of *Doctor of Philosophy*, was carried out by the candidate under my supervision at Catalysis Division, National Chemical Laboratory, Pune 411 008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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## **DECLARATION BY RESEARCH SCHOLAR**

I hereby declare that the thesis entitled "**Synthesis, characterization and catalytic application of heterogenized transition metal complexes in solid porous material**", submitted for the Degree of *Doctor of Philosophy* to the University of Pune, has been carried out by me at Catalysis Division, National Chemical Laboratory, Pune 411 008, India, under the supervision of Dr. Rajiv Kumar. The work is original and has not been submitted in part or full by me for any other degree or diploma to this or any other University.

**Amit A. Deshmukh**

*Dedicated*

*to my*

*Parents*

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## List of Abbreviations

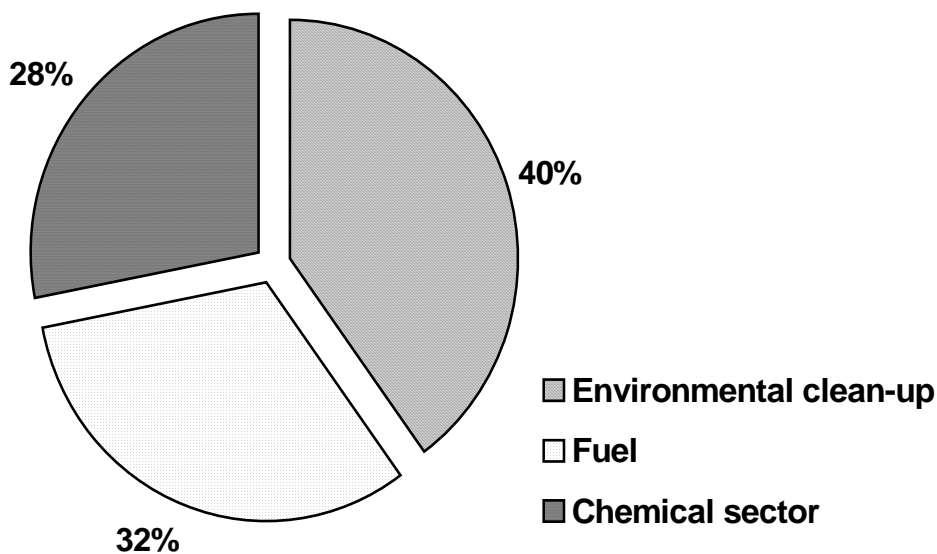
AAS	Atomic Absorption Spectroscopy
APTS	3-Aminopropyltrimethoxy silane
BE	Binding Energy
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BY	Bipyridyl
CTABr	Cetyltrimethylammonium bromide
DCM	Dichloromethane
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GCMS	Gas Chromatography – Mass Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
MCM	Mobil's Crystalline Material
NMR	Nuclear Magnetic Resonance
PHEN	Phenanthroline
PY	Pyridine
SAED	Selected Area Electron Diffraction
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl orthosilicate
TON	Turnover Number
TOF	Turnover Frequency
UV-Vis	Ultraviolet-Visible
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

# 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.



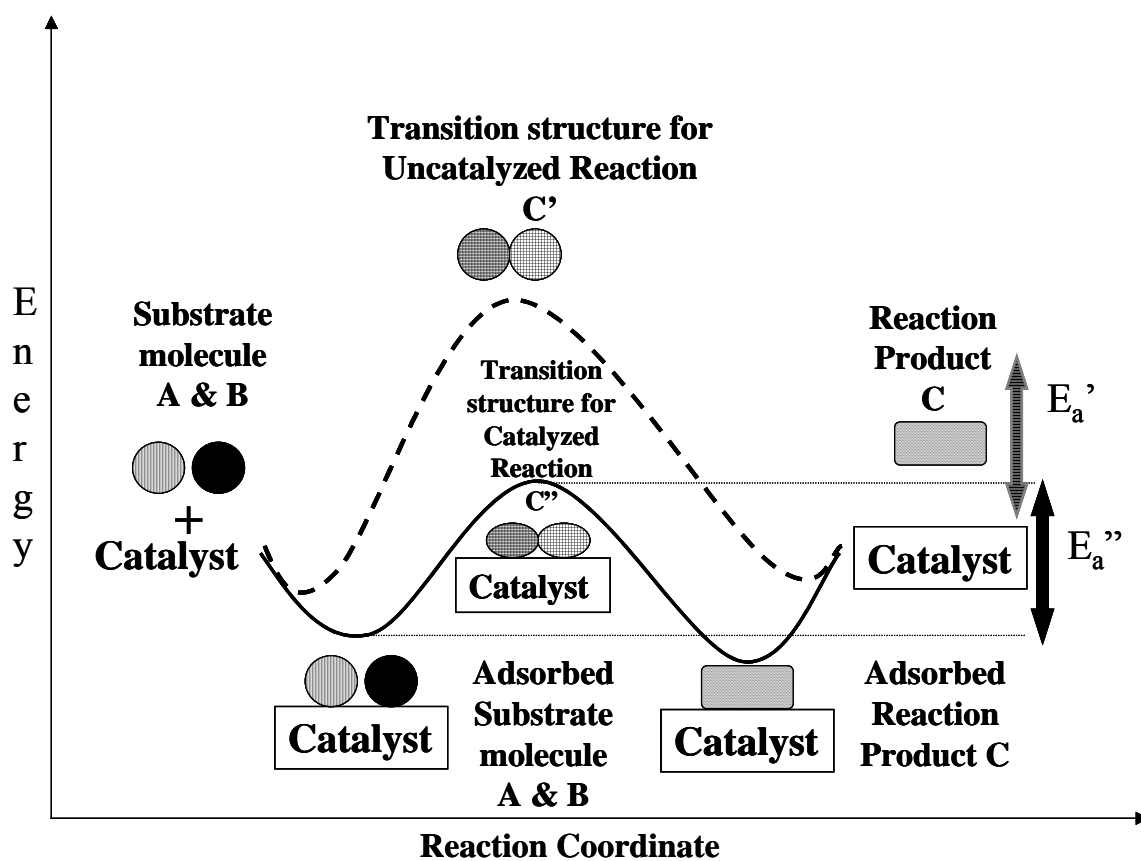
**Fig. 1.1:** Global trade expenditure for application of catalysts

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.<sup>1</sup> 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.<sup>2</sup> 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.<sup>3</sup>

### **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 become the basis of industrial and environmental chemistry during last century.

#### *1.1.2.2. Homogeneous catalysis*

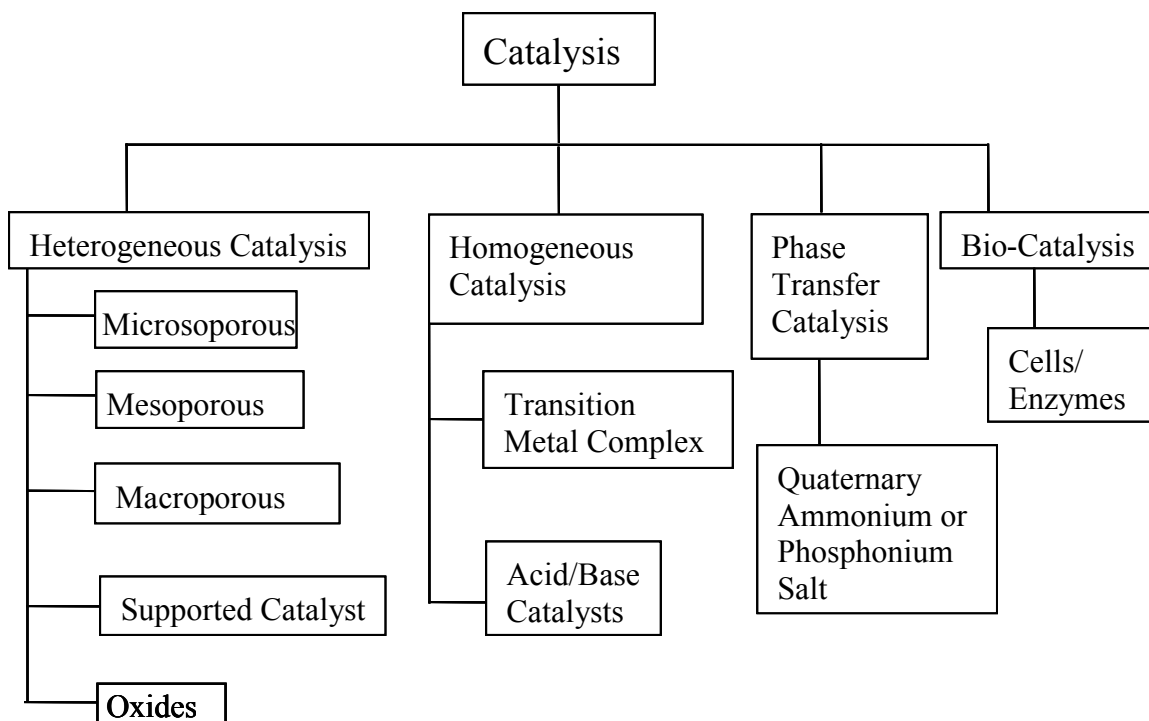
The name itself explains the term homogeneous, as in this the catalyst, reactant and product are in one phase. The homogeneous catalysts are more reactive in general mainly due to the absence of phase boundaries, diffusion limitation and physisorption phenomenon.

### 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<sup>4</sup>.



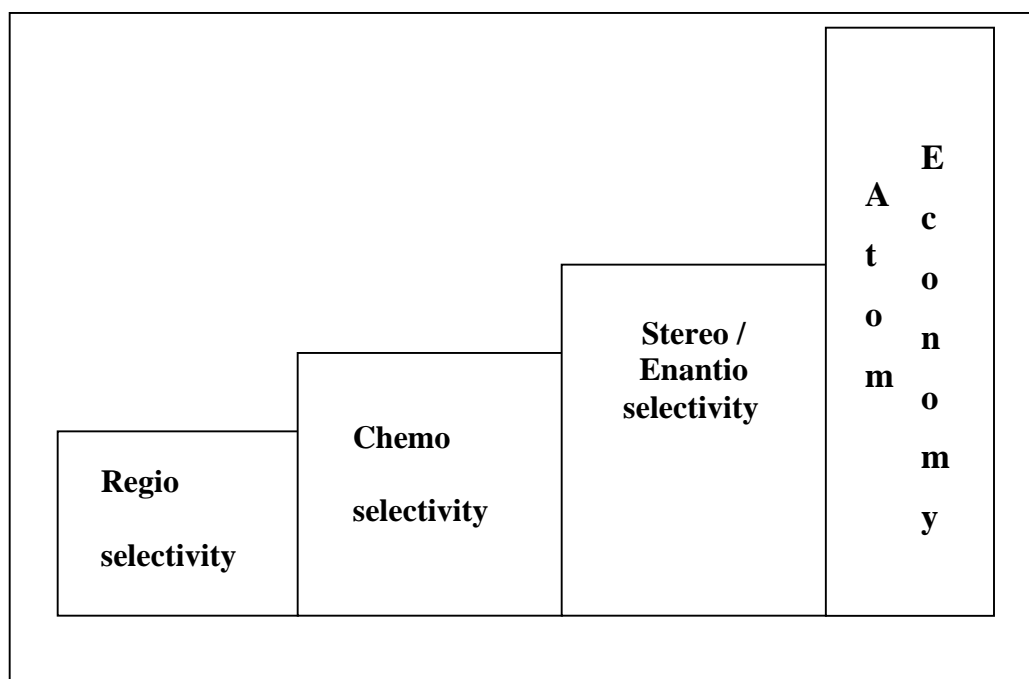
**Scheme 1.1:** Classification of catalysis

## 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<sup>5</sup> 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.<sup>6</sup>

#### 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<sub>7</sub> (Fig. 1.4 A).

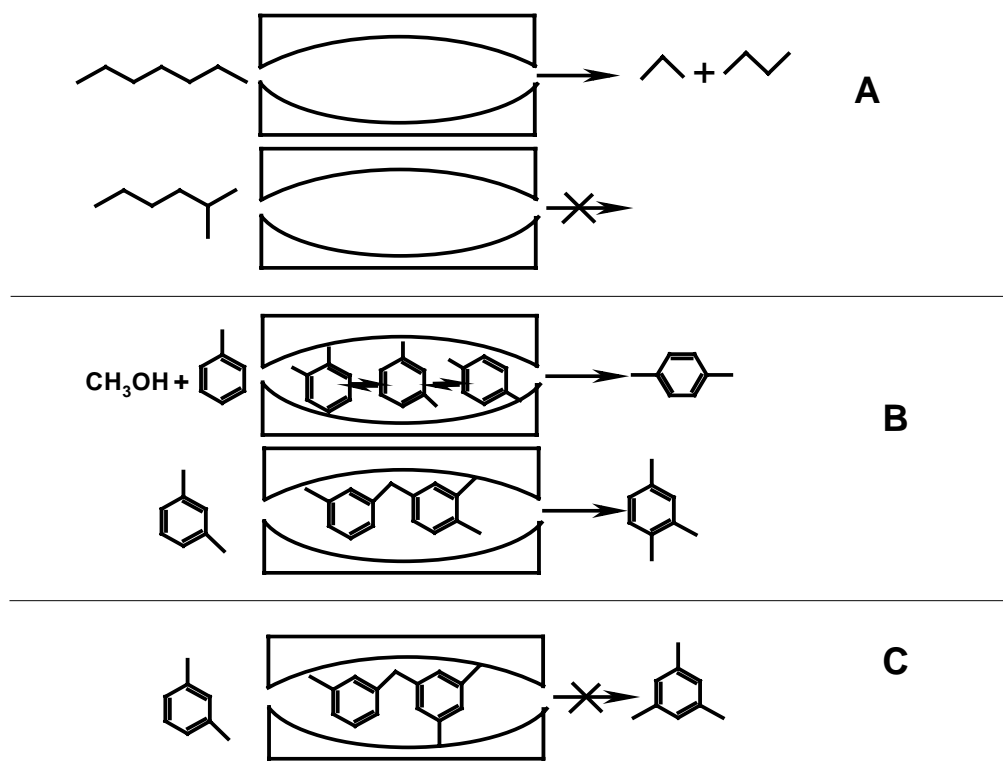
#### 1.2.1.2. Product Shape Selectivity

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.



**Fig. 1.4:** Different shape selectivities observed in microporous solid catalysts<sup>6</sup>

### 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’

exhibited by solid catalysts. Since the separation of enantiomers is rather difficult and costly, the '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-Diphenylethylenediamine) has been reported as heterogeneous catalyst for asymmetric transfer hydrogenation of prochiral ketones with very high conversions (99 %) and enantioselectivity ee = 95-99 %). The conversion and ee obtained over solid catalyst are comparable to that obtained over same metal complex under homogeneous conditions.<sup>7</sup>

#### 1.2.4. Atom Economy

The concept of atom economy where, no atom is wasted in the formation of undesired co-products,<sup>8,9</sup> 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:

$$\% \text{ Atom Economy} = (\text{no. of atoms in desired product} / \text{no. of atoms used in reactant}) \times 100$$

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 (CO<sub>2</sub> 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.<sup>10</sup> 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 high 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.<sup>11</sup> 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*.<sup>10</sup>

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 down stream 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 *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<sup>12</sup> type of mesoporous materials having very high surface area, well defined mesopore and large pore size (2 – 10 nm). These materials were aimed to over come constrain of catalytic transformation of bulkier organic materials. These M41S materials are further classified into three types depending on there 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 in to the liquid phase during the course of reaction, and at the same time shows high activity and selectivity.

The utilization of mesoporous materials for the anchoring of metal complexes is widely exploited by surface modification<sup>13</sup>. The ordered hexagonal MCM-41 and cubic MCM-48 material possess narrow and controlled pore size distribution and large pore openings, which has stimulated fundamental research in inclusion of metal<sup>14</sup>, metal oxide<sup>15</sup>, nanoclusters<sup>16</sup> and metal complexes<sup>17</sup> 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*

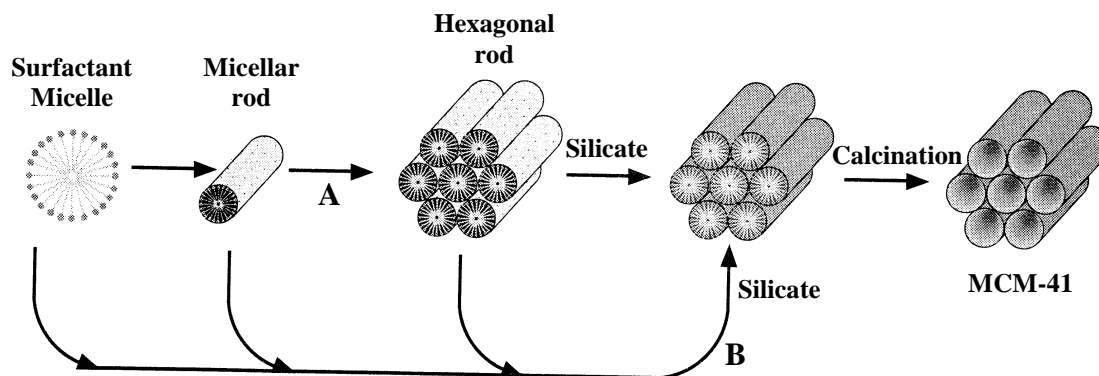
In order to explain the synthesis mechanism, Mobil researchers proposed a liquid crystal templating (LCT) mechanism, based on the similarity between liquid crystalline surfactant assemblies (i.e. lyotropic phases) and M41S. The mesostructure formation depends on the hydrocarbon chain length of the surfactant tail group,<sup>18</sup> 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 ( $CMC_1$ ). Further increase in the surfactant concentration initiates aggregation of spherical into cylindrical or rod-like micelles ( $CMC_2$ ). 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.

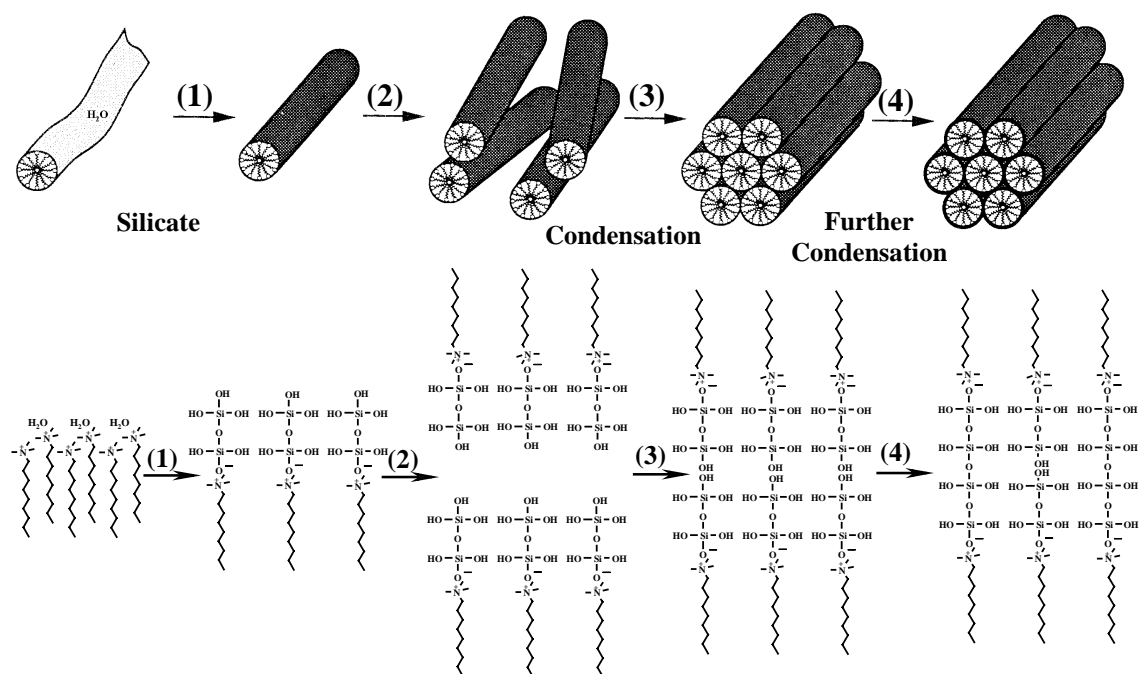
So, the negatively charged inorganic components preferentially interacted with the positively charged ammonium head groups of the surfactants and condensed into a solid. However, it was clearly shown<sup>19</sup> that pathway A (Scheme 1.2) did not take place because the surfactant concentrations used were far below the critical micelle concentration ( $CMC_2$ ) 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,<sup>20</sup> by carrying out *in situ*  $^{14}\text{N}$  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)



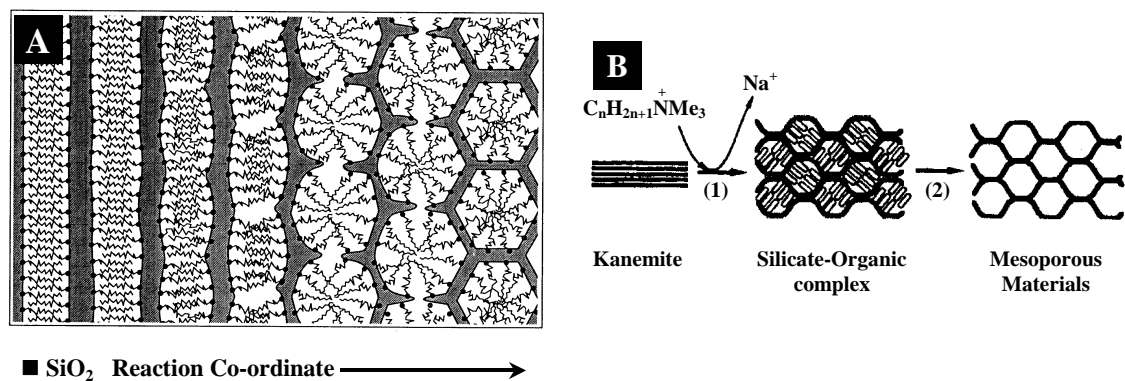
**Scheme 1.3:** Silicate rod assembly proposed for the formation of MCM-41: (1) and (2) involve the random ordering of rod-like micelles and interaction with silicate species; (3) represents the spontaneous packing of the rods and (4) is the remaining condensation of silicate species upon final heating 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.<sup>21</sup> and Stucky et al.<sup>22</sup> 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.<sup>23</sup> proposed the ‘folding sheets mechanism’ and suggested that the incorporation of surfactants by ion-exchange of interlayer  $\text{Na}^+$  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).

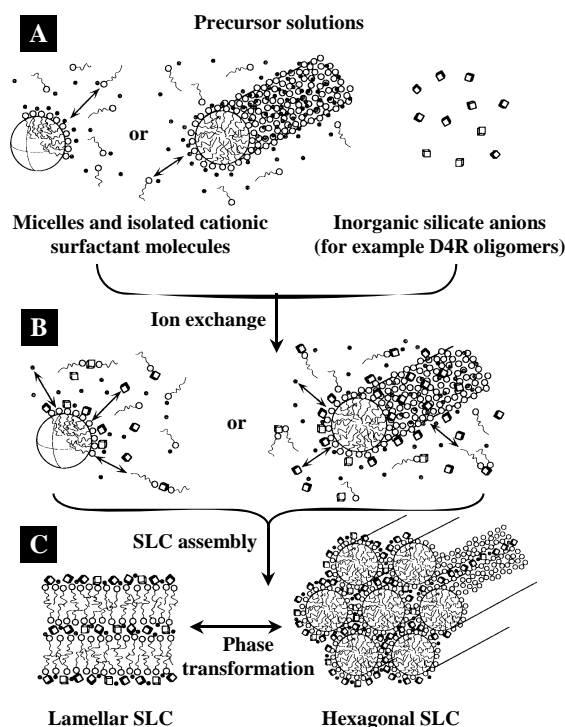


**Scheme 1.4:** Mechanism proposed for the transformation of surfactant-silicate system from lamellar to hexagonal mesophases. (A) hexagonal mesophase obtained by charge density matching and (B) folding of kanemite silicate sheets around intercalated surfactant molecules formed the hexagonal mesostructure.



#### 1.4.1.4. Silicatropic Liquid Crystals

Firouzi and co-workers<sup>24</sup> 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).



**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 co-workers.<sup>25</sup> 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  $S^+I^-$  pathway. On the other hand, anionic surfactants ( $S^-$ ) are employed for structuring cationic inorganic species ( $I^+$ ) ( $S^-I^+$  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 ( $S^+X^-I^+$  ( $X^-$  is a counter anion) and  $S^-M^+I^-$  ( $M^+$  is a metal cation) mesostructures).

#### 1.4.1.5.2. Hydrogen Bonding Interaction

Neutral amine template surfactants ( $S^0$ ) and hydroxylated TEOS ( $I^0$ ) have been used by Tanev and Pinnavaia<sup>26</sup> 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 ( $N^0$ ) of polyethylene oxide<sup>27</sup> and ethylene glycol hexadecyl ether<sup>28</sup> can also act as structure directors like the amine head group ( $S^0$ ).

#### 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.<sup>29</sup> 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.

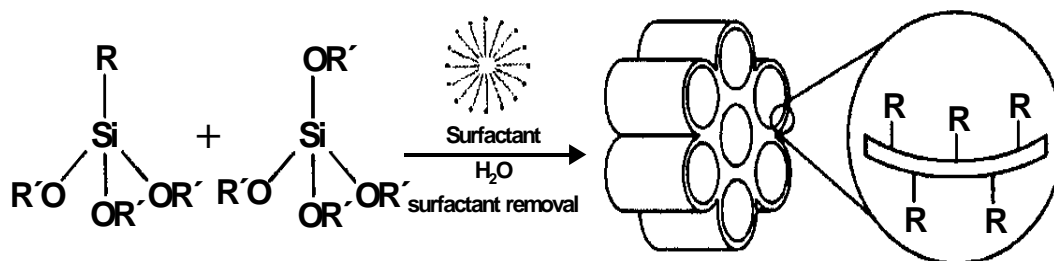
#### 1.4.2. Immobilization of Metals/Metal Complexes in Mesoporous Silicates

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,<sup>30</sup> vapor deposition,<sup>31</sup> treatment with  $(\text{NH}_4)_2\text{MF}_6$  ( $\text{M} = \text{Si}^{4+}, \text{Ti}^{4+}, \text{etc.}$ ),<sup>32</sup> metal alkoxides<sup>33</sup> and ion exchange with metal salts,<sup>34,35</sup> etc.

The immobilization of metal complex is mostly done by ion exchange followed by the complexation with ligand<sup>36</sup> and also by direct incorporation of the metal complex in the mesoporous hexagonal channels of MCM-41.<sup>37</sup>

### 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.<sup>38</sup> The presence of large amount of silanol groups  $[(-O-)_{3}SiOH]$  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.<sup>39</sup>]

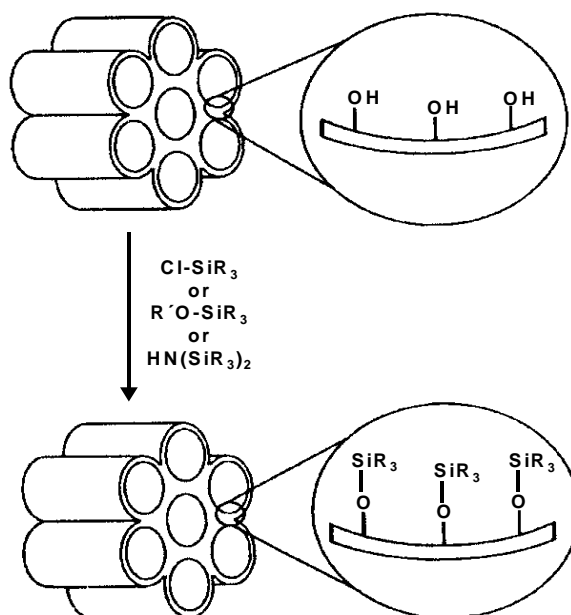
#### 1.4.3.1. In-situ Direct Synthetic Methods

Organically functionalised mesoporous silica was prepared conveniently at room temperature<sup>40</sup> or at higher temperature<sup>41</sup> by the co-condensation of tetraalkoxysilane ( $Si(OR)_4$ ) and organosiloxanes ( $R^1-Si(OR)_3$ ) 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.<sup>42</sup> Although, the organic functional groups have been introduced into mesoporous silica in both ways, *in situ* and post synthetic methods, organometallic complexes attached covalently to the pore surface are introduced only by post synthesis modifications.<sup>43,44</sup>



**Scheme 1.7:** Post Synthesis method for functionalization of mesoporous silicates  
[Source: Ref.<sup>39</sup>]

## **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 tool 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 ( $2\theta$ ) 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).<sup>45</sup> 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.<sup>46</sup> 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”.<sup>47</sup>

#### 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.<sup>48</sup> 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.<sup>49</sup> 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.<sup>50</sup>

#### 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.<sup>51</sup>

### **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.<sup>52</sup> 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.<sup>53</sup>

### **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.<sup>54</sup> 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.<sup>55</sup> TEM also provides real space image on the atomic distribution in the bulk and surface of a nano crystal.<sup>56</sup>

### **1.5.8. Porosity Measurements by N<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> adsorbed by the sample under pressure  $p$ ,  $p_0$  = saturated vapor pressure at the same temperature,  $v_m$  = volume of N<sub>2</sub> adsorbed when the surface is covered with a unimolecular layer and  $c$  = constant for a given adsorbate.<sup>57</sup> 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:

$S = \frac{N_0 v_m A}{22414m}$ , where  $N_0$  = Avogadro number,  $m$  = amount of solid adsorbent,  $A$  = cross-

section of the gas molecules (16.2 Å<sup>2</sup> for N<sub>2</sub>), and  $S$  is expressed in cm<sup>2</sup> g<sup>-1</sup> 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.<sup>58</sup> 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.<sup>59</sup> 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 1.1:** Some examples of Catalytic Liquid Phase Hydrogenation Reactions

<b>Sr. No</b>	<b>Substrate</b>	<b>Catalyst</b>	<b>Product</b>	<b>Application</b>	<b>Reference</b>
1.	2,4-Dinitrotoluene	Pd/Al <sub>2</sub> O <sub>3</sub>	Toluenediamine	Intermediate for TDI (fine chemicals)	60
2.	Chloronitrobenzenes	PtS/C	Chloroanilines	Pharmaceuticals & dyes	61
3.	o-Nitroanisole	Pd/C	o-Anisidine	Dyes & fine chemicals	62
4.	Butynediol	Pd-Zn/CaCO <sub>3</sub>	cis-Butenediol	Intermediate for vitamin-A & endosulfan	63
5.	p-Isobutylacetophenone	Pd/C, Ni/HY	p-Isobutylphenylethanol	Intermediate for Ibuprofen	64
6.	Glucose	Raney Ni	Sorbitol	Pharmaceuticals	65
7.	Adiponitrile	Raney Ni	Hexamethylenediamine	Intermediate for Nylon 66	66
8.	1,5,9-Cyclododecatriene	Pd/Al <sub>2</sub> O <sub>3</sub>	Cyclododecene	Intermediate for 121-lauro lactum	67
9.	Cinnamaldehyde	Pt-Co/C or Pt-Ru/C	Cinnamyl alcohol	Fine chemicals, perfumery	68
10.	2,8-Dichloroadenosine	Pd/BaSO <sub>4</sub>	Adenosin	Pharmaceutical Neuro-regulatory drug	69
11.	4-Aminoacetylphenol	Pd/support	Octopamine	Pharmaceuticals	70
12.	Soyabin oil	Ni /Support	Saturated oil	Fat industry	71
13.	Phenylacetylene	Pd/C, Al <sub>2</sub> O <sub>3</sub>	Styrene	Raw material for polystyrene	72
14.	Acetophenone	Ru/Al <sub>2</sub> O <sub>3</sub>	1-Phenylethanol	Pharmaceuticals, fragrance	73

### 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.<sup>74</sup> 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.<sup>75</sup> 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.<sup>76</sup> found that Ru/TiO<sub>2</sub> 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<sub>2</sub> at 773 K while with other supports, the metal support interaction doesn't occur at that temperature. With Ru/TiO<sub>2</sub> 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.<sup>77</sup> Masson et al.<sup>78</sup> 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.<sup>79</sup> 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<sup>80</sup> 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.<sup>81</sup> 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.<sup>82</sup> have used Cu based catalysts for the selective formation of 1-phenylethanol from acetophenone. Rajasekharam et al.<sup>83</sup> 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.<sup>84</sup> 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.<sup>85</sup> 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<sub>2</sub> system, is the most remarkable catalyst for the hydrogenation of olefins, ketones, imines, aldehyde. The *trans*[RuCl<sub>2</sub>(bisphosphine)-(1,2-diamine)] catalyst, combined with <sup>t</sup>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.<sup>86, 87</sup> Various substituted acetophenones and

acetylnaphthalenes are reduced quantitatively using <sup>t</sup>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.<sup>88</sup> 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.<sup>89, 90</sup> Pt-cinchona modified catalytic system is used for the asymmetric hydrogenation of prochiral ketones.<sup>91</sup> Hess et al. studied the effect of cinchona modifier ratio with metal and substrate to achieve the maximum 70 % ee.<sup>92</sup> 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  $\alpha,\beta$ -unsaturated aldehyde.<sup>93</sup> 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.<sup>94, 95, 17b</sup>

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

Sr No.	Reaction parameters			Reference	
	Catalyst	Sub	Max Yield		Condition
1	Chiral bipyridyl	Acetophenone Transfer hydrogenation	TON = 172, ee = 15 %	Sub/Rh = 200, 83 °C, IPA, KOH	96
2	Ru(diphosphine)( 1,2diamine)	Amino ketones	ee > 99 %	IPA, 8 bar H <sub>2</sub> , 25 °C, Sub:Cat:base = 2000:1:20	97
3	Ru-(4,4'- BINAP)(chiral diamine)Cl <sub>2</sub>	Acetophenone, substituted acetophenone	ee > 80 %, selectivity >95 %	IPA, 1 mol % KO <sup>t</sup> Bu, 50 bar H <sub>2</sub> , 20 h, 25 °C	98
4	Ru{N,N'-bis[o- (diphenylphosphin o)benzylidene]cyc lohexane-1,2- diamin}	Acetophenone Transfer hydrogenation	ee 97 % (S), yield 93 %	IPA, 45 °C, 7h, Substrate: Catalyst = 200,	99
5	Rh-P,P'-1,2- phenylenebis{(1R, 2S4R,5S,)-2,5- dimethyl-7- phosphabicyclo[2. 2.1]heptane}	Acetophenone & substituted acetophenone	ee 95 %	MeOH, 25 °C, 30 bar, KBr, 24 h, additives = ionic base / halides / neutral base	100
6	[Rh-(diol)Cl] <sub>2</sub> & chiral 3- alkylphenanthroli ne	Acetophenone Transfer hydrogenation	Turn over rate 10000 cycles/hour. ee 65 %	IPA, 83 °C, KOH, 10 h, [S]/[Rh] = 2000	101

Sr No.	Reaction parameters				Reference
	Catalyst	Sub	Max Yield	Condition	
7	Ru- $\eta^6$ arene (1S,2R)-2-amino- 1,2- diphenylethanol	with Acetophenone Transfer hydrogenation	conv. 98 %, ee 98 %	IPA, 35 °C, KOH, 25 h, ionic liquid	102
8	Ru <sup>II</sup> ( $\eta^6$ - C <sub>6</sub> Me <sub>6</sub> )(bipy)(H <sub>2</sub> O)	Acetophenone Transfer hydrogenation	TOF = 153, yield 97 %	70 °C, HCOONa, 4 h, water, pH ~ 4	103
9	Cr promoted Raney Nickel	Acetophenone Hydrogenation	select. >99 %	IPA & water, 80 °C, 10 bar, 2 h	104
10	RuCl <sub>2</sub> ( $\eta^6$ -C <sub>6</sub> Me <sub>6</sub> )	Acetophenone Transfer hydrogenation	ee 94 %, conv. 95 %	IPA, ligand (S)- phenylglycinol, NaOH, 25 °C, 6 h	105
11	[Ru(acac) <sub>3</sub> ]- MeC(CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub>	Esters to alcohols, bezybezoate	TOF = 2071	100 °C, 85 bar, 16 h, MeOH, additives = IPA +HBr	106
12	Ru-BINOL derived monodonor phosphorous	Acetophenone & substituted acetophenone	ee 90 %	S/C = 3000, IPA, 20 h, 10 bar, 20-22 °C,	107
13	Rh-phen containing norpinanyl substituent	Acetophenone transfer hydrogenation	TON = 510 ee 24 %	IPA, 83 °C, Sub /Rh = 200,	108
14	Ru, Rh, Ir with chiral bis(oxazoline)	Acetophenone	conv. 85 % ee 50 %	H <sub>2</sub> = 40 bar, THF, 50 °C, 15 h	109

### ***1.6.1.2. Chemoselective Hydrogenation of Unsaturated Ketones***

The  $\alpha,\beta$ -unsaturated alcohols are compounds of great commercial importance as they are used as fragrances, in pharmaceutical industries, intermediates in fine chemicals, etc.<sup>110</sup> 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 %.<sup>111</sup> Gold supported on zirconia was found to be very active catalyst for the hydrogenation of unsaturated aldehydes.<sup>112</sup> Ir/H- $\beta$  shows very high chemoselectivity towards the reduction of unsaturated ketones.<sup>113</sup>

#### *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 %.<sup>114</sup> 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.<sup>115</sup> 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.<sup>116</sup>

#### *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.<sup>117</sup> Ruthenium bipyridine metal complex was also investigated for the hydrogenation of ketones in presence of unsaturated compound.<sup>118</sup>

#### *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.<sup>119</sup> 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/Al<sub>2</sub>O<sub>3</sub> has been utilized for chemoselective hydrogenation of diketones. This modified cinchonidine on the metal surface is successfully used for asymmetric hydrogenation of ethyl pyruvate<sup>120</sup>, 2,3-butadione, 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-pentanedione 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 1.3:** Literature survey for hydrogenation of diketones.

Sr No.	Reaction parameters				Reference
	Catalyst	Sub	Max Yield	Condition	
1	Cinchona-modified Pt/ $\gamma$ Al <sub>2</sub> O <sub>3</sub>	Ethyl pyruvate & 2,3-butanedione	Ethylpyruvate = ee 86 % Butanedione = ee 47 %	50 bar H <sub>2</sub> , 20 °C, 1200rpm.	121
2	Cinchona-modified Pt/ $\gamma$ Al <sub>2</sub> O <sub>3</sub>	Butane-2,3-dione		20 ml toluene, 107 bar,	122
3	Cinchona alkaloid modified Pt	1-phenylpropane-1,2-dione	Yield 1-hydroxy-1-phenyl-2-one = 60 %	7 bar, 15 °C, 1950 rpm,	123
4	Cinchona-modified Pt/ $\gamma$ Al <sub>2</sub> O <sub>3</sub>	1-Et-4,4-diMepyrrolidine-2,3,5-trione	(R)-1-Et-3-hydroxy-4,4-di-Mepyrrolindine-2,5-dione	Toluene, 15 °C, 70 bar	124
5	Hydrosilylation of cinchonidine-Pt/ $\gamma$ Al <sub>2</sub> O <sub>3</sub>	Ethylpyruvate & 1-phenylpropane-1,2-dione	Yield = 70 % ee 70 %	Toluene, 15 °C, 10 bar	125
6	Ru(BINAP)	Various 2,4-dione	Yield of mono hydrogenated product 17 %	Sub/Cat = 5000, 60 °C, 70 bar	126
7	Ru-atropisomeric diphosphine bis(diphenylphosphino)-6,6'-di-Me-biphenyl	Pentane-2,4-dione	Yield of monohydrogenated 85 % (ee 99 %) at conv. 85 %	EtOH, 100 bar, 50°C, 24 h,	127



Sr. No.	Reaction parameters			Reference
	Catalyst	Sub	Max Yield	
8	Pt/Silica modified by cinchonidine	Butane-2,3-dione	yield 85 % of 3-hydroxy-butane-2-one [-(s)-ee 20-40 %]	25 °C, 10 bar, DCM. 128
9	Pt/Al <sub>2</sub> O <sub>3</sub> modified cinchonidine and 10,11-dihydrocinchonidine	1-phenyl-1,2-propanedione	yield 41 % for (S)-1-hydroxy-1-phenylpropanone. ee 60 %	Ethylacetate, 25 °C, 5 bar 129
10	Hydrosilylated cinchonidine on Pt/Al <sub>2</sub> O <sub>3</sub>	1-phenyl-1,2-propanedione		Ethylacetate, 25 °C, 5 bar 130
11	Cinchona modified Pt	1-phenyl-1,2-propanedione	Hydroxyketones yield 88 % at 31 % conv. (ee 57 %)	Solvents = Toluene, acetic acid. 131
12	Knitted Pt silica fibers modified with cinchonidine	1-phenyl-1,2-propanedione	Max ee 60 %	Gas flow 60 cm <sup>3</sup> min <sup>-1</sup> , 5 bars, 25 °C. 132

### 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, agrochemicals 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.<sup>133</sup> 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.<sup>134</sup> 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.<sup>135, 136</sup>

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 nano-particles. Dai and coworkers, reported use of various metal nano-particles deposited on carbon nano-tubes.<sup>137</sup> 3 % Pt on carbon nano-tubes showed very high activity for the nitrobenzene hydrogenation at ambient temperature and at atmospheric pressure.<sup>138</sup> Xu et al. investigated the Pd-macromolecule supported on copolymer for the hydrogenation of

4-nitro-phenol.<sup>139</sup> Platinum on carbon was used for the hydrogenation of nitrobenzene halides.<sup>140,141</sup> The environmentally benign process which involves the supercritical carbon dioxide has also been investigated.<sup>142</sup> The heterogenized rhodium metal on zinc aluminate spinel has been studied for chemoselective hydrogenation of nitro compounds.<sup>143</sup> The Pt and Pd clusters supported on ordered mesoporous carbon molecular sieve showed high catalytic activity towards the hydrogenation of nitro compounds.<sup>144</sup> Deshpande et al. reported the hydrogenation of substituted nitrobenzene using water-soluble iron complex catalyst under heterogeneous reaction conditions.<sup>145</sup> 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 nitro-aryls 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.<sup>146</sup> 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 a byproducts over transition metal catalysts. Among the other transition metals used in hydrogenation reactions Ru has  $4d^75S^1$  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.<sup>147</sup> 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-Cl<sub>x</sub> 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-Cl<sub>x</sub> 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, N<sub>2</sub> 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,  $\alpha$ ,  $\beta$ -unsaturated ketones. Results of hydrogenation of ketones, diketone,  $\alpha$ ,  $\beta$ -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.

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**CHAPTER 2**  
**SYNTHESIS, CHARACTERIZATION**  
**AND IMMOBILIZATION OF METAL COMPLEXES**  
**IN MESOPOROUS SILICA**



## 2.1. INTRODUCTION

The syntheses of mesoporous silicate materials have opened-up new possibilities for preparing heterogeneous catalysts containing uniform pores with high surface area in the mesoporous regime.<sup>1</sup> This new family of material, termed as M41S, is broadly classified into three categories: hexagonal (MCM-41), cubic (MCM-48) and lamellar (MCM-50). These mesoporous materials have great potential in a wide range of applications such as catalyst for the synthesis of fine chemicals, as support, sensor, etc.<sup>2</sup> Structures with uniform pore size and high surface area without catalytically active sites are also of great utility for producing carriers on which catalytically active species such as heteropolyacids, amines, transition metal complexes, oxides, etc. can be supported. Surface modification of M41S type mesoporous silicates by reactive organic functional groups have been investigated extensively.<sup>3</sup> This surface modification allows tailoring of the surface properties for variety of potential applications, *viz.*, catalysis, immobilization of catalytically reactive species, chemical sensing and fabrication of nanomaterials.<sup>2,4</sup> The inorganic part (polymeric silicate framework) of the surface modified hybrid mesoporous materials provides structural, thermal and mechanical stability; whereas the pendant organic species permit flexible control of interfacial properties to provide covalently linked anchoring site for catalytically important metals and metal complexes.

Surface modification of mesoporous materials can be achieved by two methods,

- (i) post modification
- (ii) in-situ synthesis.

In post synthesis method organo-functionalization of the internal surfaces of mesoporous silicates can be achieved by covalent grafting of various organic species on

the channel walls.<sup>3</sup> The grafting process has been widely applied to anchor desired organic functional groups *via* condensation with surface silanol groups of the mesoporous silicate. However, it is somewhat difficult to control the concentration and distribution of organic moieties in the silicate surface mainly due to non-uniform presence of silanol groups in different mesoporous samples.<sup>2</sup> Silanol groups are known to be highly accessible on the external surface towards functionalization.<sup>5</sup> Thus grafting on the external surface can be minimized by passivating the external silanol groups before functionalization of those on the internal surface.<sup>6</sup>

The direct synthesis approach is based on the co-condensation of tetraalkoxysilane with tri-alkoxyorganosilane precursors in a templating environment. The tetra-alkoxysilane precursor acts as a building block to create the mesoporous silicate framework, whereas the tri-alkoxyorganosilanes function as both framework silicate units and pendant organic functional groups.<sup>7</sup> The most frequently encountered problem in this method is the relatively different rates of hydrolysis of the tetraalkoxysilane and trialkoxy-organosilanes precursors and their self-condensation. However, using a suitable solvent in the synthesis gel to control the hydrolysis can circumvent this problem.<sup>8</sup> This one step synthesis procedure can produce mesoporous silicates with relatively high loading and homogeneous surface coverage of organic functional groups.

The present chapter deals with the detailed description for synthesis of siliceous mesoporous material particularly MCM-41, functionalization of mesoporous material by organic functional group *viz.* amine (-NH), synthesis of metal complexes. It also includes a brief description for the synthesis of encapsulated metal complexes in the pores of

functionalized mesoporous material. Additionally, the details of physico-chemical characterization of the materials are also described.

## **2.2 EXPERIMENTAL**

### **2.2.1. Material**

Fumed silica (Surface area =  $384 \text{ m}^2 \text{ g}^{-1}$ ), tetraethyl orthosilicate (TEOS), 3-X-propyltrimethoxy silane (X= amino), and ruthenium metal were purchased from Aldrich, and cetyltrimethylammonium bromide (CTABr), phenanthroline, bipyridine, pyridine was purchased from Loba Chemie, India. All the chemicals were used as received without further purification.

### **2.2.2. Synthesis of MCM-41 Mesoporous Material**

Generally, the synthesis of mesoporous materials was carried out hydrothermally in an autoclave under autogeneous pressure using surfactant like cetyltrimethylammonium halide/hydroxide as template with sodium hydroxide and/or tetramethylammonium hydroxide as mineralizer. Moreover, MCM-41 type mesoporous materials can also be synthesized by refluxing the gel mixture at atmospheric pressure under constant stirring.<sup>9</sup>

In a typical synthesis procedure of MCM-41, fumed silica (3 g) was added to a solution of 0.64 g NaOH in 25 mL H<sub>2</sub>O and stirred for 45 min. To this mixture, a solution of 3.64 g CTABr in 50 mL H<sub>2</sub>O was added drop wise under stirring condition. Stirring was continued for another 45 min. Finally 37 mL of H<sub>2</sub>O was added to the synthesis gel, stirred further for 30 min and autoclaved at 373 K for 36 h. The resultant molar gel composition was 1 SiO<sub>2</sub>: 0.32 NaOH: 0.2 CTABr: 125 H<sub>2</sub>O. The product thus obtained

after hydrothermal synthesis was filtered, washed thoroughly with distilled water followed by acetone and dried at ambient temperature under vacuum.

### 2.2.3. Surface Modification of MCM-41 Material

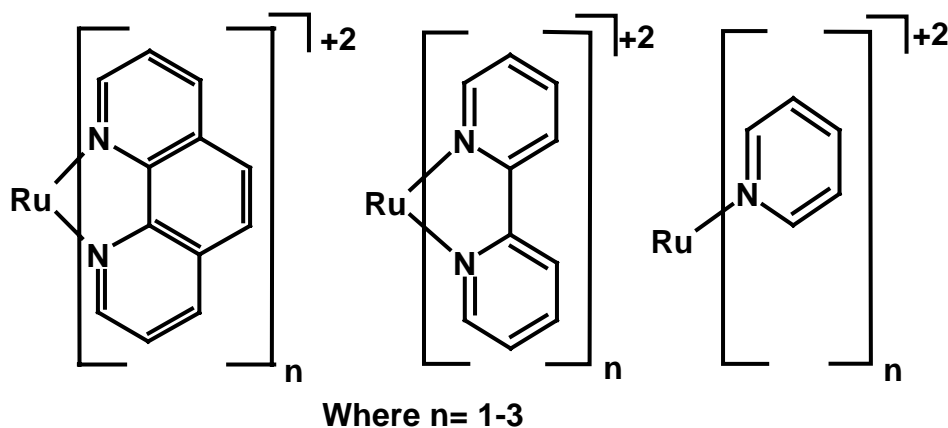
The syntheses of various organo-functionalized MCM-41 materials were carried out by *in situ* as well as post synthetic methods. For *in situ* synthesis of 3-aminopropyl-MCM-41 (NH-MCM-41) material, 3-X-propyltrimethoxysilane ( $X = \text{NH}_2$ ) was used along with TEOS in a 1: 2.5 molar ratio as the silica source. The molar gel composition was 1.0 XPTS: 2.5 TEOS: 0.42 CTABr: 0.96 NaOH: 272 H<sub>2</sub>O: 66 MeOH. Methanol was used in the initial gel mixture to reduce and control the fast hydrolysis of XPTS. All the synthesis gel mixtures were first stirred at room temperature for 12 h to remove methanol and then heated in autoclave at 368 K for 36 h under static condition. The products obtained were filtered, washed several times with *dry* toluene and then dried at ambient temperature under vacuum. From all organo-functionalized MCM-41 samples, surfactant was removed by solvent extraction containing methanol and HCl. In a typical extraction process, the surfactant was extracted from 1.0 g of solid product using 85 g of methanol and 3.25 g of HCl (35.4 wt.%) at reflux temperature for 24 h.

However, HN-MCM-41 was also synthesized by post synthesis modification, where 1.0 g of calcined Si-MCM-41 was taken in 25 mL *dry* toluene. To this stirred suspension, 0.60 g of APTS diluted in 25 mL of *dry* toluene was added very slowly through a syringe under N<sub>2</sub> atmosphere at room temperature (298 K). After complete addition of APTS, the mixture was refluxed at 353 K for 24 h in N<sub>2</sub> atmosphere. The

functionalised NH-MCM-41 was filtered, washed with *dry* toluene followed by acetone and dried at ambient temperature under vacuum.

#### 2.2.4. Synthesis of Metal Complexes

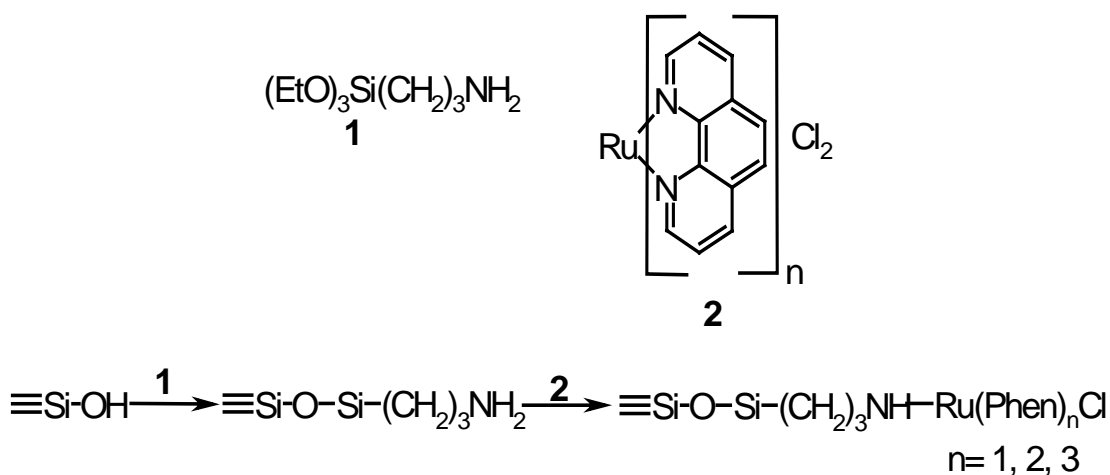
Ruthenium metal complexes were prepared according to the procedure available in literature.<sup>10</sup> Metal complex synthesis was carried out in following manner, ethanolic solution of phenanthroline ligand was added to the aqueous solution of ruthenium under stirring condition and kept over night. The over all yield of the metal complex was 85 %. Various metal complexes with different metal to ligand ratios (metal: Ligand = 1, 2, 3) were synthesized using same methodology. Ruthenium bipyridine and pyridine complexes with various metal to ligand ratios were also synthesized by the same procedure.



**Scheme 2.1:** Schematic representation of ruthenium metal complexes

### 2.2.5. Grafting of Metal Complexes onto Functionalized NH-MCM-41

The ruthenium phenanthroline complexes were grafted to the surface of functionalized MCM-41 as represented in Scheme 2.2. NH-MCM-41 (1 gm) was added to a solution containing 0.03 gm of complex dissolved in 10 mL of acetonitrile and N, N-di-methyl-formamide (9:1 ratio)<sup>11</sup> and the mixture was stirred at room temperature for 12 h under nitrogen atmosphere. Ruthenium chloride was also anchored on organo-functionalised MCM-41 in the same manner. The solid product was filtrated, washed with ethanol and dried under vacuum at 353 K.



**Scheme 2.2:** Immobilization of  $\text{Ru}(\text{Phen})_n\text{Cl}_2$  complex onto functionalised MCM-41

### 2.2.6 Catalytic Hydrogenation Reactions

The catalytic hydrogenation reactions of different ketones, diketones, unsaturated ketones, nitro compounds were performed in a 100 mL high-pressure autoclave at various temperatures (80 – 170 °C),  $\text{H}_2$  pressures 200 – 400 psig, stirring 200 - 500 rpm, different solvents and time intervals. In a typical reaction, 0.1 g solid functionalised catalyst, 10 %

of potassium *ter*-butoxide ( $t\text{BuOK}$ ) with respect to substrate as base and water as reaction medium was used. The solid catalyst was recovered by centrifugation, characterized and reused for the same substrate under identical reaction parameters to find out recyclability of the catalyst.

### 2.2.7. Instruments for Characterization

Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Rigaku Mini-Flex instrument using Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5404 \text{ \AA}$ ), in the  $2\theta$  range  $1.5 - 10^{\circ}$  at scan rate of  $1^{\circ}/\text{min}$ . The specific surface areas of the samples were determined by the BET method<sup>12</sup> from  $\text{N}_2$  adsorption isotherms at  $77 \text{ K}$  using an Omnisorb CX-100 Coulter instrument. Prior to the adsorption experiments, the samples were activated at  $523 \text{ K}$  for  $6 \text{ h}$  at  $1.333 \times 10^{-2} \text{ Pa}$ . Pore size distributions of the samples were computed by the Barrett-Joyner-Halenda (BJH) model.<sup>12</sup>

Cross-polarization magic angle spinning nuclear magnetic resonance (CP MAS NMR) spectra were recorded at  $11.7 \text{ Tesla}$  and  $202.64 \text{ MHz}$  in a Bruker DRX-500 FT NMR spectrophotometer.

The scanning electron microscopic (SEM) images were recorded on a Philips Model XL 30 instrument. The samples were loaded on stubs and sputtered with thin gold film to prevent surface charging and also to protect from thermal damage from the electron beam, prior to scanning. The samples were dispersed on Holey carbon grids and Transmission Electron Microscopic (TEM) images were scanned on a Jeol Model 1200 EX instrument operated at an accelerating voltage of  $100 \text{ kV}$ .

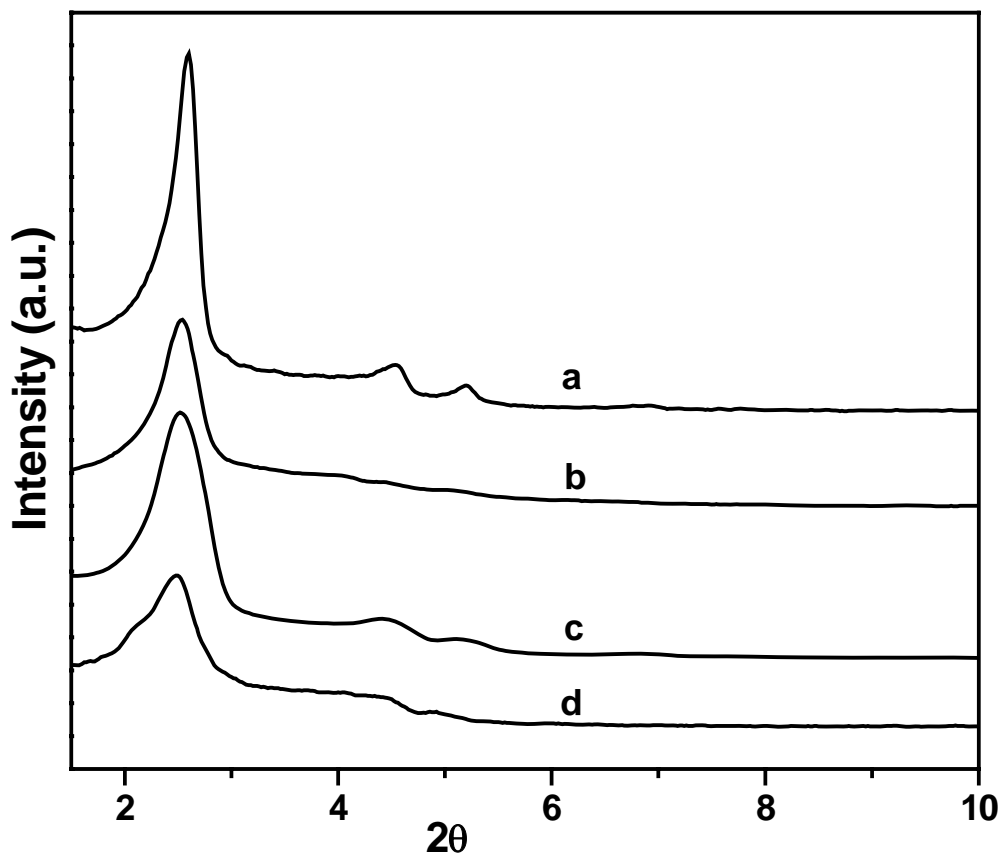
FT-IR spectra of samples were taken in the range of 4000 to 400  $\text{cm}^{-1}$  on a Shimadzu FT-IR 8201 instrument. Diffuse-reflectance UV-vis spectra were recorded with a Shimadzu UV-2101 PC spectrometer equipped with a diffuse-reflectance attachment. XPS analyses of the catalysts were recorded on a VG Microtech ESCA 3000 spectrometer using Mg  $K_{\alpha}$  radiation (photon energy = 1253.6 eV) at a pressure of 0.133  $\mu\text{Pa}$ , pass energy of 50 eV and electron take-off at angle of  $60^{\circ}$ .

## 2.3. CHARACTERIZATION

### 2.3.1. Powder X-Ray Diffraction

The XRD (powder) pattern (Fig. 2.1) of calcined Si-MCM-41 (curve (a)), organofunctionalized NH-MCM-41-P (post synthesis method) (curve (b)), NH-MCM-41-D (direct synthesis method) (curve (c)) and Ru-Phen-2-NH-MCM-41 (curve (d)) are shown. The XRD pattern of Si-MCM-41 shows characteristic four distinct low angle reflections [strong 100 reflection and weak (110), (200) and (210) reflections] at  $2\theta = 2.1^{\circ}$ ,  $3.7^{\circ}$ ,  $4.3^{\circ}$  and  $5.6^{\circ}$  respectively, and a  $d_{100}$  spacing value of  $\sim 4.3$  nm. The XRD patterns indicate high degree of order-ness amongst the hexagonal ( $p6mm$ ) mesophases of Si-MCM-41.<sup>1a,13-15</sup> These results indicate ordered mesoporous material. However, a slight decrease in the peak intensities were observed in the case of Ru-complexes containing samples, which might be due to the partial filling of Ru-complexes inside the mesoporous. The  $d$  spacing and unit cell parameters of the samples are given in Table 2.1.





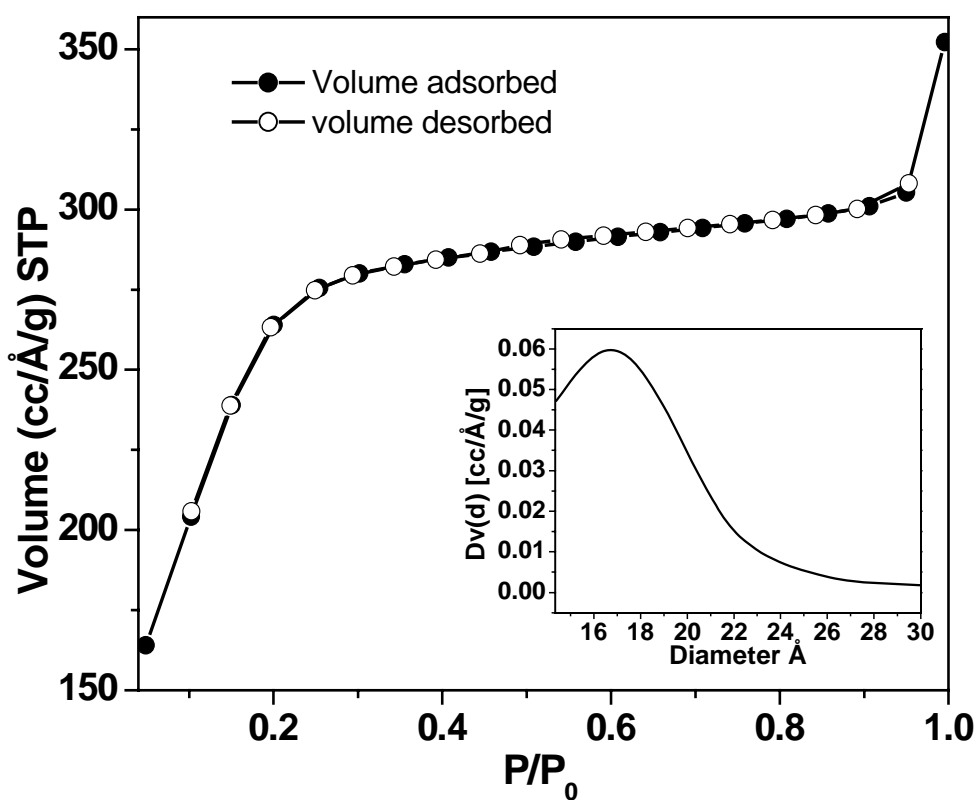
**Fig. 2.1:** XRD pattern for (a) calcined Si-MCM-41, (b) NH-MCM-41-P, (c) NH-MCM-41-D and (d) Ru-phen-2-NH-MCM-41,

### 2.3.2. Specific Surface Area

Table 2.1 depicts the effect of surface modification on the specific surface area, pore volume and pore diameter values estimated from  $N_2$  adsorption-desorption isotherms. Fig. 2.2 shows the  $N_2$  adsorption-desorption isotherm and pore size distribution curve (inset). All the samples showed similar type IV isotherm having inflection around  $P/P_0 = 0.35 - 0.8$ , characteristics of MCM-41 type ordered mesoporous material. Calcined MCM-41 shows highest surface area, which goes on decreasing after surface modification for NH-MCM-41 and Ru-(Phen) $_n$ -MCM-41 ( $n = 1, 2, 3$ ), as

expected. These results indicate that partial filling of mesopores occurred by the aforesaid coordination of compounds, which are anchored inside the pores of mesoporous material.

The pore volume, average pore diameters and BET surface area values of all the siliceous and organo-functionalized MCM-41 samples are summarized in Table 2.1. After grafting of the  $\text{-NH}_2$  functional group of the MCM-41 materials, a decrease in surface areas, pore volumes and pore diameters by *ca.* 15 – 20 %, 6 – 11% and 22 – 28 % respectively were observed. All these results strongly indicate that the organic functional groups are mainly located inside the channels.



**Fig. 2.2:**  $\text{N}_2$  adsorption-desorption isotherms and corresponding pore size distribution curves (inset) for Si-MCM-41.

**Table 2.1:** Physical characteristics of various surface modified MCM-41 before and after immobilization of metal complexes

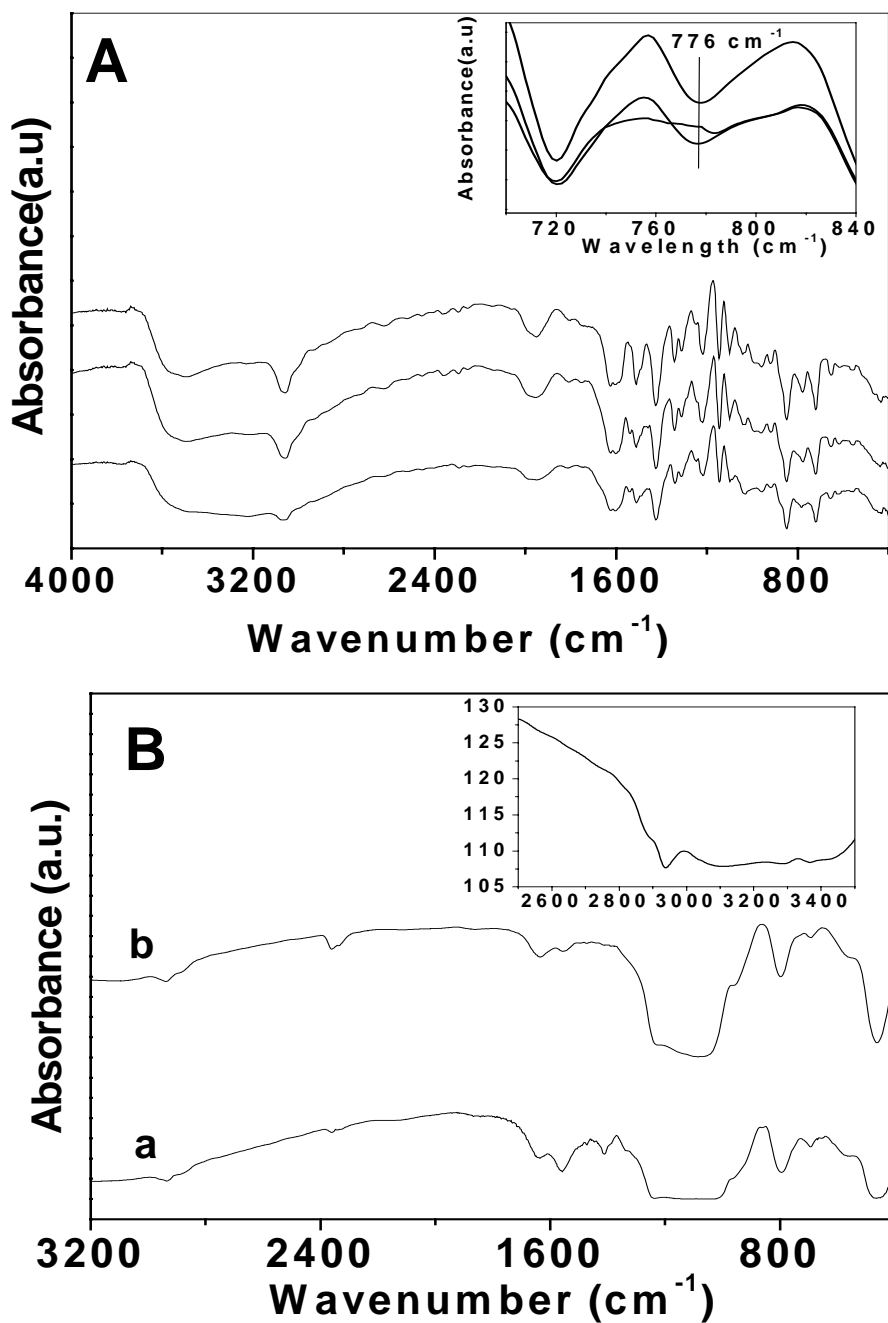
Material	$d_{hkl}$ (Å) <sup>a</sup>	$a_0$ (Å) <sup>b</sup>	Pore Diameter (Å)	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )	Surface Area (m <sup>2</sup> g <sup>-1</sup> )
Si-MCM-41	42.64	54.28	22.54	0.70	1322
NH-MCM-41	35.17	52.88	18.49	0.55	1113
Ru-Phen-1-NH-MCM-41	35.17	52.88	18.11	0.55	1104
Ru-Phen-2-NH-MCM-41	34.20	51.43	17.93	0.54	1093
Ru-Phen-3-NH-MCM-41	35.15	52.86	17.80	0.51	893

<sup>a</sup> Calculated from XRD pattern ( $n\lambda = 2d\sin\theta$ , where  $n = 1$  and  $\lambda = 1.5404$  Å)

<sup>b</sup>  $a_0 = d_{100} \times 2/\sqrt{3}$

### 2.3.3. FT-IR Spectra

FT-IR spectra of all the neat ruthenium phenanthroline complexes with different metal to ligand ratios are depicted in Fig. 2.3(A). The peaks observed between wavenumber 1000 and 1600 cm<sup>-1</sup> were attributed to bands for the framework-stretching mode of phenanthroline ligand. The band ~776 cm<sup>-1</sup> is characteristic of *Cis* confirmation of complexes is due to the out of plane C-H deformation of ligand.<sup>16</sup>



**Fig. 2.3:** FT-IR spectra of the (A) neat complex (a) Ru-Phen-1 (b) Ru-Phen-2, (c) Ru-Phen-3; and (B) (a) NH-MCM-41 (b) Ru-Phen-2-NH-MCM-41

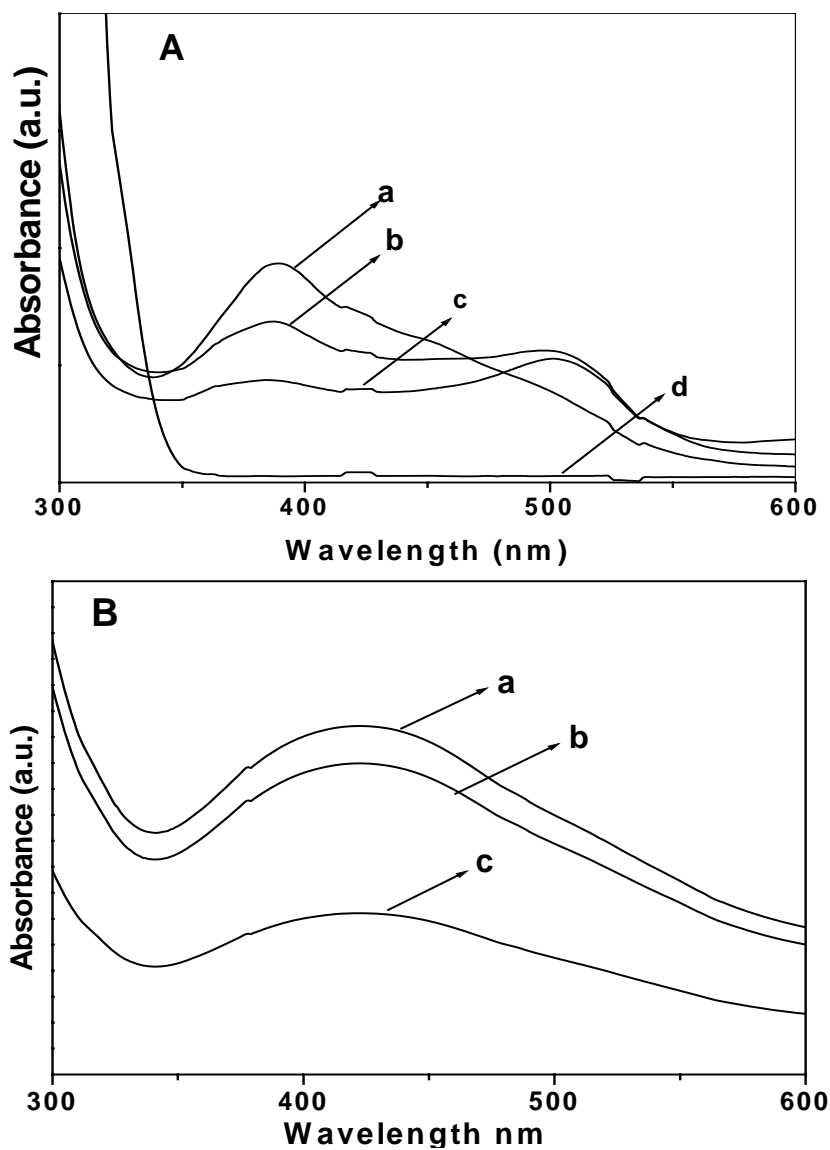
Fig. 2.3(B) shows the FT-IR spectra (a) NH-MCM-41 and (b) Ru-Phen-2-NH-MCM-41 between 3200 and 400  $\text{cm}^{-1}$ . Spectrum (Fig. 2.3 (A & B)) obtained from template-free -NH-MCM-41 shows characteristic bands at 1080, 796 and 452  $\text{cm}^{-1}$ . Bands at similar wavenumber in the spectra of the crystalline and amorphous  $\text{SiO}_2$  have been assigned to characteristic vibrations of Si-O-Si bridges cross-linking the silicate network.<sup>17</sup> In the case of NH-MCM-41 with  $-(\text{CH}_2)_3\text{NH}_2$  (NH-MCM-41), the peak at 3305 and 3428  $\text{cm}^{-1}$  corresponds to  $-\text{NH}_2$  group, whereas the transmission bands at 2935 and 2841  $\text{cm}^{-1}$  from the asymmetric and symmetric vibrations of  $-\text{CH}_2$  group of the propyl chain of the silylating agent were indicative of successful anchoring of amine moieties in the mesoporous.

#### 2.3.4. UV-Visible Spectra

The UV-visible spectra of six-coordinate  $[\text{Ru}(\text{phen})_2]^{2+}$  complexes are shown in Fig. 2.4. The absorbance spectra for these complexes in acetonitrile are characterized by the presence of intense  $\pi-\pi^*$  phenanthroline intraligand transitions in the UV-*vis* region and metal-to-ligand charge- transfer (MLCT) bands at 500-530 nm along with a second band of lesser intensity between 340-390 nm.<sup>18</sup> Interestingly the complexes show a blue shift in the range of 510-530 nm which is characteristics of *Cis* configuration attributed to the electron donating chlorine group.<sup>19</sup> The bathochromic shift in *cis*-conformation is due to the destabilization of the ruthenium  $t_{2g}$  orbital because of electron donation from the two anionic chloride ligands to ruthenium center.

The UV-*vis* patterns observed in the case of immobilized metal complexes on surface modified MCM-41 are shown in Fig. 2.4(B). Curves a-c represents Ru-Phen-1-

NH-MCM-41, Ru-Phen-2-NH-MCM-41, Ru-Phen-3-NH-MCM-41 samples respectively. The band at 510-530 nm clearly indicates the anchoring of the complex in the surface modified MCM-41 without change in the configuration of the complex.



**Fig. 2.4:** UV-visible spectra of the (A) Neat complex (a) Ru-Phen-1 (b) Ru-Phen-2 (c) Ru-Phen-3 (d) Phen; and (B) Immobilized metal complex (a) Ru-Phen-1-NH-MCM-41 (b) Ru-Phen-2-NH-MCM-41 (c) Ru-Phen-3-NH-MCM-41

### 2.3.5. X-Ray Photoelectron Spectra

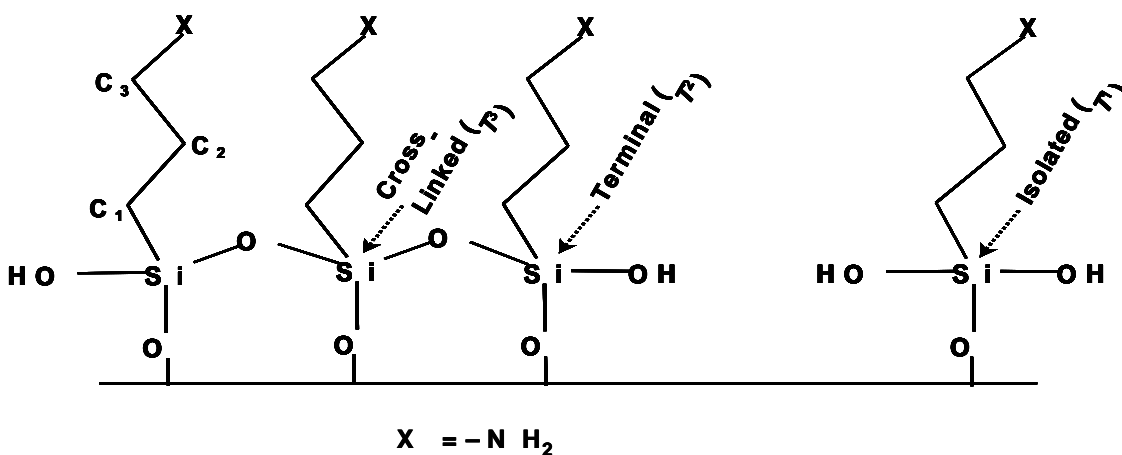
X-ray photoelectron spectroscopy (XPS) was used to find out the oxidation state of ruthenium in the neat and immobilized complex before and after reactions. Table 2.2 represents the Ru 3d<sub>5/2</sub>, Ru 3p<sub>3/2</sub> and N 1s core level binding energy (BE) obtained from XPS analysis. BE values for Ru 3d<sub>5/2</sub> and Ru 3p<sub>3/2</sub> were *ca.* 280 and 465 eV respectively making it evident that the ruthenium in the catalysts were present as Ru<sup>II</sup> species.<sup>20</sup> The binding energy of Ru 3d<sub>5/2</sub> in complexes goes on decreasing from top to bottom through the Table 2.2, which is attributed to the increase in the number of electrons in the outer most shell of the ruthenium metal donated by nitrogen atom from the ligand (as metal to ligand ratio goes on increasing). As the number of electrons in outer most shell increases, the ionization energy decreases (shielding effect) as a result the bond strength between metal and ligand decreases, which in turn decreases the binding energy.

**Table 2.2:** Core level binding energies (in eV) of various elements present in the catalyst precursors and anchored catalysts.

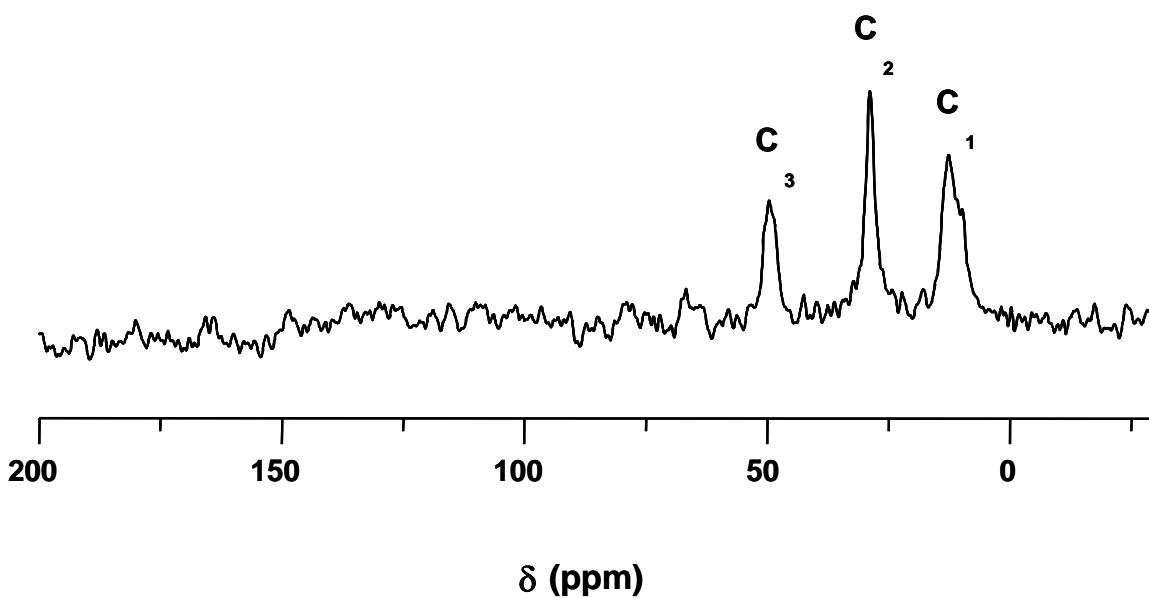
Material	Ru 3d <sub>5/2</sub>	Ru 3p <sub>3/2</sub>	N 1s	Si 2p
Ru-Phen-1	280.4	465.1	401.5	-
Ru-Phen-2	280.3	465.0	401.6	-
Ru-Phen-3	279.8	464.8	401.5	-
Ru-Phen-1-NH-MCM-41	280.5	465.2	401.5	103.4
Ru-Phen-2-NH-MCM-41	280.3	465.1	401.5	103.4
Ru-Phen-3-NH-MCM-41	279.8	465.0	401.6	103.5

### 2.3.6. $^{13}\text{C}$ CP MAS NMR Spectra

Fig. 2.5 represents the  $^{13}\text{C}$  coupled CP MAS NMR spectra of NH-MCM-41 sample. The spectra of the NH-MCM-41 (Fig. 2.5) sample reveal three distinct  $^{13}\text{C}$  signals at  $\delta \approx 11$ , 29 and 50 ppm, which can be assigned to  $\text{C}_1$ ,  $\text{C}_2$  and  $\text{C}_3$  atoms respectively, of the propyl chain (Scheme 2.3).



**Scheme 2.3:** Schematic representation of different chemical environments of carbon (C) and silicon (Si) atoms



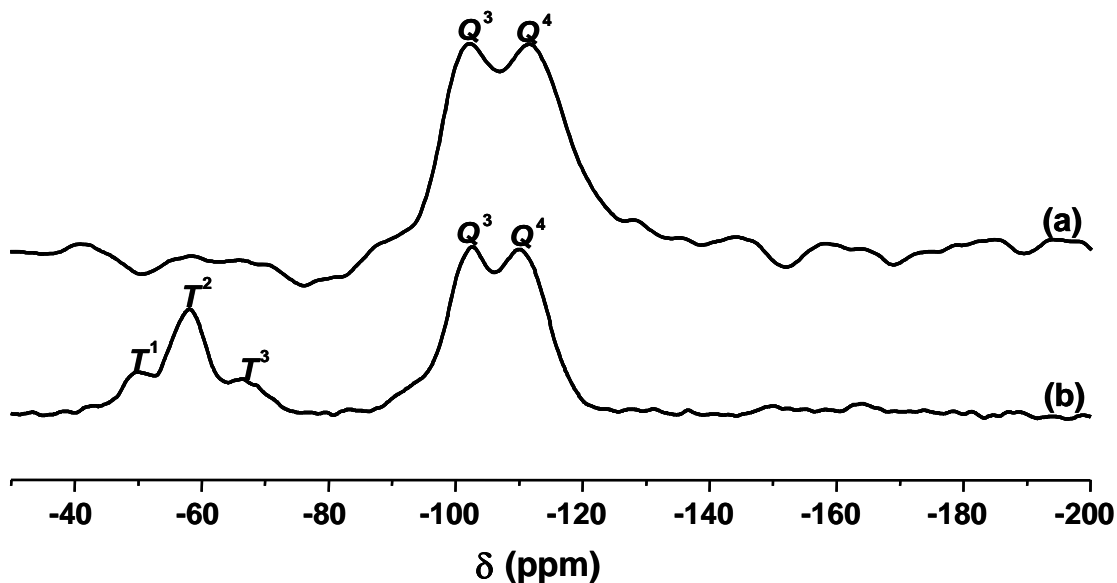
**Fig. 2.5:**  $^{13}\text{C}$  coupled CP MAS NMR spectra of NH-MCM-41



### 2.3.7. $^{29}\text{Si}$ CP MAS NMR Spectra

Fig. 2.6 shows the  $^{29}\text{Si}$  CP MAS NMR spectra of the (a) Si-MCM-41 and (b) NH-MCM-41 samples. In all the spectra, the strong resonances at  $\delta \approx -101$  and  $-110$  ppm are attributed to  $Q^3$   $[(\text{SiO})_3\equiv\text{Si}-\text{OH}]$  and  $Q^4$   $[(\text{SiO})_3\equiv\text{Si}-\text{O}-\text{Si}\equiv]$  species respectively, present in the silicate framework of MCM-41 materials.

The three additional peaks were observed at  $\delta \approx -49$ ,  $-57$  and  $-66$  ppm, which correspond to three different environments for the siloxane groups in the functionalized monolayers that shows evidence for the close-packed conformation of propyl chains in the functionalized materials (Fig. 2.6, curve b). These peaks are due to the presence of isolated ( $T^1$ ), terminal ( $T^2$ ) and cross-linked ( $T^3$ ) siloxane moieties (Scheme 2.3), respectively. Among the three, the strongest peak comes from the terminal group ( $T^2$ ).

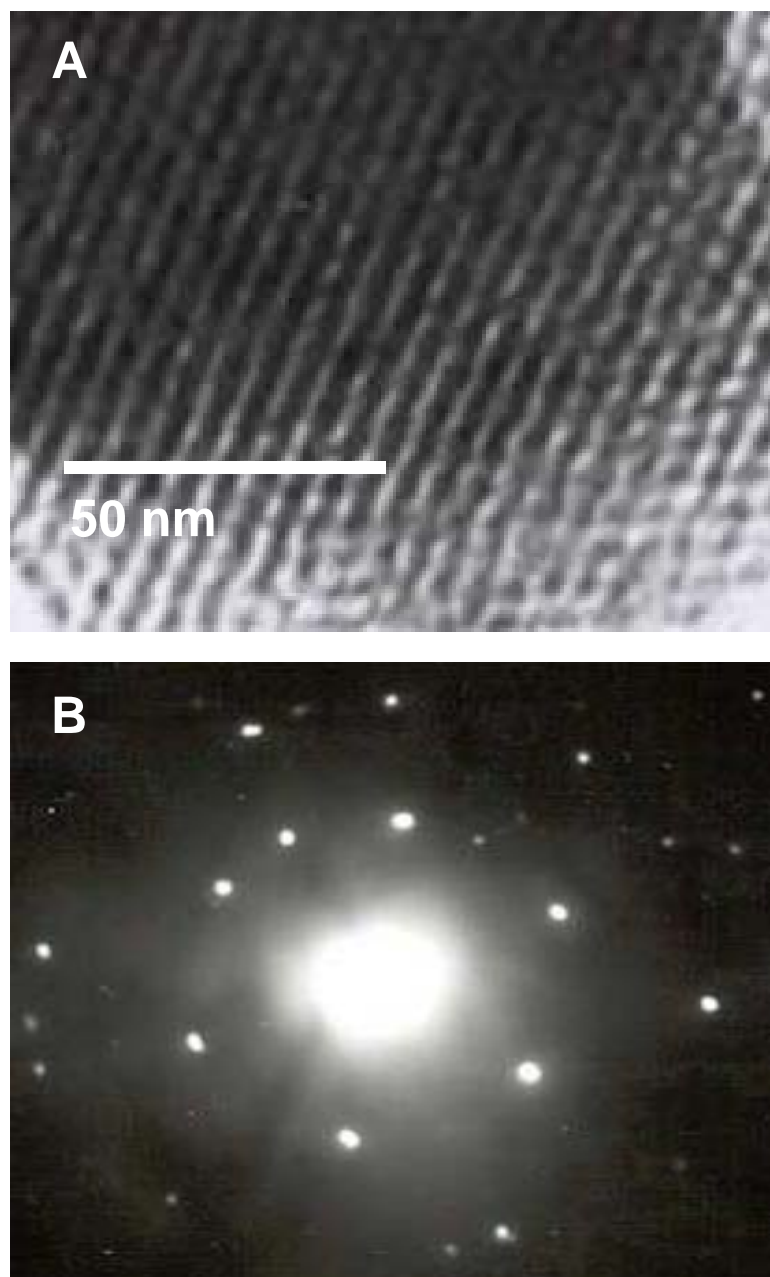


**Fig. 2.6:**  $^{29}\text{Si}$  CP MAS NMR spectra of (a) Si-MCM-41, (b) NH-MCM-41

### 2.3.8. Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is used as an indispensable tool for characterization of mesoporous supports.<sup>21</sup> Moreover, TEM has also been applied extensively to envisage 3D structures of the mesoporous solids, imaging metal nanoparticle catalysts inside mesoporous hosts and determine the occluded structure-directing organic species.<sup>22</sup> Fig. 2.7 (A) represents the TEM images of Ru-Phen-NH-MCM-41 materials, showing clear hexagonal pattern of lattice fringes along the pore direction. Parallel fringes due to the side-on view of the long pores were also observed. The equidistant parallel fringes in the images show unique feature of separate layers and the addition of the layers one after other results in the formation of bunch of layers.

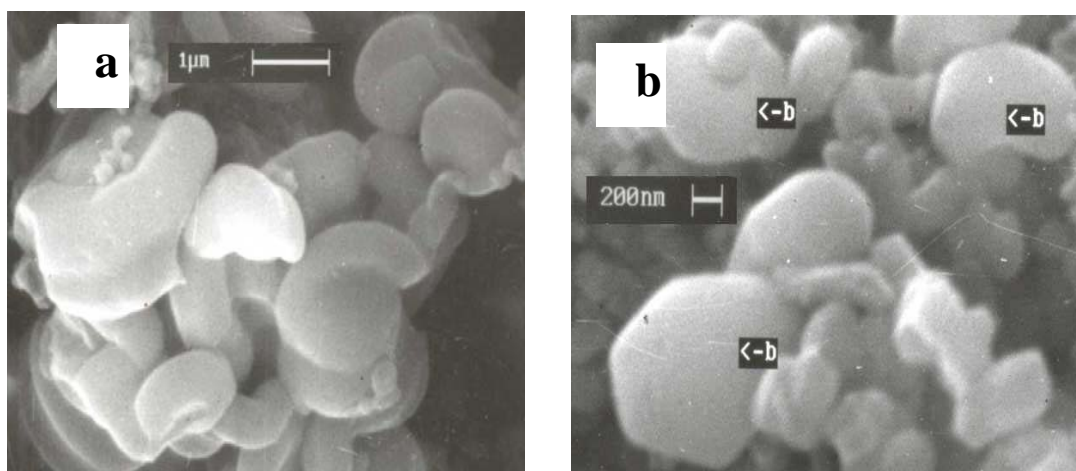
The selected area electron diffraction (SAED) pattern of the sample (Ru-Phen-2-NH-MCM-41) is given in Fig. 2.7 (B). The TEM images and SAED patterns are well consistent with the regular hexagonal mesophases of MCM-41, with homogeneity in patterns indicating the retention of ordered patterns of MCM-41 after anchoring of the abovementioned Ru-Phen complexes. These results corroborate the XRD results presented earlier (Fig. 2.1).



**Fig. 2.7:** TEM images recorded from (A) Ru-NH-MCM-41, (B) SAED patterns

### 2.3.9. Scanning Electron Microscopy

The SEM photographs of Si-MCM-41 sample, given in Fig. 2.8, are typical of MCM-41 type materials. The particle size and morphology of MCM-41 samples are determined by scanning electron microscopy. Two types of particle morphology are obtained. For the samples obtained under reflux and stirred condition, the crystal morphology is worm like (Fig. 2.8 a). However, when synthesis was done in autoclave under static condition hexagonal type crystals were obtained (Fig. 2.8 b).



**Fig. 2.8:** Scanning electron micrographs of calcined Si-MCM-41 sample having different types of particle morphology: (a) winding worm type and (b) hexagonal type

## 2.4. CONCLUSION

From the above-mentioned detailed characterization it is clear that

- (i) Ru-(Phen)<sub>n</sub> (n = 1, 2, 3) complexes were prepared and characterized.
- (ii) Amminopropyl organo-functionalized MCM-41 samples were successfully prepared.
- (iii) The anchoring of Ru(Phen)<sub>n</sub> (n = 1, 2 and 3) complexes in organofunctionalized MCM-41 have been successfully achieved.

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**CHAPTER 3**  
**CHEMOSELECTIVE HYDROGENATION**  
**OF CARBONYL COMPOUNDS**

Chapter 3 describes the detailed study of chemoselective hydrogenation of carbonyl compounds. This chapter is divided in following three sections:

Section 3.1 deals with the selective hydrogenation of ketones.

Section 3.2 deals with the chemoselective hydrogenation of  $\alpha,\beta$ -unsaturated ketones.

Section 3.3 deals with the chemoselective hydrogenation of diketones.

The details about synthesis procedure and characterization of both the neat ruthenium metal complexes and immobilized on organo-functionalised MCM-41 have already been presented in chapter 2. The catalyst samples were utilized for the hydrogenation of carbonyl compounds. The influence of various catalytic and reaction parameters on the conversion and selectivity are mentioned below;

1. Effect of Ligand (mono- and bi- dentate)
2. Effect of Solvent / Reaction Medium
3. Effect of Reaction Time
4. Effect of Metal to Ligand Ratio
5. Effect of Temperature
6. Effect of Pressure
7. Catalyst Recycle Study
8. Effect of Substrates with Different Substituent Group



### 3.1. HYDROGENATION OF MONO-KETONES

#### 3.1.1. Introduction

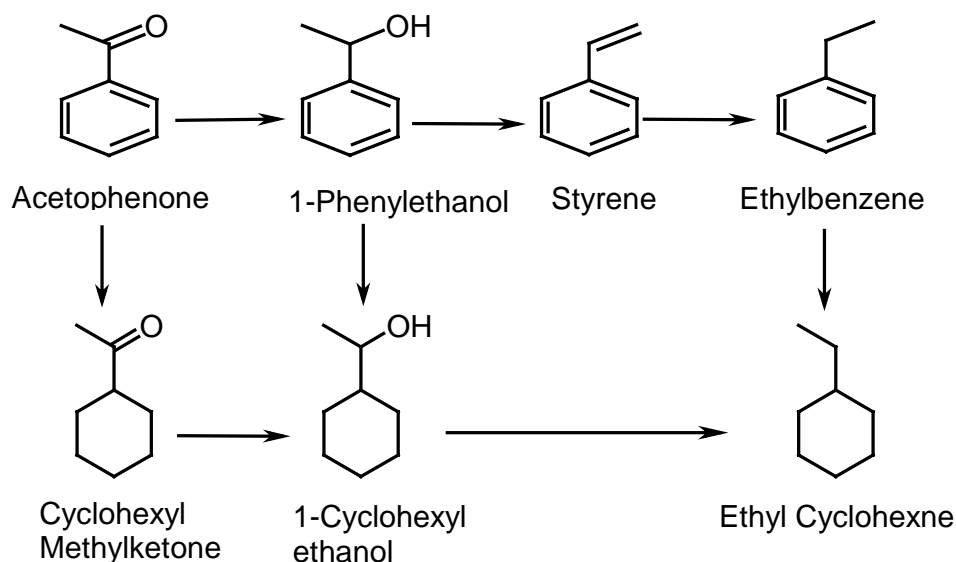
Hydrogenation of carbonyl compounds to corresponding alcohols is an important reaction. The secondary alcohols are of great significance in pharmaceuticals, fine chemicals, agrochemicals and perfumeries.<sup>1</sup> Catalysis plays crucial role in the production of secondary alcohols from ketones.<sup>2</sup> The synthesis of secondary alcohols can be achieved using catalyst, which can selectively reduce carbonyl group under mild reaction condition. This can also be achieved by using another method such as transfer hydrogenation<sup>3</sup> and hydrosilylation.<sup>4</sup> Ruthenium and rhodium are frequently used catalyst for reduction of ketones with various phosphorous or nitrogen containing ligands either alone or in combination to give high conversion and selectivity for secondary alcohols.<sup>5-8</sup> Phosphorous containing complexes are sensitive in nature towards the reaction conditions and are rather costly vis-à-vis nitrogen containing ligands. In recent years, transition metal complexes with nitrogen containing ligands like 1,10-phenanthroline, 2,2'-bipyridine, ethylene amine have found wide applications. These nitrogen-containing ligands were used for transfer hydrogenation reaction. Gladiali et al. reported the use of modified phenanthroline, bipyridine metal complexes for the transfer hydrogenation of acetophenone.<sup>9</sup> Epoxides were also reduced by the rhodium containing phenanthroline ligands to corresponding alcohols.<sup>10</sup> Generally, organic solvents are used for catalytic hydrogenation reactions.<sup>11</sup> However, in such cases down-stream processing and product recovery poses environmental problems and causing cumbersome workup.

The present section deals with the hydrogenation of different ketones with an emphasis of acetophenone as model substrate. The effect of mono and bi-dentate ligands

(such as pyridine, phenanthroline, bipyridine) and the effect of solvent on hydrogenation of acetophenone are highlighted. The use of water as reaction medium gives significant advantage over the organic solvent system.

### 3.1.2. Catalytic Hydrogenation Reaction

Aromatic ketones can undergo hydrogenation by two ways: (i) hydrogenation of  $>C=O$  functional group resulting in the formation of corresponding alcohol and (ii) hydrogenation of the aromatic ring giving rise to saturated ketone. However, saturated alcohols can also be formed from saturated ketones. In general, Scheme 3.1 represents reaction path involved.

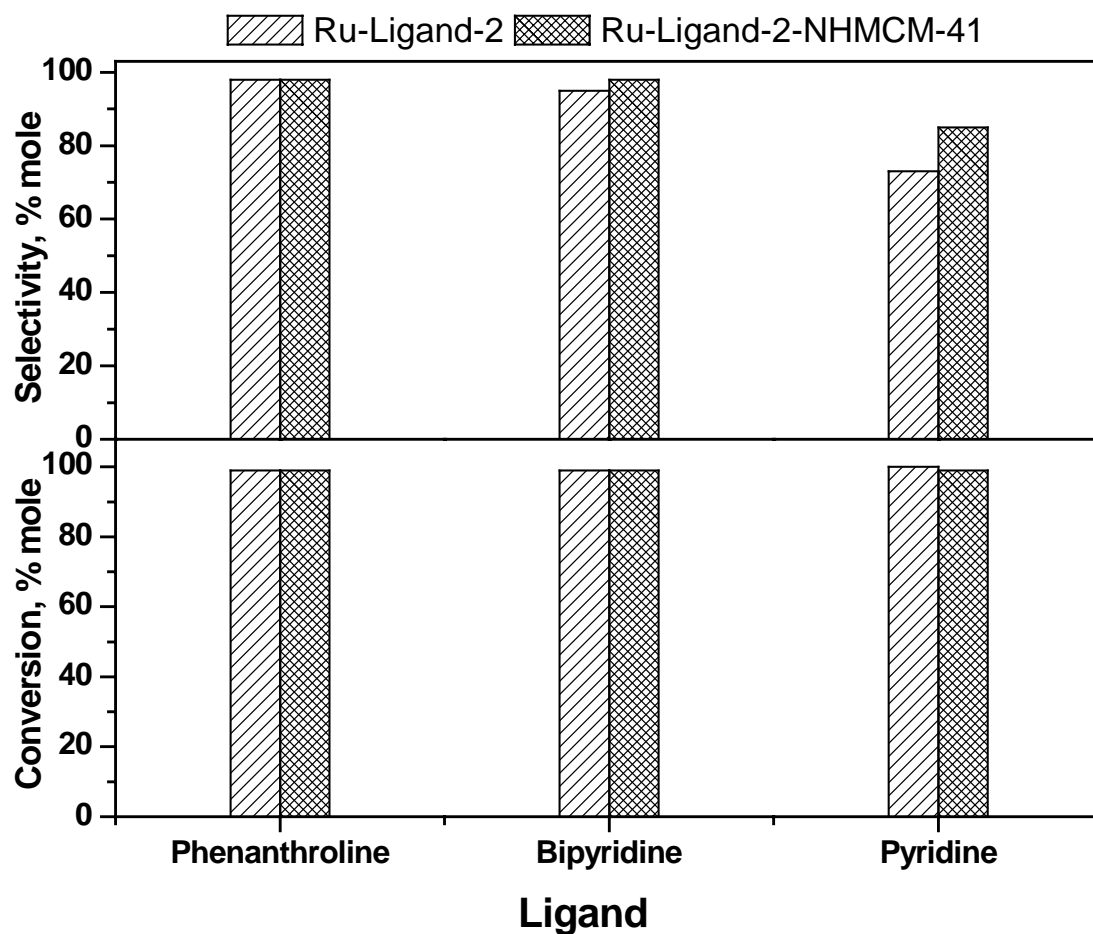


**Scheme 3.1.** Reaction scheme for hydrogenation of acetophenone

### 3.1.2.1. *Effect of Different Ligand*

Initially, to study the effect of dentateness of the ligand (pyridine as a mono- or 2,2'-bipyridine and 1,10-phenanthroline as a bi-dentate) in Ru-complex on the activity and selectivity in the hydrogenation reaction of acetophenone to 1-phenylethanol was studied. The reactions were carried out using Ru-Py-2, Ru-Phen-2 and Ru-Bipy-2 as homogeneous catalysts. The same metal complexes were also anchored in NH-MCM-41 and were used as heterogeneous catalyst. The reactions were carried out at 100 °C and at 300 psig using water as reaction medium and the results are given in Fig. 3.1.

The conversion exhibited by Ru-complexes using all the three ligands as well as the same metal complex anchored in organo-functionalised MCM-41 is comparable. However, there was significant loss of selectivity towards alcohol (due to the formation of styrene, ethylbenzene), when mono-dentate ligand (pyridine) was used, whereas styrene can be formed by dehydration of 1-phenylethanol and ethylbenzene can be formed by hydrogenation of styrene. Although, the conversions using homogeneous as well as heterogeneous catalyst system were comparable, the selectivity towards 1-phenylethanol was slightly higher in the case of heterogeneous catalyst.



**Fig. 3.1:** Effect of ligand on conversion and selectivity in hydrogenation of acetophenone to 1-phenylethanol

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.002 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Reaction medium = 30 mL water, Time = 4 h.

## 3.1.2.2. Effect of Solvent / Reaction Medium

Table 3.1 compares the results obtained over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41 catalyst in the presence of organic solvents (methanol, iso-propanol) and water. Almost complete conversion and very high selectivity could be obtained when water was used as reaction medium in hydrogenation of acetophenone (Table 3.1).

**Table 3.1:** Effect of solvent on selectivity in hydrogenation of acetophenone<sup>a</sup>

Sr. No.	Catalyst	Solvent	Conv. (mol. %)	Selectivity (%)		
				>C-OH	STY	EB
1	Ru-Phen-2		92	65	24	11
2	Ru-Phen-2-NH-MCM-41	Methanol	90	69	21	10
3	Ru-Phen-2		99	78	14	8
4	Ru-Phen-2-NH-MCM-41	Iso-propanol	99	88	8	4
5	Ru-Phen-2	Water	100	95	5	-
6	Ru-Phen-2-NH-MCM-41		98	99	1	-

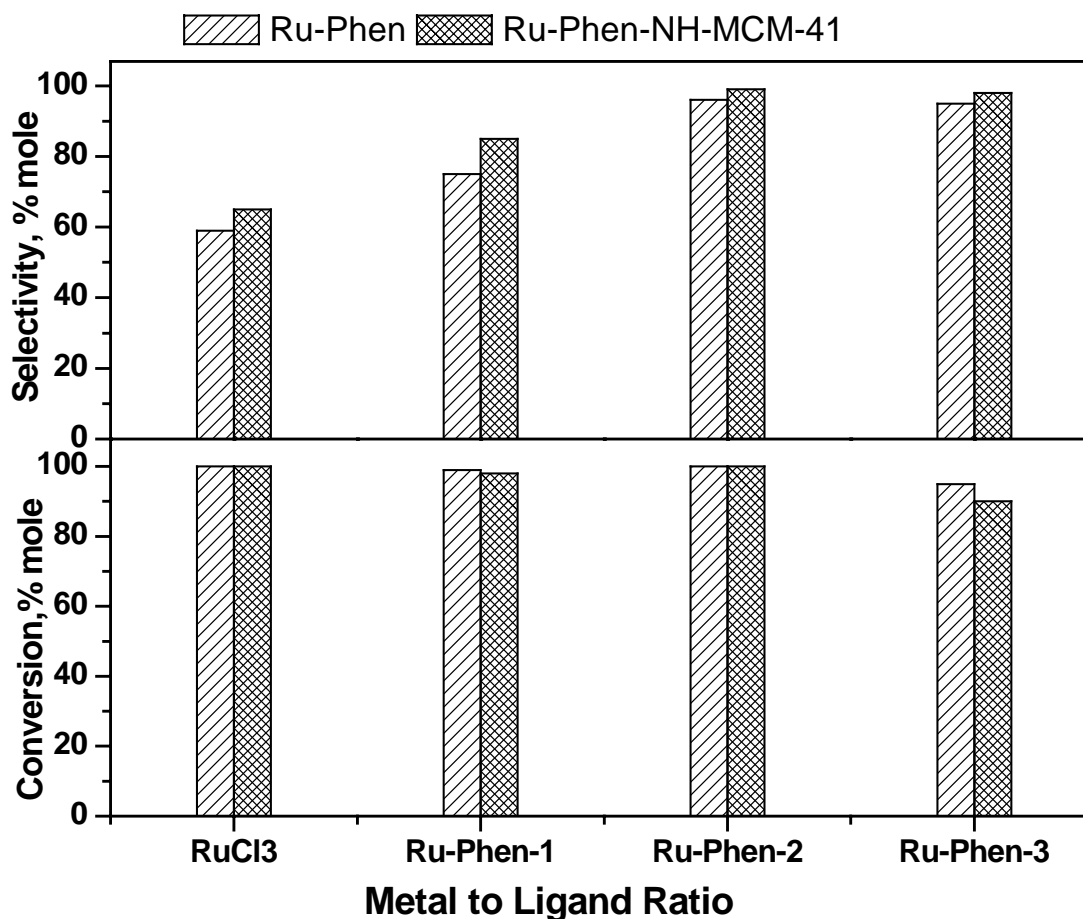
<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.002 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Solvent = 30 mL, Time = 4 h.

Solvent or reaction medium plays an important role in removing phase boundaries as well as in heat and mass transfer. Every solvent is having large degree of attractive forces acting in liquid, including dispersive, dipolar and the most significant H-bonding contribution. All these properties are the measure of the *cohesive energy density* (CED), which is one of the measures of pressure (MPa).<sup>12</sup> Use of water, as reaction medium was

found to be most effective in the hydrogenation with respect to conversion and chemoselectivity as compared to other organic solvent like methanol and iso-propanol. This may be attributed to the lower cohesive energy density of these organic solvents used during the reaction.

### *3.1.2.3. Effect of Metal to Ligand Ratio*

To understand the performance of metal to ligand ratio, different complexes with different ruthenium to phenanthroline ratios were studied using water as reaction medium and the results are shown in Fig. 3.2. Except Ru-Phen-3 catalyst, other catalyst gave nearly complete conversion. However, the selectivity towards secondary alcohol follows the order:  $\text{RuCl}_3 < \text{Ru-Phen-1} < \text{Ru-Phen-2} \approx \text{Ru-Phen-3}$ . The same trend was observed in homogeneous and heterogeneous system. Further, anchored solid catalyst showed slightly lower conversion particularly in Ru-Phen-3 complex anchored in NH-MCM-41. The selectivity towards formation of 1-phenylethanol was always higher, when solid catalyst was used due to suppression of secondary products. This may be attributed to specific geometry and the steric effect due to ligand molecule, which controls approach of reactant molecule towards reactive metal center in complex. Therefore all further studies in this section were carried out using Ru-Phen-2 catalyst.

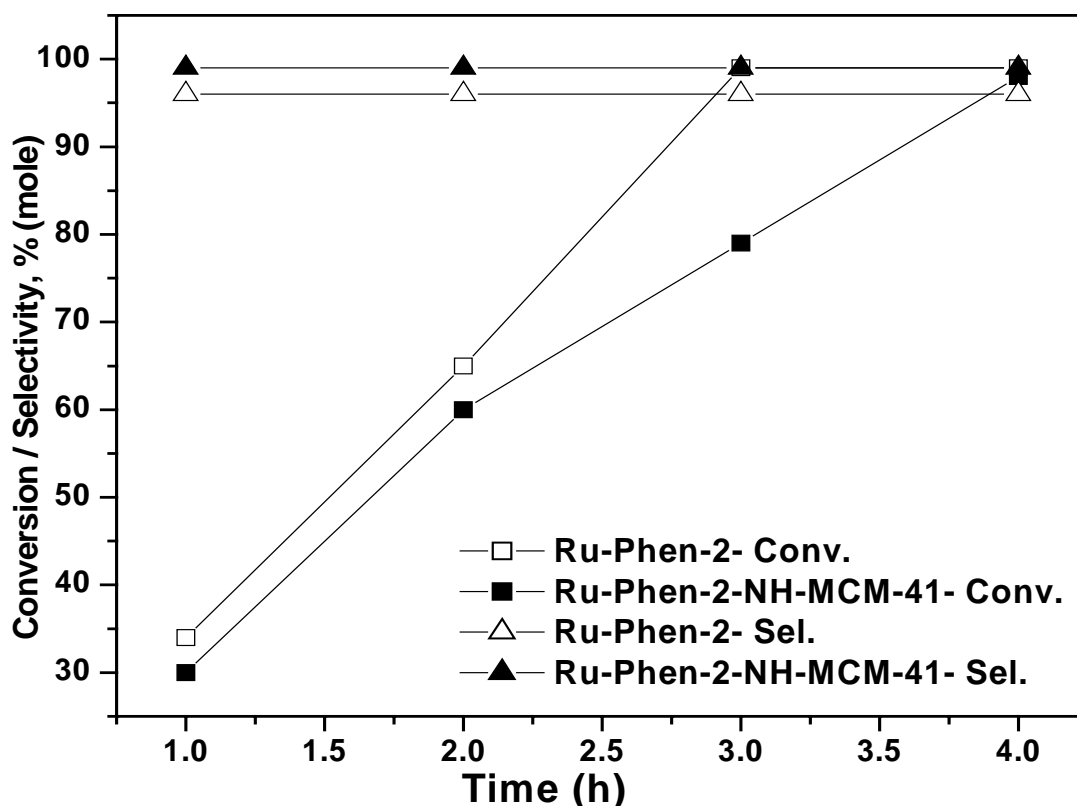


**Fig. 3.2:** Effect of metal to ligand on conversion and selectivity in hydrogenation of acetophenone to 1-phenylethanol over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41.

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.002 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Reaction medium = 30 mL water, Time = 4 h.

## 3.1.2.4. Effect of Time Profile

Fig. 3.3 compares the reaction profile (conversion and selectivity) as a function of time for neat Ru-Phen-2 catalyst. As expected, the reaction is faster in the case of homogeneous catalyst. Almost complete conversion was achieved in 3 or 4 hours of reaction time in homogeneous and heterogeneous conditions respectively, mainly due to lack of diffusion barrier in the case of homogeneous system. However, the selectivity towards primary product (1-phenylethanol) was slightly higher (by ca. 5 %) in the case of heterogeneous catalyst, due to suppression of further hydrogenation.



**Fig. 3.3:** Effect of time profile on conversion and selectivity in hydrogenation of acetophenone to 1-phenylethanol over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.002 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Reaction medium = 30 mL water.

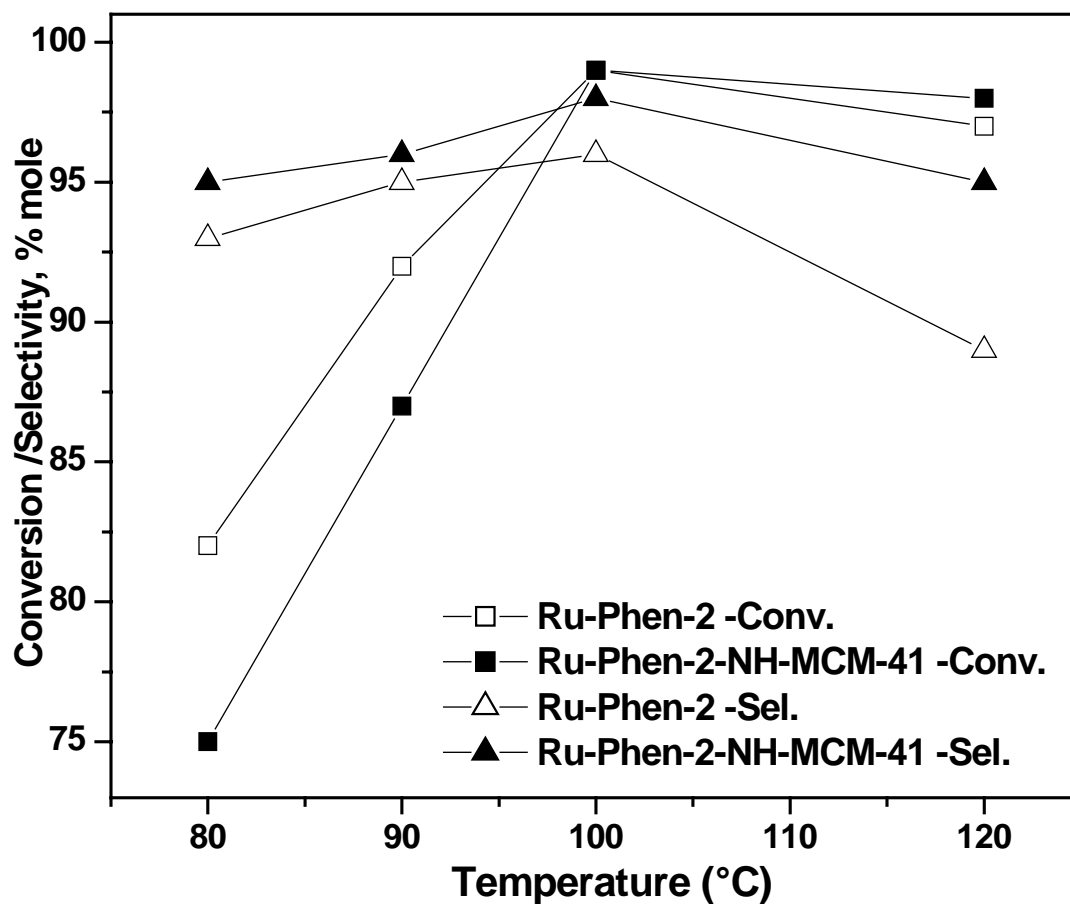


#### 3.1.2.5. *Effect of Temperature*

The Fig. 3.4 shows the effect of temperature on activity and selectivity in catalytic hydrogenation of acetophenone. With increase in temperature from 80 to 100 °C it was observed in both the homogeneous as well as in heterogeneous cases that the conversion and selectivity was increased, as expected. The highest conversion (100 %) as well as selectivity (99 %) was observed at 100 °C in both the homogeneous and heterogeneous catalytic system. The reaction was faster in the presence of neat complex compared to that over anchored solid catalyst below 100 °C. However, at all the reaction temperatures, the selectivity for desired 1-phenylethanol was slightly higher in the case of heterogenized catalyst. Quite interestingly, the selectivity at 120 °C dropped due to increased secondary reaction at higher severity of reaction condition. Hence, further studies were conducted at 100 °C.

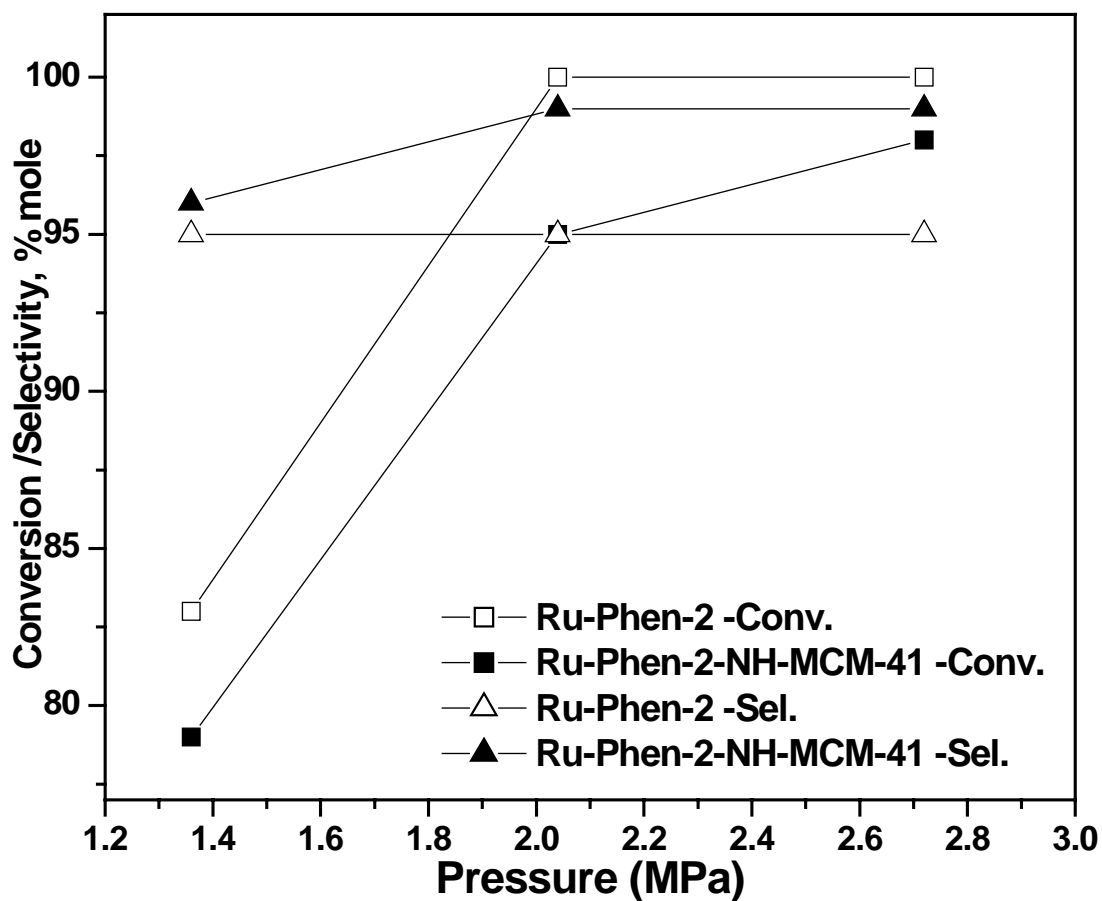
#### 3.1.2.6. *Effect of Pressure*

Fig. 3.5 depicts the effect of pressure on acetophenone hydrogenation at 100 °C using water as solvent. When pressure was increased from 1.3 to 2.1 MPa, the conversion increases significantly in both, the homogeneous and heterogeneous catalyst system. The high conversion at higher hydrogen pressure in both homogeneous and heterogeneous reaction conditions was obtained. There is no change in the selectivity of 1-phenylethanol with increase of H<sub>2</sub> pressure indicating that only C=O was hydrogenated.



**Fig. 3.4:** Effect of temperature on conversion and selectivity in hydrogenation of acetophenone to 1-phenylethanol over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.002 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Pressure = 2.04 MPa, Reaction medium = 30 mL water, Time = 4 h.



**Fig. 3.5:** Effect of pressure on conversion and selectivity in hydrogenation of acetophenone to 1-phenylethanol over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41.

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.002 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Reaction medium = 30 mL water, Time = 4 h.

Table 3.2 depicts the effect of pressure at various temperatures for the hydrogenation of acetophenone to 1-phenyl-ethanol. Results clearly indicate that comparable conversion and selectivity was obtained at all the pressures up to 100 °C. However, in case of 120 °C, selectivity for 1-phenyl ethanol goes on increasing up to 300 psig, which in turn decreases (ca. 85-87 %) at 400 psig. This is due to the presence of excess of molecular hydrogen. Further at higher temperature 1-phenylethanol starts getting converted to styrene and ethylbenzene.

**Table 3.2:** Effect of pressure on hydrogenation of acetophenone to 1-phenylethanol at various temperatures <sup>a</sup>

Sr. No.	Press. (psig)	Temp. (°C)	Conv. (mole %)		Selectivity (mole %)	
			Ru-Phen-2	Ru-Phen-2-NH-MCM-41	Ru-Phen-2	Ru-Phen-2-NH-MCM-41
1	200		78	75	91	93
2	300	90	92	92	90	92
3	400		90	89	92	93
4	200		83	79	95	96
5	300	100	99	99	96	98
6	400		99	97	94	98
7	200		78	80	88	90
8	300	120	98	89	98	95
9	400		99	99	85	87

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.002 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Reaction medium = 30 mL water, Time = 4 h.

### 3.1.2.7. Catalyst Recycle Studies

The heterogenized catalyst were effectively filtrated and recycled for three times with slight decrease in activity and selectivity (Table 3.3), which is attributed to the leaching, as confirmed by atomic absorption spectroscopic analysis. Almost 0.8 % of total ruthenium present in the catalyst was found to leach out in to mother liquor after third cycle.

**Table 3.3:** Recycle studies of the heterogeneous catalysts for hydrogenation of acetophenone

No. of Cycle	Conv. (mole %)	>C=O Selectivity (%)
Fresh Catalyst	98	99
Recycle 1	98	97
Recycle 2	91	95
Recycle 3	87	89

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.002 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Reaction medium = 30 mL water, Time = 4 h.

### 3.1.2.8. Effect of Different Substrates

Efficient hydrogenation of ketones to secondary alcohols was accomplished over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41 at 100 °C and 2.0 MPa pressure using water as reaction medium. From Table 3.4, it is evident that all the substrates showed very high conversion (>99 %) over ruthenium phenanthroline complex in homogeneous and heterogeneous reaction condition. The yield of secondary alcohol was observed as high

as 99 % after heterogenization of ruthenium phenanthroline metal complex. The reactivity of substituted compound was found to be slightly lower as expected due to the bulkier group.

**Table 3.4:** Effect of substrate on catalytic activity of neat and heterogenized catalyst for hydrogenation reaction <sup>a</sup>

$$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 + \text{H}_2 \xrightarrow[\text{tBuOK, water}]{\text{Catalyst}} \text{R}^1-\text{CH}(\text{OH})-\text{R}^2$$

Entry	Catalyst	Substrate	>C=O % Yield
1	Ru-Phen-2	R <sup>1</sup> = CH <sub>3</sub> , R <sup>2</sup> = C <sub>2</sub> H <sub>5</sub>	98
2	Ru-Phen-2-NH-MCM-41		99
3	Ru-Phen-2	R <sup>1</sup> = CH <sub>3</sub> , R <sup>2</sup> =	98
4	Ru-Phen-2-NH-MCM-41	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	99
5	Ru-Phen-2	R <sup>1</sup> = Ph, R <sup>2</sup> = CH <sub>3</sub>	95
6	Ru-Phen-2-NH-MCM-41		99
7	Ru-Phen-2	R <sup>1</sup> = p-CH <sub>3</sub> -Ph, R <sup>2</sup> =	93
8	Ru-Phen-2-NH-MCM-41	CH <sub>3</sub>	95
9	Ru-Phen-2	R <sup>1</sup> = p-Cl-Ph, R <sup>2</sup> = CH <sub>3</sub>	94
10	Ru-Phen-2-NH-MCM-41		97
11	Ru-Phen-2	R <sup>1</sup> = Ph, R <sup>2</sup> = C <sub>2</sub> H <sub>5</sub>	92
12	Ru-Phen-2-NH-MCM-41		95

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.002 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Reaction medium = 30 mL water, Time = 4 h. Complete conversion was obtained in all the cases.

## 3.2. CHEMOSELECTIVE HYDROGENATION OF $\alpha,\beta$ -UNSATURATED KETONES

### 3.2.1. Introduction

The  $\alpha,\beta$ -unsaturated alcohols are of great commercial importance as they are widely used in fragrances, pharmaceutical industries, intermediates in fine chemicals synthesis etc.<sup>13</sup> The chemoselective hydrogenation of  $\alpha,\beta$ -unsaturated ketones to corresponding unsaturated alcohols using molecular hydrogen is quite challenging because of the higher reactivity of C=C bond compared with that of C=O group<sup>14</sup> due to favorable thermodynamics for hydrogenation of C=C bond compared to the C=O by ca. 35 kJ/mol.<sup>15</sup> Hence, it is quite challenging to achieve unsaturated alcohols via selective reduction of unsaturated ketones. In addition to this, the product formed in reaction may isomerize to corresponding saturated ketones resulting in lower unsaturated alcohol selectivity.<sup>16</sup>

The reduction of unsaturated aldehydes or ketones have been reported using various transition metals catalyst in the form of homogeneous metal complexes viz. diamine (ether-phosphine) ruthenium (II)<sup>17</sup>,  $\eta^6$ -*p*-cymene/Ru (II)<sup>18</sup>, phenyldimethylphosphine-copper (I).<sup>19</sup> Supported metals like Ir or Ru on H- $\beta$  zeolite<sup>20</sup>, immobilized Zr and Hf alkoxide on mesoporous material<sup>21</sup>, gold supported on Fe<sub>2</sub>O<sub>3</sub><sup>22,23</sup> and MgO<sup>24</sup> have been used as heterogeneous catalyst for selective hydrogenation. The cinchonidine metal complexes were also used for the hydrogenation of unsaturated ketones to saturated ketones.<sup>25</sup> In all above reactions relatively low to moderate chemoselectivity towards unsaturated alcohols was obtained. Several attempts have been

made to develop suitable heterogeneous catalysts for the chemoselective hydrogenation of the C=O group in  $\alpha,\beta$ -unsaturated aldehyde.<sup>26</sup>

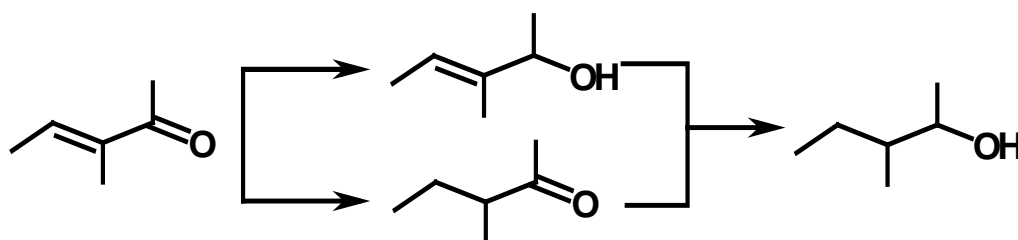
The ruthenium metal, owing to its  $4d^75s^1$  electron configuration, has wide range of possible oxidation states<sup>27</sup> and thereby can stabilize various coordination geometries in each electron configuration. Particularly, the lower oxidation states of ruthenium complexes normally prefer trigonal-bipyramidal and octahedral structures, such variety of structural geometry of ruthenium complex has great potential for use in selective hydrogenation reactions.

The use of nitrogen containing metal complexes for hydrogenation of unsaturated carbonyl compounds to unsaturated alcohol has not been extensively studied till date. Also due to increasing environmental concern in recent years for eco-friendly catalytic systems, the use of water as a reaction medium or the reaction medium has become an important factor. The present section details with chemoselective hydrogenation of  $\alpha,\beta$ -unsaturated ketones with particular emphasis on 3-methyl-pent-3-en-2-one over homogeneous Ru-Phen-2 as well as heterogenized Ru-Phen-2-NH-MCM-41 catalyst.

### 3.2.2. Catalytic Hydrogenation Reactions

The hydrogenation of  $\alpha,\beta$ -unsaturated ketones give saturated alcohols in two paths. In one path the double bond gets hydrogenated first, and possibly followed by hydrogenation of carbonyl group. In second path carbonyl group get hydrogenated first to give unsaturated alcohol, which on further hydrogenation may give saturated alcohol as shown in scheme 3.2.



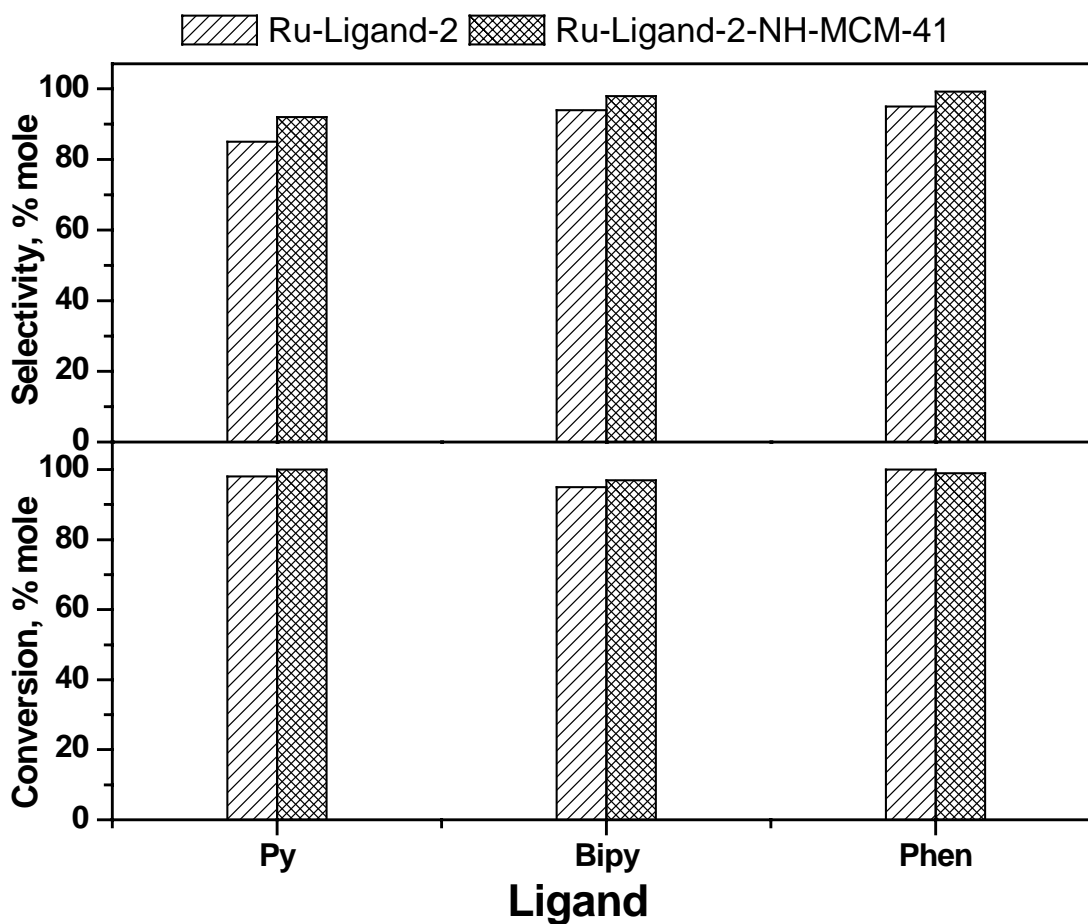


**Scheme 3.2:** Reaction scheme for hydrogenation of 3-methyl-pent-3-en-2-one

### 3.2.2.1. Effect of Different Ligand

The effect of ligand (pyridine as a mono or 2,2'-bipyridyl and 1,10-phenanthroline as a bi-dentate) on the activity and selectivity in the hydrogenation reaction of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol was studied. The reactions were carried out using Ru-Py-2, Ru-Phen-2 and Ru-Bipy-2 as homogeneous catalysts. The same metal complexes, anchored in NH-MCM-41 were used as heterogeneous catalyst. The reactions were carried out at 100 °C and at 2.0 MPa using water as reaction medium and the results are given in Fig. 3.6.

The conversion exhibited by Ru-complexes using all the three ligands was more or less comparable ranging between 96 – 100 %, whereas Ru-Phen-2 was giving nearly quantitative conversion. However, the selectivity for unsaturated alcohol was lower when mono-dentate ligand pyridine was used, due to the formation of 3-methylpentane-2-ol. Although, the conversions using homogeneous as well as heterogeneous catalyst system were comparable, the selectivity towards 3-methylpent-3-en-2-ol was slightly higher in the case of heterogeneous catalyst in accordance with the trend observed in the case of ketones hydrogenation (Section 3.1).



**Fig. 3.6:** Effect of ligand on conversion and selectivity in hydrogenation of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.005 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Reaction medium = 30 mL water, Time = 4 h.

3.2.2.2. *Effect of Solvent / Reaction Medium*

Table 3.5 depicts the effect of different solvents for hydrogenation of 3-methylpent-3-en-2-one using Ru-Phen-2 and Ru-Phen-2-NH-MCM-41 catalyst. Except in n-butanol almost complete conversion was obtained in other solvent (methanol and iso-propanol) or reaction medium (water). It is quite interesting that inspite of biphasic (in the case of homogeneous catalyst or tri-phasic in the case of heterogeneous catalyst) the reaction was complete in the presence of water. However, the selectivity for primary product (unsaturated alcohol) was significantly lower in the case of organic solvent vis-à-vis water. In fact the selectivity trend follows the order: n-butanol < methanol < iso-propanol < water. This may be due to high cohesive energy density of water over other organic solvents used during the reaction.

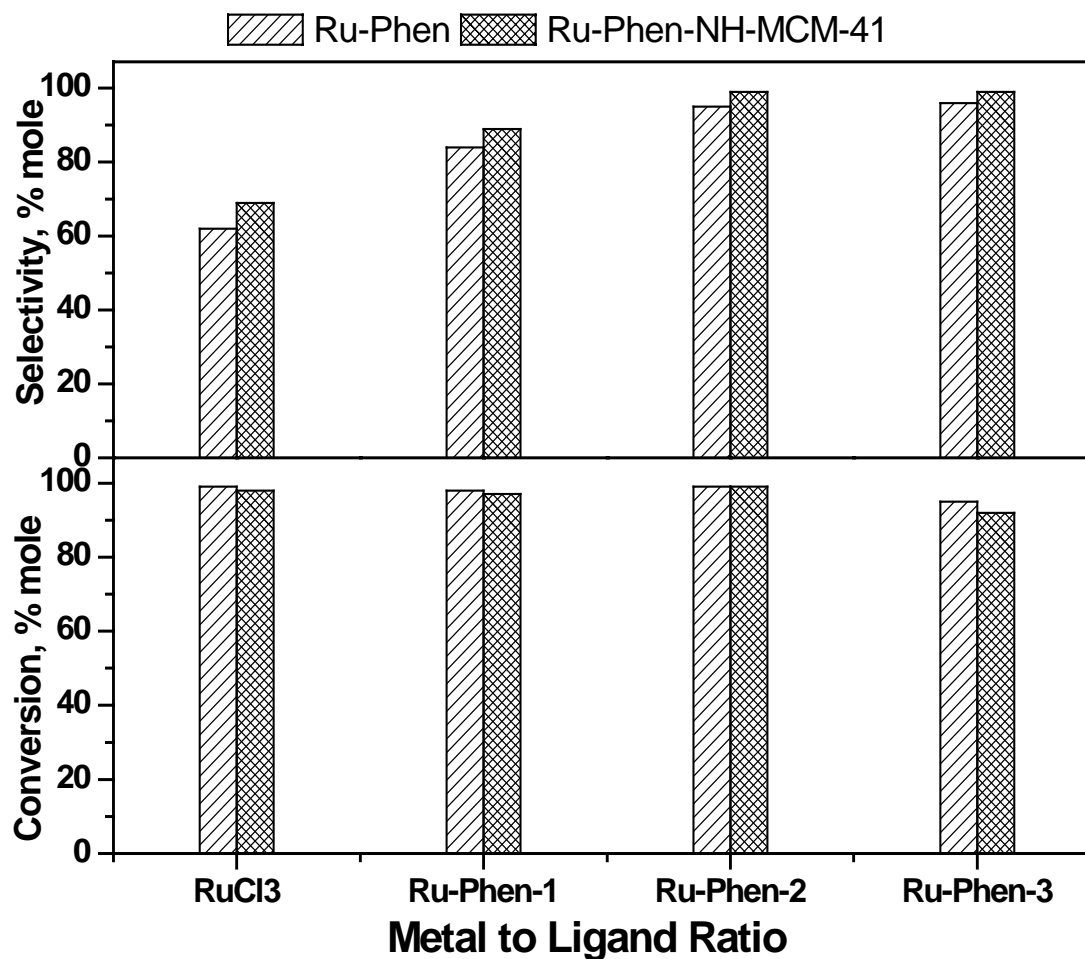
**Table 3.5:** Effect of solvent on selectivity and conversion for hydrogenation of 3-methylpent-3-en-2-one<sup>a</sup>

Sr. No.	Catalyst	Solvent	Conv. % (mole)	>C=O Sel. % (mole)
1.	Ru-Phen-2	n-Butanol	81	69
2.	Ru-Phen-2-NH-MCM-41		80	75
3.	Ru-Phen-2	Methanol	100	79
4.	Ru-Phen-2-NH-MCM-41		100	87
5.	Ru-Phen-2	Iso-propanol	100	86
6.	Ru-Phen-2-NH-MCM-41		99	92
7.	Ru-Phen-2	Water	100	95
8.	Ru-Phen-2-NH-MCM-41		99	99

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.005 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Reaction medium = 30 mL water, Time = 4 h.

### 3.2.2.3. *Effect of Metal to Ligand Ratio*

To understand the performance of metal to ligand ratio, different complexes with ruthenium to phenanthroline ratios were studied at the 100 °C, 2.0 MPa and using water as reaction medium and the results are shown in Fig. 3.7.  $\text{RuCl}_3$  as well as  $\text{RuCl}_3\text{-NH-MCM-41}$  were also included in the studies for comparative purpose. In homogeneous conditions  $\text{RuCl}_3$  showed complete conversion but lower selectivity compared to  $\text{RuCl}_3$  on MCM-41, which clearly support the above conclusion that the accessibility of reactant molecule to metal is higher in  $\text{RuCl}_3$ , while the conversion remains comparable except for Ru-Phen-3. The selectivity of unsaturated alcohol goes on increasing in both cases (homogeneous and heterogeneous conditions), as ruthenium to phenanthroline ratio increases from one to three. This may be attributed to the steric effect of ligand molecule, which controls the approach of reactant molecule towards reactive metal center in complex leading to slower reaction over Ru-Phen-3 or Ru-Phen-3-NH-MCM-41 catalyst. Further work was carried out using Ru-Phen-2 and Ru-Phen-2-NH-MCM-41 catalyst as we got best results with these catalyst systems.



**Fig. 3.7:** Effect of metal to ligand ratio on conversion and selectivity in hydrogenation of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.005 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Reaction medium = 30 mL water, Time = 4 h.

#### 3.2.2.4. *Effect of Time*

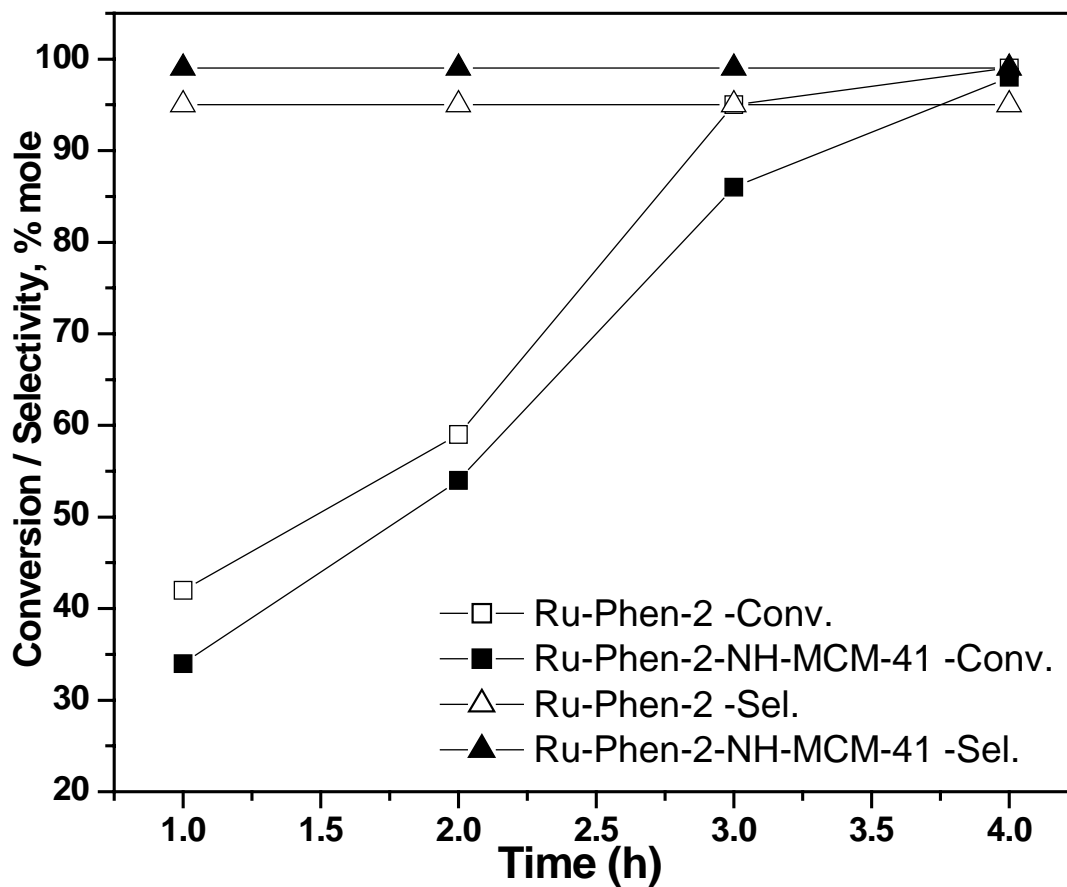
Fig. 3.8 shows typical time profile for the hydrogenation of 3-methylpent-3-en-2-one over Ru-Phen-2 and heterogenized Ru-Phen-2-NH-MCM-41 catalysts at 100 °C, 300 psig pressure. In both the cases conversion goes on increasing with reaction time till 4 h, where as selectivity remains comparable through out the reaction. The reaction is faster in the case of homogeneous catalyst compared to heterogeneous catalyst, as there is no diffusion barrier / transport limitation for reactant to adsorb on surface of catalyst in the case of homogeneous catalyst system. The conversion after 4 h is almost 100 %, however, the selectivity in heterogeneous catalyst (99 %) was found to be slightly higher compared to homogeneous catalyst (96 %).

#### 3.2.2.5. *Effect of Temperature*

The Fig. 3.9 shows the effect of temperature on activity and selectivity in catalytic hydrogenation of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol. As the conversion increased from 80 °C to 100 °C, the yield of unsaturated alcohol increased sharply from ca. 75 % to 99 %. However, further increase in temperature resulted in decrease in selectivity towards unsaturated alcohol. This is quite expected, as at higher temperature, saturated alcohols will also be formed due to further hydrogenation.

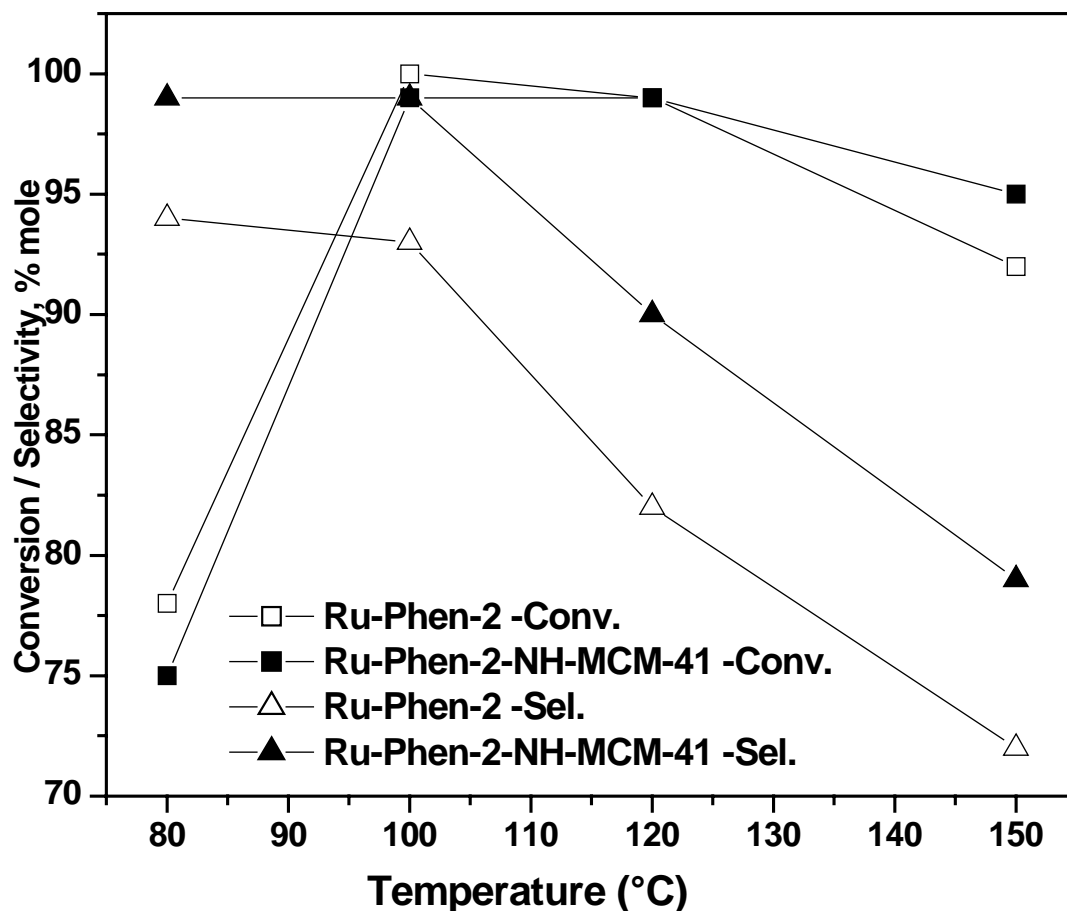
#### 3.2.2.6. *Effect of Pressure*

Fig. 3.10 depicts the effect of pressure on conversion of 3-methylpent-3-en-2-ol at 100 °C using water as reaction medium. The hydrogen pressure shows pronounced effect over conversion. There is decrease in the selectivity of 3-methylpentane-2-ol with increase in hydrogen pressure. At higher hydrogen pressure further hydrogenation of 3-methylpent-3-en-2-ol to 3-methylpentane-2-ol may be possible and as a result selectivity decreases.



**Fig. 3.8:** Effect of time on conversion and selectivity in hydrogenation of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

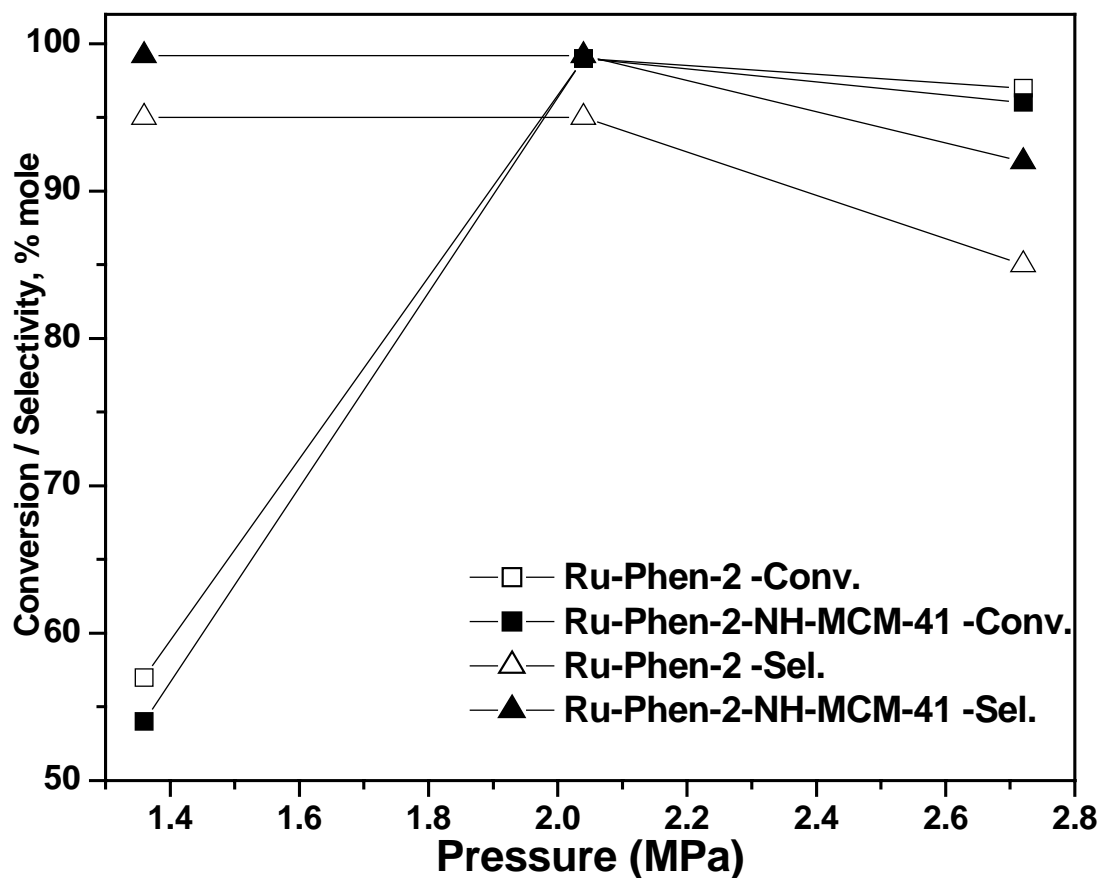
<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.005 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Water = 30 mL water, Time = 4 h.



**Fig. 3.9:** Effect of temperature on conversion and selectivity in hydrogenation of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.005 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Water = 30 mL water, Time = 4 h.





**Fig. 3.10:** Effect of pressure on conversion and selectivity in hydrogenation of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41.

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.005 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Water = 30 mL water, Time = 4 h.

Further detailed study has been carried out to find out the effect of pressure on the hydrogenation of 3-methylpent-3-en-2-one at various temperatures. The results in Table 3.6 indicate that conversion goes on increasing as temperature goes on increasing, but selectivity reaches maximum only at 300 psig, which decrease as hydrogen pressure increases to 400 psig due to increase in secondary reaction.

**Table 3.6:** Effect of pressure on hydrogenation of 3-methylpent-3-en-2-one at various temperatures <sup>a</sup>

Sr. No.	Press. (psig)	Temp. (°C)	Conv. (mole %)		Selectivity (mole %) <sup>a</sup>	
			Ru-Phen-2	Ru-Phen-2-NH-MCM-41	Ru-Phen-2	Ru-Phen-2-NH-MCM-41
1	200		62	60	87	91
2	300	80	80	79	93	95
3	400		82	80	83	90
4	200		57	54	95	99
5	300	100	99	98	93	99
6	400		97	96	87	92
7	200		68	65	83	86
8	300	120	98	98	85	90
9	400		99	99	80	84

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.005 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Substrate: Base = 10 (wt/wt), Water = 30 mL water, Time = 4 h.

### 3.2.2.7. Catalyst Recycle Studies

The solid anchored catalyst was filtered and recycled for three times with slight decrease in the activity and selectivity. The decrease in conversion is due to the partial leaching of ruthenium (ca. 0.9 %) that of total ruthenium present in solid catalyst. However, there is very minor decrease in selectivity using recycled catalyst. This takes the process towards green chemistry route in which the use of non-environment pollutant solvent, easily separable and recyclable catalyst is used.

**Table 3.7:** Recycle studies of the heterogeneous catalysts for hydrogenation of acetophenone

No. of Cycle	Conv. (mole %)	>C=O Selectivity (%)
Fresh Catalyst	98	99
Recycle 1	98	97
Recycle 2	95	97
Recycle 3	92	97

<sup>a</sup>Reaction Conditions: Substrate = 1 g, Neat Catalyst = 0.005 g (mole/mole) (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation = 300 rpm, Substrate: Base = 10 (wt/wt), Temperature = 100 °C, Pressure = 2.04 MPa, Water = 30 mL water, Time = 4 h.

### 3.2.2.8. Effect of Different Substrate

Table 3.8 shows the hydrogenation of unsaturated ketones with the substitution of C=C by pentane, phenyl. The increase in the turn over frequency (TOF) value in case of phenyl substituted compound is attributed to the less steric hindrance as compared to that

of pentane, as the phenyl ring always remain in one plane. However, in both the cases selectivity remains unaffected. This indicates, that only the functional group (C=O) is reduced over the catalyst and the double bond remains protected giving very high selectivity of unsaturated alcohol. The increase in selectivity and decrease in TOF was observed in case of heterogenized metal complex due to the diffusion barrier.

**Table 3.8:** Effect of different substrate on the catalytic activity <sup>a</sup>

Catalysts	Substrate	% Conv	>C=O % Select	TOF (h <sup>-1</sup> ) <sup>b</sup>
Ru-Phen-2	R <sub>1</sub> = C <sub>2</sub> H <sub>5</sub> , R <sub>2</sub> = CH <sub>3</sub>	99	95	246
Ru-Phen-2-NH-MCM-41		99	99	212
Ru-Phen-2	R <sub>1</sub> = C <sub>5</sub> H <sub>11</sub> , R <sub>2</sub> = CH <sub>3</sub>	100	98	241
Ru-Phen-2-NH-MCM-41		98	>99	201
Ru-Phen-2	R <sub>1</sub> = Ph, R <sub>2</sub> = CH <sub>3</sub>	99	96	257
Ru-Phen-2-NH-MCM-41		99	98	247
Ru-Phen-2	Cyclohex-2-ene-one	100	94	363
Ru-Phen-2-NH-MCM-41		97	97	339

<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), Neat Catalyst = 0.005 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Temperature = 100 °C, Pressure = 2.04 MPa, Agitation speed = 300 rpm, 30 mL water, Time = 4 h.

<sup>b</sup>TOF = Turn over frequency = mole of product formed / Mole of Ru per hour.

### 3.3. CHEMOSELECTIVE HYDROGENATION OF DI-KETONES

#### 3.3.1. Introduction

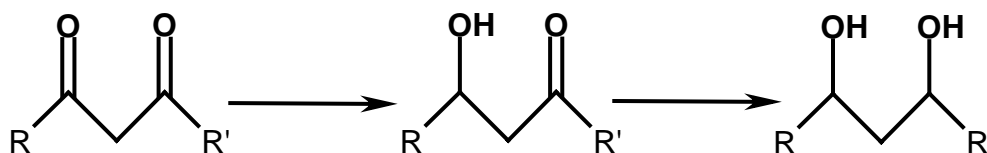
Ketols are of immense importance for the synthesis of fine chemicals<sup>28</sup>, as they provide two different functionalities in the same molecule ready for manipulation. For example, 4-hydroxypentan-2-one is used as flavoring agent. Several attempts have been made to hydrogenate diketones over cinchonidine<sup>29-33</sup>, BINAP<sup>34</sup> and cyclooctadine<sup>35</sup> metal complexes. In all above studies significant formation of diol was obtained resulting in low chemoselectivity towards ketol formation. Transition metal complexes of ruthenium, rhodium, palladium and platinum containing nitrogen ligand viz. phenanthroline and bipyridine were also utilized for the transfer hydrogenation of carbonyl compounds.<sup>36</sup> It may worth recalling that among the other transition metals Ru has  $4d^75s^1$  electronic configuration and hence it has wide range of oxidation states from – 2 to +8. Therefore it forms various coordination geometry in each electronic configuration. It also has great potential for exploitation of novel catalytic reactions and variety of Ru complexes are prepared and used for various reactions. Because of steric hindrance, Ru II phenanthroline complex posses the *cis* geometrical configuration.<sup>37</sup> Therefore, it is very interesting to utilize these complexes in hydrogenation of acetylacetone to 4-hydroxypentan-2-one. To the best of our knowledge this is not reported in the literature. The increased environmental concerns in recent years advocate the replacement of organic solvents by water for environmentally benign catalytic systems and also to use easily separable and recyclable catalyst in the reaction.

In this section, Ru-Phen-2 (ruthenium: phenanthroline = 1:2) and heterogenized Ru-Phen-2-NH-MCM-41 (Ru-Phen-2 encapsulated in amino functionalised MCM-41)

catalyzed highly chemoselective hydrogenation of acetylacetone to 4-hydroxypentan-2-one using water as preferred reaction medium under triphasic reaction conditions, are reported for comparison. Some other diketones were also included in study.

### 3.3.2. Catalytic Hydrogenation Reactions

The diketones on complete hydrogenation give diols. The diol formation occurs via hydrogenation of diketones to hydroxy-ketones (ketols), which is shown in Scheme 3.3.



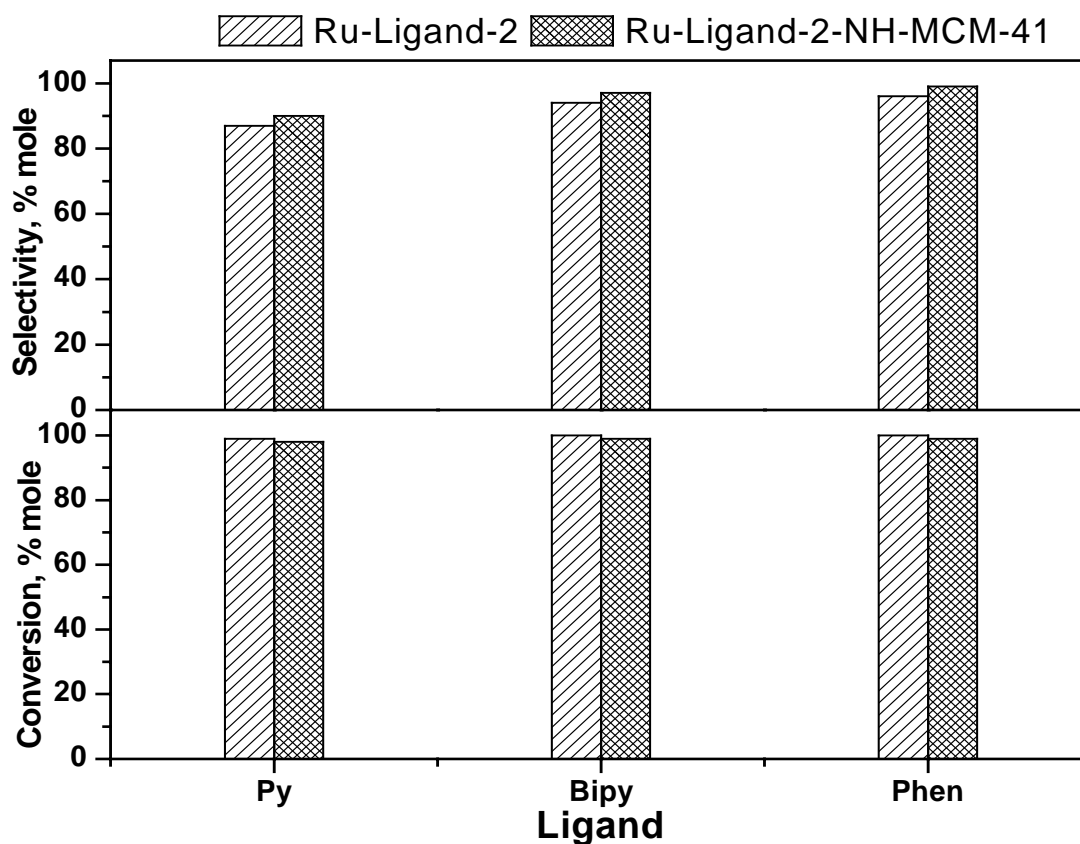
**Scheme 3.3:** Reaction scheme for hydrogenation of diketones

#### 3.3.2.1. Effect of Different Ligand

The effect of type of ligand (pyridine as a mono or 2,2'-bipyridyl and 1,10-phenanthroline as a bi-dentate) on the activity and selectivity in the hydrogenation reaction of acetylacetone to 4-hydroxypentan-2-one was also studied here like previous section. The results obtained are shown in Fig. 3.11. The reactions were carried out using Ru-Py-2, Ru-Phen-2 and Ru-Bipy-2 as homogeneous catalysts. The same metal complexes anchored in NH-MCM-41 were also used as heterogeneous catalyst. The reactions were carried out at 120 °C and at 300 psig using water as reaction medium and the results are given in Fig. 3.11.

The conversion exhibited by Ru-complexes using all the three ligands was comparable. However, there was significant loss of selectivity towards ketol (due to the

formation of diol, namely 2,4-dihydroxypentane), when mono-dentate ligand (pyridine) was used. The cause of this is may be the less steric hindrance around the active metal center (as compared to bi-dentate ligand), which facilitates ketol to interact and further hydrogenate to diol. Although, the conversions using homogeneous as well as heterogeneous catalyst system were comparable, the selectivity for 4-hydroxy-pentan-2-one was slightly higher in the case of heterogeneous catalyst.



**Fig. 3.11:** Effect of different ligand on conversion and selectivity in hydrogenation of acetylacetone to 4-hydroxypentan-2-one over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), Neat Catalyst = 0.005 g (Ru-Phen-2), Solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), Temperature = 120 °C, Pressure = 2.04 MPa, Agitation speed = 300 rpm, 30 mL water, Time = 10 h.

### 3.3.2.2. Effect of Solvent / Reaction Medium

To find out the suitable reaction medium for the hydrogenation of acetylacetone, the reactions were carried out over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41 catalysts in the presence of different solvents / reaction medium (Table 3.9). The conversion and ketol selectivity followed the trend: n-butanol < methanol < isopropanol < water. However, in the case of alcoholic solvents, except water as reaction medium, the conversion was slightly higher when homogeneous Ru-Phen-2 vis-à-vis Ru-Phen-2-NH-MCM-41 and opposite trend was observed in ketol selectivity. This may be due to high cohesive energy density of water over other organic solvents used during the reaction as mentioned early. Therefore, for further studies water, a universal and environmentally benign solvent was used.

**Table 3.9:** Effect of different solvents on conversion and selectivity for hydrogenation of acetylacetone

Sr. No.	Catalyst	Solvent	% Conv.	Ketol Sel. (%)
1	Ru-Phen-2		85	75
2	Ru-Phen-2-NH-MCM-41	n-Butanol	80	79
3	Ru-Phen-2		90	82
4	Ru-Phen-2-NH-MCM-41	Methanol	88	85
5	Ru-Phen-2		100	87
6	Ru-Phen-2-NH-MCM-41	Iso-propanol	98	92
7	Ru-Phen-2		100	99
8	Ru-Phen-2-NH-MCM-41	Water	100	99

<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), Neat Catalyst = 0.005 g (Ru-Phen-2), 0.1 g (Ru-Phen-2-NH-MCM-41), Temp. = 120 °C, Pressure = 2.04 MPa, Agitation speed = 300 rpm, 30 mL water, Time = 10 h. <sup>b</sup>TOF = Turn over frequency = mole of product formed / Mole of Ru per hour.

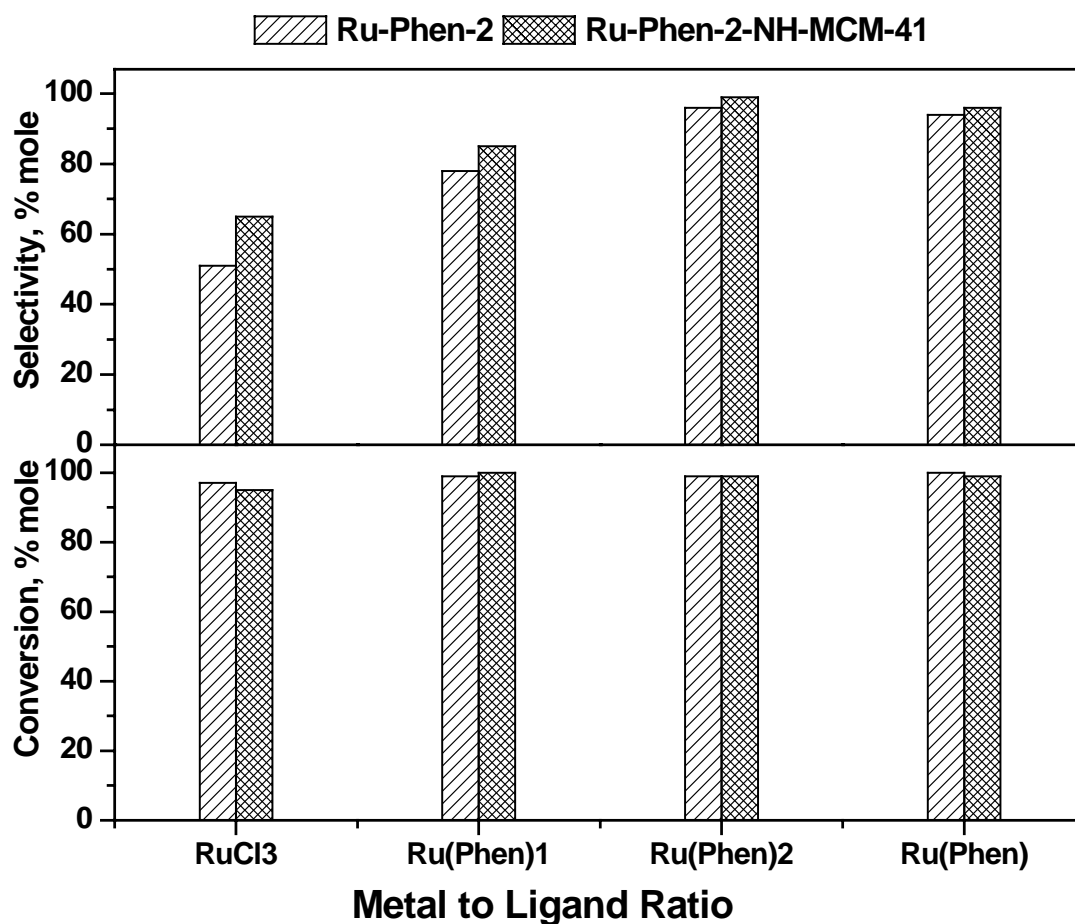


### 3.3.2.3. *Effect of Metal to Ligand Ratio*

Fig. 3.12 depicts the performance of metal concentration, different complexes with different ruthenium to phenanthroline ratios were studied at the 120 °C, 300 psig and using water as reaction medium. Although, comparable conversions were obtained in case of homogeneous as well as heterogeneous condition, heterogenized metal complex showed increase in selectivity, which is due to the diffusion barrier for reactant. The selectivity of 4-hydroxypentan-2-one, in both cases, homogeneous and heterogeneous conditions, increased as ruthenium to phenanthroline ratio decreased from one to three. This may be attributed the steric effect of ligand molecule, which controls approach of reactant molecule towards reactive metal center in complex.

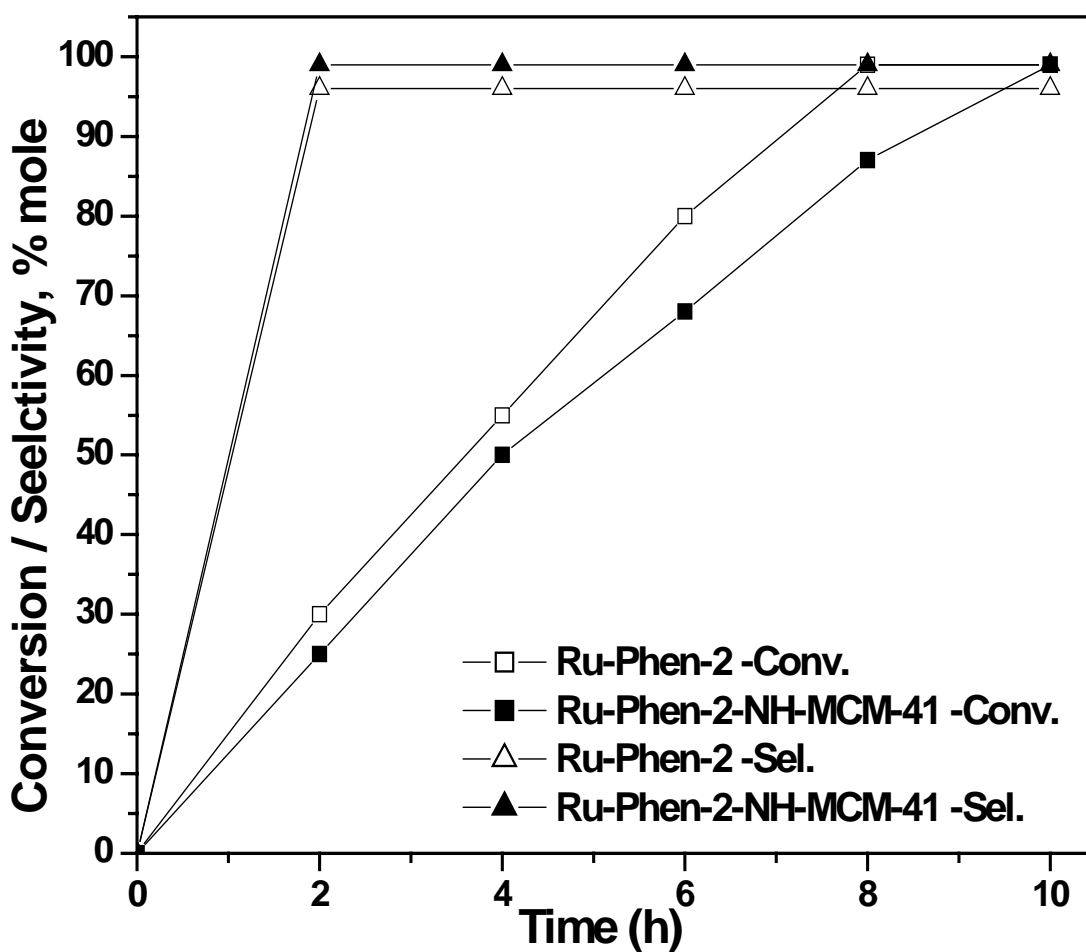
### 3.3.2.4. *Effect of Time Profile*

Fig. 3.13 shows effect of reaction time on conversion and selectivity in the hydrogenation of acetylacetone to 4-hydroxypentan-2-one over neat and heterogenized Ru-Phen-2 complex at 120 °C and 300 psig pressure. The conversion is comparable in homogeneous and heterogeneous catalyst system. However, the chemoselectivity is slightly low in homogeneous condition, as there is no diffusion barrier for reactant to adsorb on surface of catalyst in case of neat complex. Almost complete conversion was obtained after 10 h, however, the selectivity in heterogeneous catalyst is 99 % as compared to that of homogeneous catalyst (96 %).



**Fig. 3.12:** Effect of metal to ligand ratio on conversion and selectivity in hydrogenation of acetylacetone to 4-hydroxypentan-2-one over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), 0.005 g (Ru-Phen-2), 0.1 g (Ru-Phen-2-NH-MCM-41), Temperature = 120 °C, Pressure = 2.04 MPa, Agitation = 300 rpm, 30 mL water, Time = 10 h.



**Fig. 3.13:** Effect of reaction time on conversion and selectivity in hydrogenation of acetylacetone to 4-hydroxypentan-2-one over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

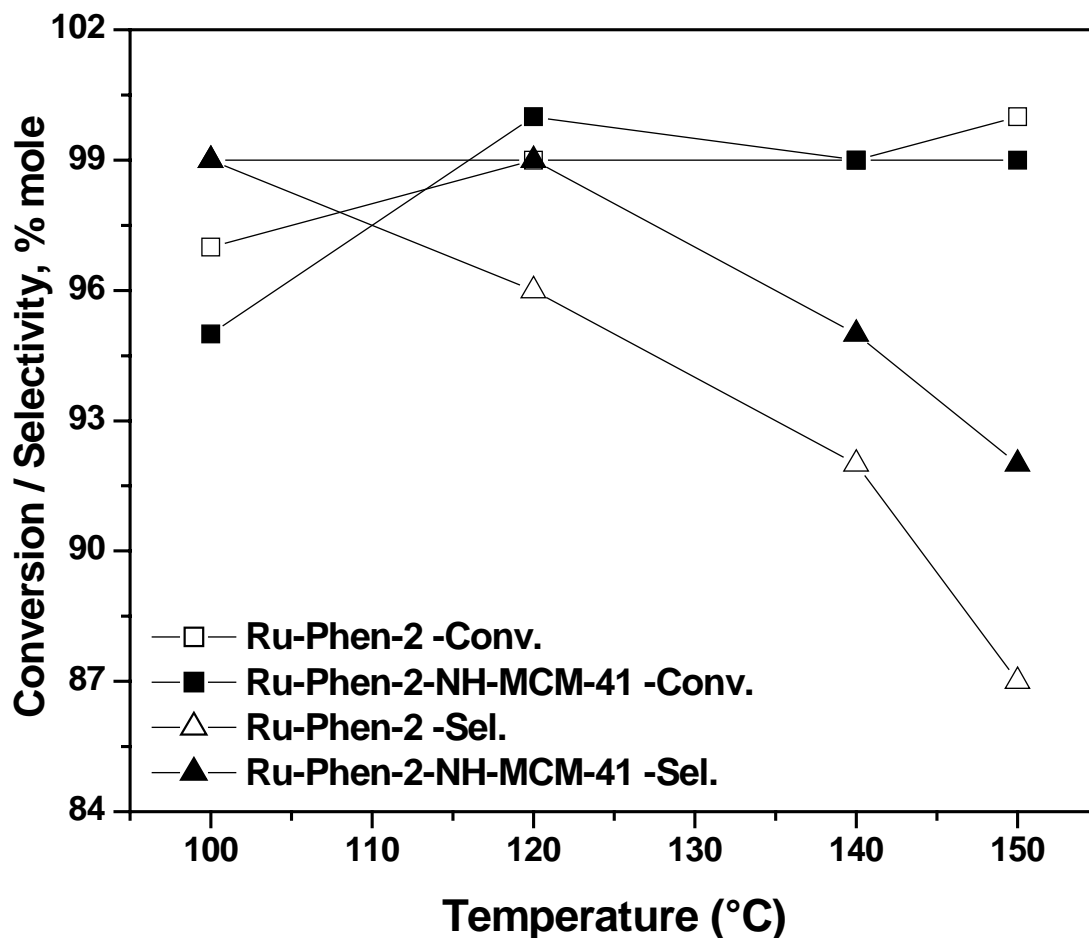
<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), 0.005 g (Ru-Phen-2), 0.1 g (Ru-Phen-2-NH-MCM-41), Temperature = 120 °C, Pressure = 2.04 MPa, Agitation speed = 300 rpm, 30 mL water.

#### 3.3.2.5. *Effect of Temperature*

To find out optimized reaction temperature for the hydrogenation of acetylacetone, reactions were carried out at various temperatures and the results are shown in Fig. 3.14. It was observed in both the homogeneous as well as heterogeneous cases that, with increase in temperature from 100 to 150 °C the conversion increases and selectivity of 4-hydroxypentan-2-one decreases. The highest selectivity (99 %) was observed at 120 °C reaction temperature. However, the selectivity decreases from 120 °C onwards due to further hydrogenation of 4-hydroxypentan-2-one to form 2, 4-pentane-diol. In heterogeneous condition the selectivity of 4-hydroxypentan-2-one are higher compare to that of homogeneous condition at all the temperatures.

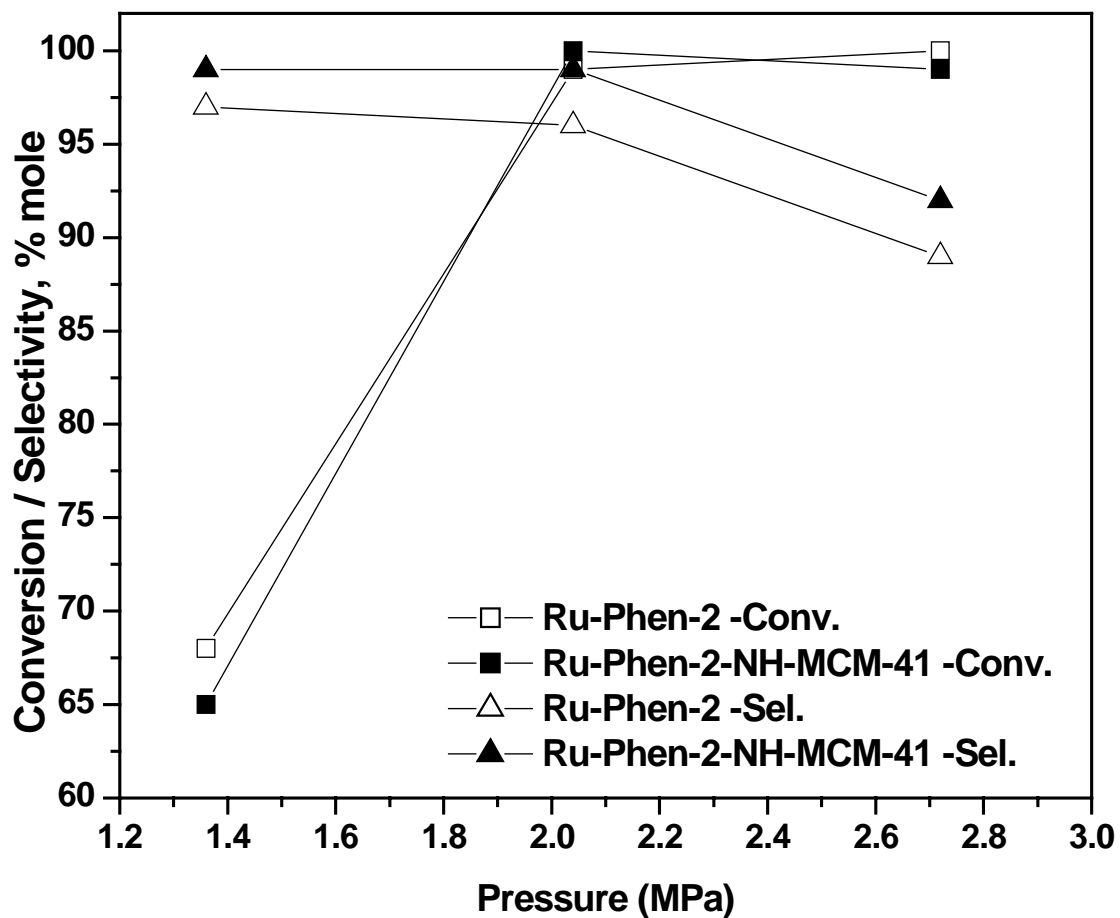
#### 3.3.2.6. *Effect of Pressure*

Fig. 3.15 depicts the effect of pressure on chemoselectivity of 4-hydroxypentan-2-one at 120 °C using water as reaction medium. The hydrogen pressure shows pronounced effect over the conversion and selectivity. As expected, the high conversion and low selectivity was obtained at higher pressure of hydrogen in both homogeneous and heterogeneous reaction conditions. There is decrease in the selectivity of 4-hydroxypentan-2-one as hydrogen pressure increases for 300 – 400 psig as more hydrogen is available to further hydrogenation of 4-hydroxypentan-2-one to diol. The heterogeneous catalyst shows higher chemoselectivity than homogeneous catalyst although the conversion is higher for homogeneous catalyst.



**Fig. 3.14:** Effect of temperature on conversion and selectivity in hydrogenation of acetylacetone to 4-hydroxypentan-2-one over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41

<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), 0.005 g (Ru-Phen-2), 0.1 g (Ru-Phen-2-NH-MCM-41), Pressure = 2.04 MPa, Agitation speed = 300 rpm, 30 mL water, Time = 10 h.



**Fig. 3.15:** Effect of pressure on conversion and selectivity in hydrogenation of acetylacetone to 4-hydroxypentan-2-one over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41  
<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), 0.005 g (Ru-Phen-2), 0.1 g (Ru-Phen-2-NH-MCM-41), Temperature = 120 °C, Agitation speed = 300 rpm, 30 mL water, Time = 10 h.

The pronounced effect of pressure was observed at higher temperature. The selectivity decreases from ca. 98 % to ca. 86 % at reaction temperature 150 °C as compared to the selectivity at reaction temperature 120 °C at hydrogen pressure 300 psig. The selectivity goes on decreasing as the pressure goes on increasing in case of reaction temperature 150 °C. This is due to the extra energy available to the formed intermediate, which further get hydrogenate to form diol.

**Table 3.10:** Effect of pressure on hydrogenation of acetylacetone at various temperature<sup>a</sup>

Sr. No.	Press. (psig)	Temp. (°C)	Conv. (mole %)		Selectivity (mole %) <sup>a</sup>	
			Ru-Phen-2	Ru-Phen-2-NH-MCM-41	Ru-Phen-2	Ru-Phen-2-NH-MCM-41
1	200		63	65	90	93
2	300	100	96	95	98	98
3	400		92	89	85	88
4	200		68	65	97	98
5	300	120	99	99	96	99
6	400		90	99	89	92
7	200		72	72	84	88
8	300	150	99	97	86	92
9	400		99	98	81	85

<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), 0.005 g (Ru-Phen-2), 0.1 g (Ru-Phen-2-NH-MCM-41), Agitation speed = 300 rpm, 30 mL water, Time = 10 h.

### 3.3.2.7. Catalyst Recycle Studies

Table 3.11 depicts the recyclability of the heterogenized catalyst. The heterogenized catalyst can be recycled for three times. The selectivity and conversion decreases to 95 % and 89 % respectively, at the time of third recycle. The decrease in the conversion and selectivity is attributed to the partial leaching (~ 1 % of the total Ru present) of ruthenium from the catalyst.

**Table 3.11:** Recycle studies of the heterogeneous catalysts for hydrogenation of acetylacetone

Entry	Catalyst	% Conv	Ketol Sel. (%)	TON <sup>a</sup>
1	Ru-Phen-2-NH-MCM-41	98	99	1921
2	Ru-Phen-2-NH-MCM-41-R1	97	98	1902
3	Ru-Phen-2-NH-MCM-41-R2	98	95	1745
4	Ru-Phen-2-NH-MCM-41-R3	89	95	1504

<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), 0.005 g (Ru-Phen-2), 0.1 g (Ru-Phen-2-NH-MCM-41), Temperature = 120 °C, Pressure = 2.04 MPa, Agitation speed = 300 rpm, 30 mL water, Time = 10 h. <sup>b</sup>TON = Turn over number = mole of product formed / Mole of Ru.

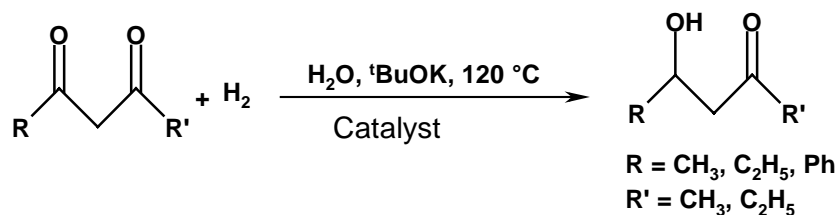
### 3.3.2.8. Effect of Different Substrate

Efficient hydrogenation of diketones to ketols was accomplished over ruthenium phenanthroline metal complex at 120 °C and under 300 psig pressure using water as reaction medium. From the Table 3.12, it is evident that all the substrates show very high conversion (>99 %) over ruthenium phenanthroline complex in homogeneous and heterogeneous reaction condition. The yield of ketol was observed as high as 99 % after



heterogenization of ruthenium phenanthroline metal complex. The reactivity of  $\alpha$  substituted compound was found low as expected due to the bulkier group in the vicinity of carbonyl group as that of the  $\beta$ -substituted compounds.

**Table 3.12:** Effect of different substrate on catalytic activity



Catalyst	Substrate	Ketol Yield (%)	TOF ( $\text{h}^{-1}$ ) <sup>b</sup>
Ru-Phen-2	R & R <sup>1</sup> = CH <sub>3</sub> , n = 1	96	240
	R = Ph, R <sup>1</sup> = CH <sub>3</sub> , n = 1	93	197
	R = Ph, R <sup>1</sup> = CH <sub>3</sub> , n = 0	95	197
	R = C <sub>3</sub> H <sub>7</sub> , R <sup>1</sup> = CH <sub>3</sub> , n = 1	96	219
	1,3-Cyclopentanedione	95	163
Ru-Phen-2-NH-	R & R <sup>1</sup> = CH <sub>3</sub> , n = 1	99	186
	R = Ph, R <sup>1</sup> = CH <sub>3</sub> , n = 1	98	105
	R = Ph, R <sup>1</sup> = CH <sub>3</sub> , n = 0	98	105
MCM-41	R = C <sub>3</sub> H <sub>7</sub> , R <sup>1</sup> = CH <sub>3</sub> , n = 1	98	133
	1,3-Cyclopentanedione	98	143

<sup>a</sup>Reaction conditions: Substrate = 1 g, Substrate: Base = 10 (wt/wt), Neat Catalyst = 0.005 g (Ru-Phen-2), 0.1 g (Ru-Phen-2-NH-MCM-41), Temperature = 120 °C, Pressure = 2.04 MPa, Agitation speed = 300 rpm, 30 mL water, Time = 10 h. <sup>b</sup>TOF = Turn over frequency = mole of product formed / Mole of Ru per hour.

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**CHAPTER 4**  
**CHEMOSELECTIVE HYDROGENATION**  
**OF NITROARYLS**

#### 4.1. INTRODUCTION

The selective synthesis of amines from the hydrogenation of nitro compounds is commonly used to manufacture important intermediates for dyes, urethanes, agrochemicals and pharmaceuticals. Aniline is mainly used:

- (i) for the production of methylene diphenyl diisocyanate (MDI)
- (ii) as an additive for rubber process
- (iii) as an intermediate for the synthesis of 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 vapor or liquid phase using supported metal catalysts and organic solvents such as alcohols, acetone, benzene, ethyl acetate or aqueous acidic solutions.<sup>1</sup> The use of these solvents has several drawbacks owing to their toxicity, flammability and environmental hazards. Therefore the choice of environmentally benevolent solvent has become an important factor, which can be overcome by the use of green solvent like water 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.<sup>2</sup> 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

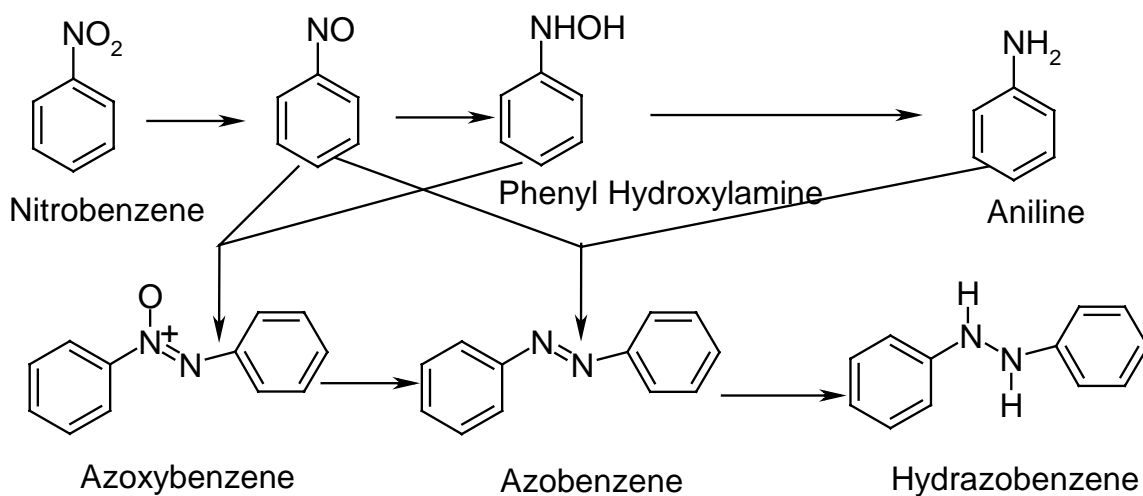
multiphase catalytic reactions) has emerged as a cleaner alternative to the conventional Béchamp process with better selectivity and yields.<sup>3,4</sup>

Metal nano-clusters are also used for the hydrogenation of nitro compounds exhibiting high activity and selectivity. Carbon nano-tubes are used as support for the deposition of metal nano-particles. Dai and coworkers have reported the use of various metal nano-particles deposited on carbon nano-tubes.<sup>5</sup> About 3 wt. % Pt on carbon nano-tubes showed very high activity for the nitrobenzene hydrogenation at ambient temperature and at atmospheric pressure.<sup>6</sup> Xu et al. investigated the Pd-macromolecule supported on copolymer for the hydrogenation of 4-nitro-phenol.<sup>7</sup> Hydrogenation of nitrobenzene halides was carried out using platinum on carbon.<sup>8,9</sup> The heterogenized rhodium metal on zinc aluminate spinel has been studied for chemoselective hydrogenation of nitro compounds.<sup>10</sup> The Pt and Pd clusters supported on ordered mesoporous carbon molecular sieve showed high catalytic activity towards the hydrogenation of nitro compounds.<sup>11</sup> The use of supercritical carbondioxide has also been investigated for the hydrogenation of nitrobenzene.<sup>12,13</sup> Deshpande et al. reported the hydrogenation of substituted nitrobenzene using water-soluble iron complex catalyst under biphasic reaction conditions to achieve 98 % selectivity towards aniline.<sup>14</sup>

However, use of water, as reaction medium has not been reported to our knowledge for hydrogenation of nitro-aromatics to corresponding amine. Similarly Ru(Phen)<sub>x</sub> complexes have also not been used for such reaction. The present chapter deals with the utilization of universal solvent, water, as reaction medium in the hydrogenation of nitro aryls using both homogeneous and heterogeneous catalyst to overcome the drawbacks of organic solvents.

## 4.2. CATALYTIC HYDROGENATION REACTION

The hydrogenation of nitrobenzene was carried out in 100 cm<sup>3</sup> high-pressure and high temperature autoclave equipped with magnetic stirrer, at different pressure (200-400 psig) and at different temperature (120 –180 °C) using water as reaction medium. The effect of different metal to ligand ratios and different types of substrates (substituted nitro-aryls) at 160 °C, at 400 psig pressure was studied. The effect of different organic solvent was also tested at 160 °C at 400 psig pressure for comparative purpose. The reaction mixture was extracted using toluene and analyzed by GC on a capillary column with FID detector. The products were confirmed by GCMS. The Scheme 4.1 represents various reaction pathways and possible products, which can be obtained during hydrogenation of nitrobenzene.



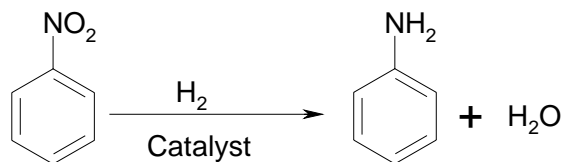
**Scheme 4.1:** Reaction path for the hydrogenation of nitrobenzene



#### 4.2.1. Effect of Different Ligand

The effect of ligand (Pyridine as a mono or bi-pyridine and phenanthroline as a bi-dentate) on the activity and selectivity in the hydrogenation reaction of nitrobenzene to aniline was studied. The reaction was carried out over  $RuL_2$  type complexes, [where L = Pyridine (PY), bipyridyl (BP) and phenanthroline (Phen)], 160 °C and 400 psig using water as reaction medium. The results are given in Table 1, which depicts that nearly complete conversion was obtained over all the catalyst studied with ca. 92 – 99 % selectivity towards aniline. However, the selectivity towards aniline followed the order:  $RuCl_3 < Ru-Py-2 < Ru-Bp-2 \approx Ru-Phen-2$ . The Ru-Phen-2-NH-MCM-41 solid catalyst was also used for the same reaction. It was found that the time required for complete conversion increases from 6 h to 8 h, which is due to the diffusional / adsorptional constrains of solid catalyst.

After reaction, the heterogenized catalyst was subjected for XRD and the mother liquor was analyzed by AAS in order to determine the phase stability of MCM-41 and leaching of ruthenium in to mother liquor. XRD pattern showed decrease in intensity of 100 peak ( $2\theta = 2.1^\circ$ ) where as no other characteristic peaks ( $2\theta = 3.7^\circ, 4.3^\circ$  and  $5.6^\circ$ ) of MCM-41 were observed. AAS showed almost complete leaching of ruthenium metal, clearly indicating that under the reaction conditions particularly in the presence of aniline and water the MCM-41 disintegrates and therefore results in the leaching of metal complex from solid. Hence, all the further experiments were conducted using neat metal complex.

**Table 4.1:** Hydrogenation of nitrobenzene with different ruthenium metal complexes <sup>a</sup>

Sr. No.	Catalyst	% Conversion (mole)	% Selectivity (mole) <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>
1	RuCl <sub>3</sub>	100	92	168
2	Ru-PY-2	100	96	113
3	Ru-BP-2	99	97	112
4	Ru-Phen-2	99	99.5	123
5 <sup>d</sup>	Ru-Phen-2-NH-MCM-41	98	99	109

<sup>a</sup> Reaction conditions: Substrate = 1 g, Pressure = 400 psig, Temperature = 160 °C, water 20 cm<sup>3</sup>, 0.89 mmol K<sup>t</sup>BuO, Time = 6 h, <sup>b</sup> remaining is phenyl hydroxylamine and azobenzene, <sup>c</sup> TOF = number of moles of amino product formed per moles of ruthenium per hour, <sup>d</sup> Time 8 h.

#### 4.2.2. Effect of Metal to Ligand Ratio

To study the performance of metal to ligand ratio, three different ruthenium to phenanthroline ratios were used as catalyst for hydrogenation of nitrobenzene at 160 °C and 400 psig (Table 2). Although, RuCl<sub>3</sub> shows faster reaction, the aniline selectivity was lower (92 %) compared to Ru-L<sub>2</sub> complex (> 99 %). Except for Ru-Phen-3 catalyst, the conversion was nearly comparable in 6 h as compared to others. The reaction was relatively sluggish over Ru-Phen-3, mainly due to bulkiness of ligand around metal

leading to steric constraints, thereby restricting the approach of reactant molecule towards reactive metal center in complex.

**Table 4.2:** Effect of metal to ligand ratio in hydrogenation of nitrobenzene <sup>a</sup>

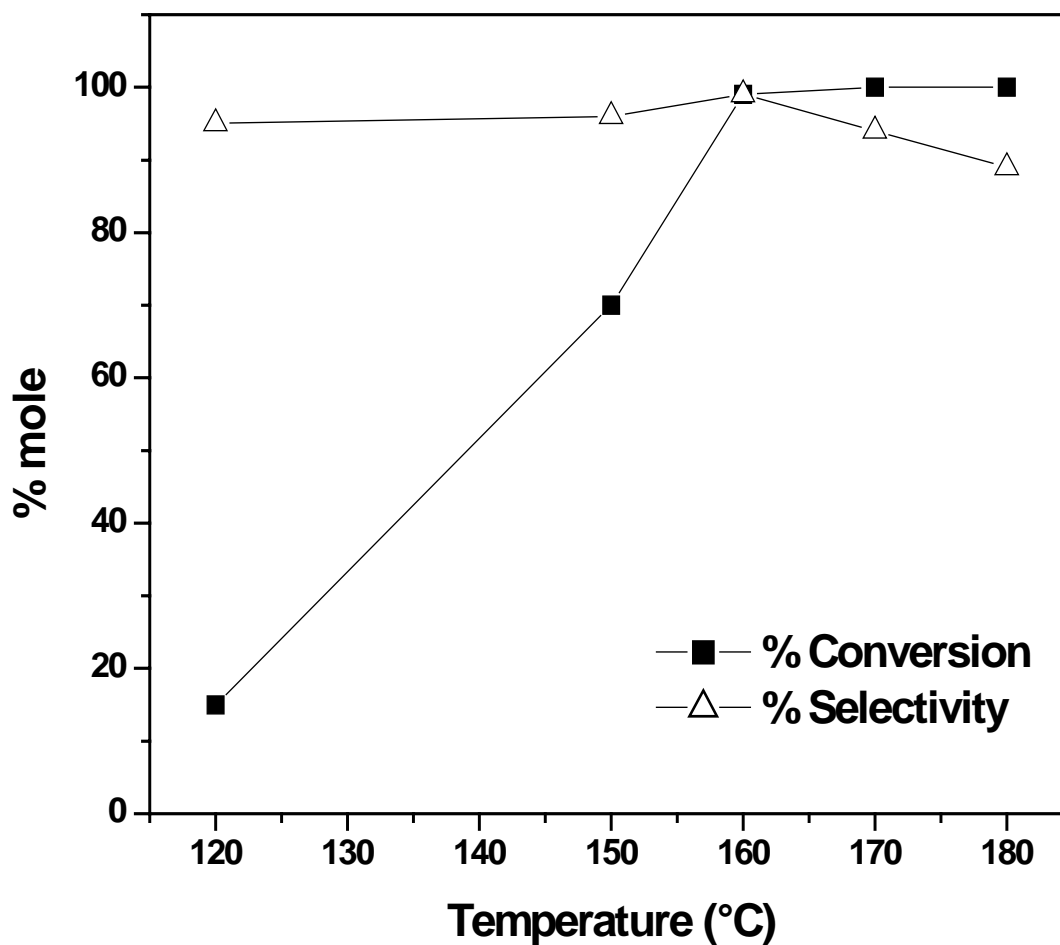
Sr. No.	Catalyst	Conversion (% Mole)	Aniline Selectivity (% Mole) <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>
1	RuCl <sub>3</sub>	100	92	168
2	Ru-Phen-1	100	96	111
3	Ru-Phen-2	99	99.5	112
4	Ru-Phen-3	80	98	91

<sup>a</sup> Reaction conditions: Substrate = 1 g, Pressure = 400 psig, Temperature = 160 °C, water 20 cm<sup>3</sup>, K<sup>t</sup>BuO = 0.1 g, Time = 6 h, <sup>b</sup> remaining is phenyl hydroxylamine and azobenzene, <sup>c</sup> TOF = number of moles of amino product formed per moles of ruthenium per hour.

#### 4.2.3. Effect of Temperature

Fig. 1 shows the effect of temperature on activity and selectivity on catalytic hydrogenation of nitrobenzene. It was observed that with increase in temperature from 120 to 160 °C the nitrobenzene conversion increases, whereas selectivity passes through a maximum at 160 °C. The highest selectivity and conversion (>99 %) was observed at reaction temperature 160 °C. The slightly lower selectivity of aniline at temperature lower than 160 °C was due to the formation of hydroxylamine as an intermediate. However, aniline selectivity decreases at reaction temperature higher than 160 °C due to

the formation of condensed products (azoxybenzene) as shown in the scheme 4.1. Thus, the optimized temperature for getting highest selectivity towards aniline by hydrogenation of nitrobenzene using water as solvent was 160 °C.

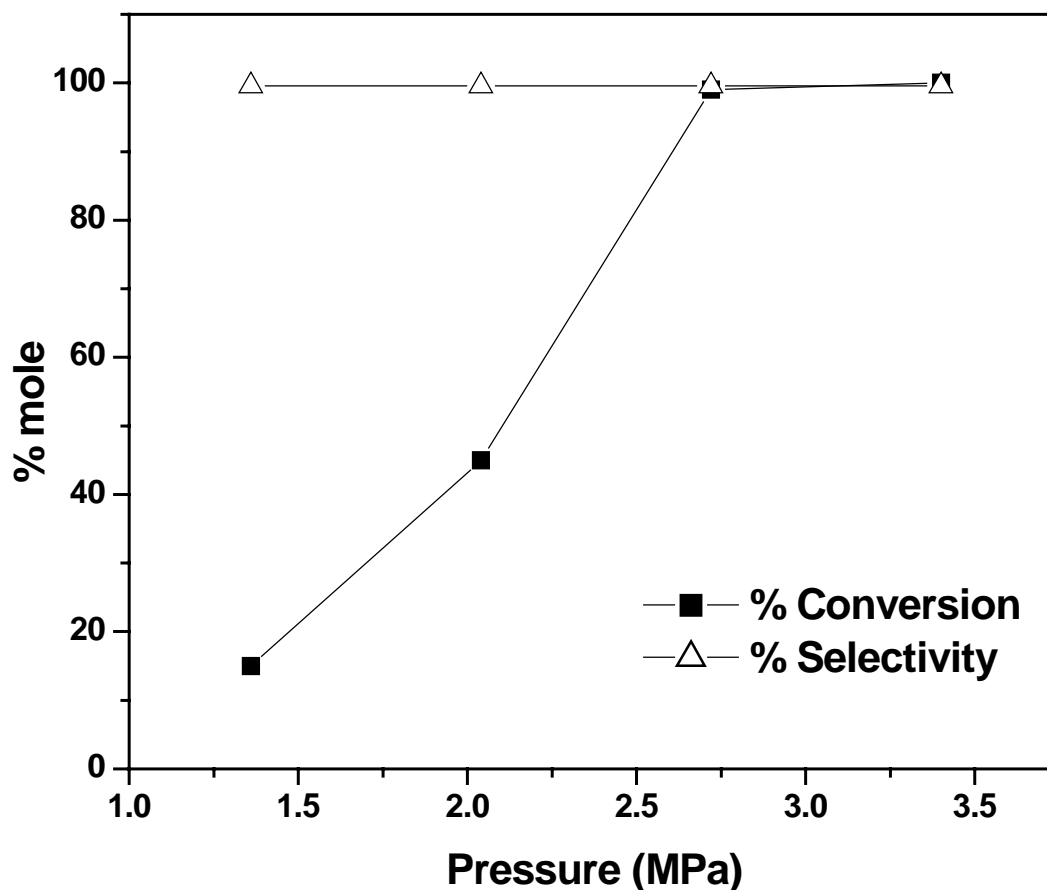


**Fig. 4.1:** Effect of temperature on the hydrogenation of nitrobenzene over Ru-Phen-2

<sup>a</sup> Reaction conditions: Substrate = 1 g, Pressure = 400 psig, water = 20 cm<sup>3</sup>, K<sup>t</sup>BuO = 0.1 g, Time = 6 h.

#### 4.2.4. Effect of Pressure

Fig. 4.2 depicts the effect of pressure on nitrobenzene conversion and aniline selectivity at 160 °C over Ru-Phen-2 catalyst. The hydrogen pressure shows pronounced effect over conversion, as expected. The conversion increased with increasing hydrogen pressure. There were no changes observed in conversion after 400 psig pressure. There was also no change in the selectivity of aniline with increase in hydrogen pressure. Thus, for all the studies the reaction temperature was maintained at 160 °C and hydrogen pressure was 400 psig.



**Fig. 4.2:** Effect of pressure on the hydrogenation of nitrobenzene over Ru-Phen-2

<sup>a</sup> Reaction conditions: Substrate = 1 g, Temperature = 160 °C, water = 20 cm<sup>3</sup>, K<sup>t</sup>BuO = 0.1 g, Time = 6 h.

#### 4.2.5. Effect of Solvent

In Table 4.3 the effect of organic protic solvents and water on the conversion and selectivity is reported. Although, complete conversion and selectivity (>99 %) was obtained in the presence of water as reaction medium for the hydrogenation of nitrobenzene, the conversion followed the order methanol < n-butanol < iso-propanol < water. However, the aniline selectivity ranged between 97 to 99.5 %. Use of water as solvent, in reaction was found most effective in the hydrogenation of nitrobenzene compare to the other solvents (n-butanol, methanol and iso-propanol). Use of water as reaction mixture allows easy phase separation thereby making the downstream processing rather easy, cost effective and eco-friendly.

**Table 4.3:** Effect of solvent on selectivity and conversion for hydrogenation of nitrobenzene<sup>a</sup>

Sr. No.	Solvent	Conversion (Mole %)	Aniline	
			selectivity (Mole %)	TOF (h <sup>-1</sup> ) <sup>b</sup>
1.	Methanol	65	97	66
2.	n-Butanol	70	98	71
3.	Iso-propanol	90	98	92
4.	Water	99	99.5	124

<sup>a</sup> Reaction conditions: Substrate = 1 g, Temperature = 160 °C, water = 20 cm<sup>3</sup>, K<sup>t</sup>BuO = 0.1 g, Time = 6 h, <sup>b</sup> TOF = number of moles of amino product formed per moles of ruthenium per hour.

#### 4.2.6. *Effect of Substitution on the Aromatic Ring*

The effect of different substrates having different substituted group is shown in Table 4.4. The hydrogenation of 4-nitrobenzaldehyde and 4-nitrobenzoic acid gives corresponding amino derivatives without affecting the other functional groups, which shows the chemoselective nature of the catalyst. The hydrogenation of Chloro-nitrobenzene also showed high yield of 4-chloro-aniline without any dehalogenation of 4-chloro-nitrobenzene. The variation in the activity observed for the hydrogenation of the different compounds could be attributed to the influence of the substituent on the ring as well as the solubility of the substrate in water. The limited solubility of the substrate in water maintains sufficient productivity.

### 4.3. CONCLUSION

The successful use of water as reaction medium has shown great promises in eliminating the necessity of using organic solvent, thereby making the process more eco-friendly. The highly selective hydrogenation of nitro aryl in biphasic aqueous medium using ruthenium metal complexes has been shown for the first time. The simplicity of the catalyst preparation, recycling and the low cost, coupled the prospect of solvent-free operations. Due to the leaching of ruthenium metal and breaking of MCM-41 structure, this heterogenized catalyst cannot be used as it follows the homogeneous path.

**Table 4.4:** Effect of substitution on hydrogenation in biphasic medium <sup>a</sup>

Sr. No.	Substrate	Product	Conv. (mole %)	Amine Selectivity (mole %)	TOF <sup>b</sup> (h <sup>-1</sup> )
1	Ph-NO <sub>2</sub>	Ph-NH <sub>2</sub>	>99	100	110
2	4-CH <sub>3</sub> - Ph-NO <sub>2</sub>	4-CH <sub>3</sub> - Ph-NH <sub>2</sub>	99	100	83
3	4-OCH <sub>3</sub> - Ph-NO <sub>2</sub>	4-OCH <sub>3</sub> - Ph-NH <sub>2</sub>	98	100	124
4	4-OH- Ph-NO <sub>2</sub>	4-OH- Ph-NH <sub>2</sub>	99	100	106
5	3,4-OH- Ph-NO <sub>2</sub>	3,4-OH- Ph-NH <sub>2</sub>	98	100	88
6	4-Cl- Ph-NO <sub>2</sub>	4-Cl- Ph-NH <sub>2</sub>	99	100	103
7	4-NH <sub>2</sub> - Ph-NO <sub>2</sub>	4-NH <sub>2</sub> - Ph-NH <sub>2</sub>	99	100	106
8	4-COOH- Ph-NO <sub>2</sub>	4-COOH- Ph-NH <sub>2</sub>	85	99	67
9	4-CHO- Ph-NO <sub>2</sub>	4-CHO- Ph-NH <sub>2</sub>	99	100	89

<sup>a</sup> Reaction conditions: Substrate = 1 g, Temperature = 160 °C, Pressure = 400 psig, water = 20 cm<sup>3</sup>, K<sup>t</sup>BuO = 0.1 g, Time = 6 h, <sup>b</sup> TOF = Mole of product formed per moles of ruthenium per hour.



**4.4. REFERENCE**

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# CHAPTER 5

## SUMMARY AND CONCLUSIONS

### 5.1. SUMMARY

The present thesis gives an account of

- (I) Effective synthesis of Ru-metal complexes using nitrogen containing mono dentate and bi-dentate ligand. During synthesis simple and cost effective method was utilized.
- (II) Synthesis of mesoporous MCM-41 material and its functionalization
- (III) The syntheses of inorganic–organic hybrid mesoporous materials by immobilization of ruthenium complexes in the functionalised MCM-41.
- (IV) Detail structural, morphological and chemical characterization of these composite materials.
- (V) Application of these materials as catalysts in chemo-selective hydrogenation of
  - (i) ketones to secondary alcohols
  - (ii)  $\alpha,\beta$ -unsaturated ketones to  $\alpha,\beta$ -unsaturated alcohols
  - (iii) diketones to ketols
  - (iv) nitro-aryls to amino-aryls
- (VI) Another major achievement of the present work is the preferred use of biphasic system using water as reaction medium vis-à-vis organic solvents.

**Chapter 1** presents a general introduction about various physicochemical aspects of mesoporous materials with particular emphasis to different synthesis routes and different approaches for their surface modification. Similarly different synthesis routes and different approaches for the synthesis of transition-metal complexes are also included. The various applications of mesoporous materials as supports for different catalytically active transition metal complexes and characterization

techniques of these composite materials are also discussed in brief. The general concepts of green chemistry in developing catalytic processes are discussed. Some of the concepts like chemo-selectivity, regio-selectivity, stereo/enantio-selectivity and atom economy for developing new industrially important reactions are discussed in detail. The scope of the work includes synthesis of Ru-metal complexes and immobilization of these metal complexes in functionalised MCM-41 and their use in catalyzing environmentally benign hydrogenation of (i) ketones to secondary alcohols (ii) diketones to ketols (iii)  $\alpha,\beta$ -unsaturated ketones to  $\alpha,\beta$ -unsaturated alcohols and (iv) nitro-aryls to amino-aryls using principles of green chemistry, water as preferred reaction medium. Based on the above scope the objectives of work on synthesizing Ru-metal complexes using mono-dentate and bi-dentate nitrogen containing ligands, their characterization and application for above mentioned hydrogenation reaction.

**Chapter 2** provides detailed experimental results on synthesis of Ru-metal complexes using pyridine as mono-dentate ligand (Ru-Py) and bi-pyridine (Ru-By) and phenanthroline  $\text{Ru(Phen)}_x$  as bi-dentate ligands. The synthesis procedure for siliceous MCM-41 material and its surface modification by reactive organic functional groups by two different methods viz. (i) post-synthesis grafting and (ii) "one-pot" co-condensation were discussed in detail. The immobilization procedure of Ru-Phenanthroline complex in the organofunctionalised MCM-41 (Ru-Phen-NH-MCM-41) was also discussed. The complete characterizations of these samples were carried out by various spectroscopic techniques like XRD, FTIR, UV-vis, NMR and elemental analysis. The microscopic techniques like SEM and TEM were used for morphological confirmation of the MCM-41 structure before and after immobilization of Ru-Phen complex. The volumetric technique was used for surface area and pore

size measured for MCM-41 structure before and after immobilization of Ru-Phen complex. The detail experimental procedure for hydrogenation of ketones to secondary alcohols,  $\alpha,\beta$ -unsaturated ketones to  $\alpha,\beta$ -unsaturated alcohols diketones to ketols, and nitro-aryls to amino-aryls are discussed.

**Chapter 3** deals with an effective utilization of synthesized Ru-metal complexes and immobilized Ru-phenanthroline complexes on surface modified MCM-41 as novel heterogeneous catalyst system for hydrogenation reactions in batch type reactor. The tri-phasic (Solid-Liquid-Liquid) reaction condition was employed when heterogenized metal complex as catalyst and water as reaction medium were used. However, when neat complexes were used as catalyst in the presence of water, the system was biphasic (Liquid-Liquid). The effects of reaction parametric effects were studied to obtain optimized reaction conditions for maximization of conversion and selectivity in the hydrogenation of (i) ketones to secondary alcohols (ii)  $\alpha,\beta$ -unsaturated ketones to  $\alpha,\beta$ -unsaturated alcohols (iii) diketones to ketols. The optimization of ligand, solvent and reaction parameters was also studied. The comparison between homogeneous and heterogeneous condition was carried out. Heterogeneous catalyst was found highly chemoselective as that of homogeneous catalyst in all the hydrogenation reactions. The use of water as reaction medium, not only gives high activity and selectivity in hydrogenation reaction, but also helps in developing environmentally safer process. Heterogenized ruthenium complex are easily separable and reusable.

**Chapter 4** focuses on the use of Ru(II) Phenanthroline [Ru-Phen-2] complex as highly selective catalyst for hydrogenation of nitro aryls using molecular hydrogen

in an aqueous medium. Probably this is the first report where water is used as reaction medium in catalytic hydrogenation of nitro-aryls. The selectivity of aniline as well as substituted anilines was as high as > 99 % at about complete conversion of nitro-benzene. The effects of solvent, ligand, metal to ligand ratio, temperature and pressure were studied in detail. The substituted nitro-aryls having other functional groups were also studied as different substrates.

## 5.2. CONCLUSIONS

### 5.2.1. Surface Modification and Characterization of Mesoporous Silica

- ♦ Highly order MCM-41 was synthesized by hydrothermal method and it was successfully functionalised by aminopropyl trimethoxysilane.
- ♦ Toluene was found to be the best solvent compared to methanol and dichloromethane in the post-synthesis functionalization process at room temperature.
- ♦ For functionalization of MCM-41 the post synthesis method was found to be better as compared to co-condensation.

### 5.2.2. Immobilization of Transition Metal Complexes

- ♦ An efficient heterogeneous catalyst system for chemoselective hydrogenation of carbonyl and nitro compounds was synthesized by a simple and easier approach, involving anchoring of Ru<sup>II</sup>-phenanthroline containing complex on the inner surfaces of organo-functionalized MCM-41 materials.
- ♦ Highly ordered hexagonal pattern of the organo-functionalized MCM-41 materials was retained even after incorporation of Ru-complex as shown by powder XRD patterns and TEM images.

- ♦ The integrity and geometry of the Ru-complex was retained before and after immobilization into the mesoporous hosts, which was confirmed from FTIR, UV-*vis* and XPS analyses.

### 5.2.3. Chemoselective Hydrogenation of Ketones

- ♦ The presence of bi-dentate ligand is essential to achieve high chemoselectivity for hydrogenation of ketones to secondary alcohols,  $\alpha,\beta$ -unsaturated ketones to  $\alpha,\beta$ -unsaturated alcohols and diketones to ketols compared to mono-dentate ligand.
- ♦ Ru-Phen-2complex was found highly chemoselective in hydrogenation of ketones.
- ♦ Water as reaction medium was found more suitable compared to other organic solvents. For the first time use of environmentally benevolent solvent / reaction medium i.e. water for hydrogenation reaction made this a green process.
- ♦ The immobilized Ru-phenanthroline complex in MCM-41 as heterogeneous catalyst found to be a promising catalyst in the chemoselective hydrogenation of ketones to secondary alcohols, diketones to ketols,  $\alpha,\beta$ -unsaturated ketones to  $\alpha,\beta$ -unsaturated alcohols. As high as 99 % chemoselectivity could be obtained using this solid catalysts under heterogeneous reaction conditions in aqueous triphasic (SLL) system.
- ♦ The functionalised solid catalyst was effectively recycled several times with marginal change in activity and selectivity

### 5.2.4. Chemoselective Hydrogenation of Nitro-aryls

- ♦ The ruthenium metal complexes exhibit promising catalytic activity in the chemoselective hydrogenation of nitro compounds in presence of water as green solvent.



- ♦ The presence of aldehydic, acidic and halide functionalities on aromatic ring in nitrobenzene did not interfere with the chemoselectivity for the hydrogenation of nitro group using Ru-Phen-2 metal complex.
- ♦ The immobilized Ru-phenanthroline complex in MCM-41 catalyst was not suitable for this reaction because the catalyst was disintegrated under the reaction conditions probably due to the presence of aniline and water coupled with high temperature required for this reaction.