“SUPPORTED TRANSITION METAL CATALYSTS FOR CARBON-CARBON, CARBON-HETEROATOM CROSS COUPLING AND SELECTIVE OXIDATION OF ORGANIC MOLECULES”

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CERTIFICATE

Certified that the work incorporated in the thesis, ***“Supported transition metal catalysts for carbon-carbon, carbon-heteroatom cross coupling and selective oxidation of organic molecules”*** *submitted by* **Mr. Ganesh D. Kokate**, *for the Degree of Doctor of Philosophy, was carried out by the candidate under my supervision in the Catalysis Division, National Chemical Laboratory, Pune-411008, India. Materials obtained from other sources have been duly acknowledged in the thesis.*

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DECLARATION BY RESEARCH SCHOLAR

I hereby declare that the thesis entitled ***"Supported transition metal catalysts for carbon-carbon, carbon-heteroatom cross coupling and selective oxidation of organic molecules"*** submitted for the Degree of Doctor of Philosophy in chemistry to the University of Pune, has been carried out by me at the Catalysis Division, National Chemical Laboratory, Pune –411008, India, under the supervision of Dr. C.V.V. Satyanarayana. 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.

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TO

MY BELOVED PARENTS

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CONTENTS

Contents i

List of Abbreviations vii

1 Introduction

- 1.1. Catalysis 1
  - 1.1.1. Classification of catalysts 1
    - 1.1.1.1. Homogeneous catalysis 2
    - 1.1.1.2. Heterogeneous catalysis 3
- 1.2. Heterogenization of homogeneous catalysts 3
  - 1.2.1. Heterogenization on solid supports 4
    - 1.2.1.1. Immobilization on polymeric resin 4
    - 1.2.1.2. Immobilization on inorganic supports 5
- 1.3. Techniques of immobilization 6
  - 1.3.1. The flexible ligand method 7
  - 1.3.2. Insitu zeolite synthesis method 7
  - 1.3.3. Cationic exchange of inorganic complexes 8
  - 1.3.4. Ligand adsorption on metal ion exchanged zeolites 8
  - 1.3.5. Chemical grafting method 8
  - 1.3.6. Grafting with passive surface groups 9
  - 1.3.7. Grafting with reactive surface groups 9
  - 1.3.8. Site-selective grafting 9
  - 1.3.9. Co-condensation method 10
- 1.4. Advantages/ Disadvantages of immobilized catalysts 11
- 1.5. Coupling reactions 11
  - 1.5.1. Transition metals in coupling reactions 12
    - 1.5.1.1. Heck reaction 14
    - 1.5.1.2. Suzuki reaction 15
    - 1.5.1.3. Sonogashira reaction 16
    - 1.5.1.4. Ullmann reaction 17
    - 1.5.1.5. Carbon-Sulfur cross coupling 17
- 1.6. Selective Oxidation of hydrocarbons 18
  - 1.6.1. Oxidation of aromatics 18

1.6.1.1. Oxidation of p-cresol 19
1.6.1.2. Oxidation of p-xylene 20
1.7. Objective of the present investigation 21
1.8. References 23

2 Synthesis and characterization of catalysts

2.1. Introduction 33
2.2. Catalyst preparation 33
2.2.1. Preparation of KOMS-2 33
2.2.2. Preparation of mesoporous SBA-15 34
2.3. Characterization of catalysts 34
2.3.1. Atomic absorption spectrophotometry 34
2.3.2. Surface area determination by BET method 34
2.3.3. Powder X-ray diffraction 35
2.3.4. Electron microscopy 36
2.3.4.1. Transmission electron microscopy 37
2.3.4.2. Scanning electron microscopy 37
2.3.5. Thermal analysis 38
2.3.6. Solid-state nuclear magnetic resonance spectroscopy 38
2.3.7. Infra-red spectroscopy 39
2.3.8. X-ray photoelectron spectroscopy 40
2.4. References 42

3 C-C Cross Coupling reactions on Pd-K-OMS-2 catalysts

3.1. Introduction 43
3.1.1. Heck reaction 44
3.1.1.2 Reaction mechanism 44
3.1.2. Suzuki reaction 46
3.1.2.1. Reaction mechanism 46
3.1.3. Sonogashira reaction 47
3.1.3.1. Mechanism of Sonogashira reaction 48
3.1.3.2. The copper-co-catalyzed Sonogashira reaction 48

3.1.3.3. The copper-free Sonogashira reaction 50

3.1.4. Homogeneous catalysts in coupling reactions 50

3.1.5. Heterogeneous catalysts in coupling reactions 51

3.1.6. Octahedral molecular sieves as catalyst supports 52

3.2. Experimental procedures 54

3.2.1. Preparation of catalysts 54

3.2.2. Characterization of catalysts 55

3.2.3. General experimental Procedure for coupling reactions 56

3.2.3.1. Heck reaction 56

3.2.3.2. Suzuki reaction 56

3.2.3.3. Sonogashira reaction 56

3.2.3.4. Test for heterogeneous nature of reaction 57

3.3. Results and Discussion 57

3.3.1. Characterization 57

3.3.1.1. X-ray diffraction 57

3.3.1.2. Scanning electron microscopy 58

3.3.1.3. Transmission electron microscopy 58

3.3.1.4. BET surface area by N_2 sorption 60

3.3.1.5. X-ray photoelectron spectroscopy 61

3.3.1.6. Thermal analysis 61

3.4. Evaluation of catalyst activity 62

3.4.1. Heck reaction 62

3.4.1.1. Effect of base 62

3.4.1.2. Effect of catalyst weight 64

3.4.1.3. Effect of temperature and Pd metal content in the catalyst 64

3.4.1.4. Heck reaction of different arylhalides with styrene over Pdcat- II 65

3.4.1.5. Effect of solvent on Heck reaction 66

3.4.1.6. Heck reaction of different olefins with bromobenzene over Pdcat-II 67

3.4.1.7. Recycle study 67

3.4.2. Suzuki reaction 68

3.4.2.1. Effect of Pd content in Catalyst 68

3.4.2.2. Effect of base 69

3.4.2.3. Effect of solvent 70
3.4.2.4. Effect of water to co-solvent ratio 70
3.4.2.5. Recycle study 71
3.4.3. Sonogashira reaction 72
3.4.3.1. Effect of catalyst concentration 72
3.4.3.2. Effect of base 73
3.4.3.3. Effect of solvent 73
3.4.3.4. Sonogashira reaction of different aryl halides with phenylacetylene on Pdcat-II 74
3.4.3.5. Recycle study 75
3.5. Conclusions 76
3.6. References 77

4 C-O and C-S Cross Coupling reactions

4.1. Introduction 84
4.1.1. C-O cross coupling 85
4.1.1.1. Reaction mechanism 87
4.1.2. C-S cross coupling 88
4.2. Experimental procedures 90
4.2.1. Materials 90
4.2.2. Preparation of catalysts 90
4.2.2.1. Preparation of mesoporous SBA-15 90
4.2.2.2. Immobilization of Cu on modified SBA-15 90
4.2.3. Characterization of catalysts 92
4.3. General Procedure for testing catalysts in coupling reactions 93
4.3.1. C-O cross coupling reactions 93
4.3.2. C-S cross coupling reactions 93
4.4. Results and Discussion 94
4.4.1. Characterization of catalysts 94
4.4.1.1. X-ray diffraction 94
4.4.1.2. Scanning electron microscopy 95
4.4.1.3. Transmission electron microscopy 96
4.4.1.4. BET surface area by N_2 sorption 96

4.4.1.5. Thermal analysis 97
4.4.1.6. ^{13}C & ^{1}H MASNMR studies 98
4.4.1.7. FT-IR spectroscopy 99
4.5. Catalytic activity of CuSBA-15 catalysts in cross coupling reactions 100
4.5.1. Ullmann reaction 100
4.5.1.1. Activity of various copper catalysts 100
4.5.1.2. Effect of base 102
4.5.1.3. Effect of solvent 103
4.5.1.4. Catalyst recycle study 103
4.5.2. C-S cross coupling reaction 104
4.5.2.1. Effect of base 104
4.5.2.2. Effect of solvent 105
4.5.2.3. Activity of various catalysts 106
4.5.2.4. Comparison of substrate reactivity 106
4.5.2.4. Recycle and leaching study 108
4.6. Conclusions 109
4.7. References 110

5 Selective Oxidation of Hydrocarbon

5.1. Introduction 116
5.1.1. Oxidation of p-cresol 116
5.1.2. Oxidation of p-xylene 119
5.1.3. Octahedral molecular sieves as oxidation catalysts 121
5.2. Experimental procedures 122
5.2.1. Materials 122
5.2.2. Preparation of catalysts 122
5.2.3. Characterization of catalysts 123
5.2.4. General Procedure for oxidation reactions 124
5.2.4.1. Oxidation of p-cresol 124
5.2.4.2. Oxidation of p-xylene 125
5.3. Results and Discussion 125
5.3.1. Characterization 125

5.3.1.1. X-ray diffraction 125
5.3.1.2. Scanning electron microscopy 127
5.3.1.3. Transmission electron microscopy 128
5.3.1.4. BET surface area by N_2 sorption 128
5.3.1.5. X-ray photoelectron spectroscopy 130
5.3.1.6. Thermal analysis 130
5.4. Catalytic activity in Oxidation reactions 131
5.4.1. Oxidation of p-cresol 131
5.4.1.1. Effect of catalyst concentration 132
5.4.1.2. Variation of p-cresol : NaOH mole ratio 132
5.4.1.3. Effect of catalyst content on performance 133
5.4.1.4. Effect of temperature 133
5.4.1.5. Recycle study 134
5.4.2. Oxidation of p-xylene 135
5.4.2.1. Effect of temperature 135
5.4.2.2. Effect of type of initiator and its content 136
5.4.2.3. Effect of cobalt content on p-xylene oxidation 137
5.4.2.4. Effect of catalyst content on performance 138
5.4.2.5. Recycle study 138
5.5. Conclusions 139
5.6. References 141

6 Summary and Conclusions

6.1. Summary 146
6.2. General Conclusions 148
6.3. Suggestions for future research 150

LIST OF ABBREVIATIONS

KOMS-2	Potassium octahedral molecular sieves-2 (Cryptomelane)
BE	Binding energy
BET	Brunauer-Emmett-Teller
GC	Gas chromatography
FID	Flame Ionization detector
FTIR	Fourier Transform Infra-red
I.D.	Internal diameter
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
PXRD	Powder X-ray diffraction
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
XPS	X-ray photoelectron spectroscopy
SBA-15	Santa Barbara amorphous
P123	Poly(ethylene glycol)-block-poly(propylene glycol)- poly(ethylene glycol)
HRTEM	High-Resolution Transmission Electron Microscopy
C-C	Carbon - Carbon
PHB	p-hydroxybenzaldehyde
TPA	Terephthalic acid
NHPI	N-hydroxy phthalimide
NAPI	N-acetoxy phthalimide

Chapter-I

Introduction

1.1. Catalysis

Long before chemists recognized the existence of catalysts, ordinary people had been using the process of catalysis for a number of purposes: making soap or fermenting wine to create vineger or leavening bread. Early in the nineteenth century, chemists began to take note of this phenomenon. In 1812, Russian chemist Gottlieb Kirchhof observed different result for suspension of starch in water by adding few drops of concentrated acid before boiling to form glucose, “a simple sugar”, while the acid which clearly had facilitated the reaction underwent no change. Around the same time, English chemist Sir Humphry Davy observed that in certain organic reactions, platinum acted to accelerate the reaction without undergoing any change. Later British physicist and chemist Michael Faraday demonstrated the ability of platinum to recombine hydrogen and oxygen that had been separated by the electrolysis of water. In 1831, Peregrine Phillips patented the role of platinum in the oxidation of sulphur dioxide and later this became the basis for sulphuric acid manufacture [1].

In general, anything that increases the rate of a process is called “catalyst”, a term derived from Greek words ***kata*** means down and ***lyein*** meaning to loosen. The phrase “catalyzed processes” was coined by Jöns Jakob Berzelius in 1836 [2] to describe reactions that are accelerated by substances that remain unchanged after the reaction. In the 1880, Wilhelm Ostwald at Leipzig University started a systematic investigation into reactions that were catalyzed by the presence of acids and bases, and found that chemical reactions occur at finite rates and that these rates can be used to determine the strengths of acids and bases. For this work, Ostwald was awarded the 1909 Nobel Prize in chemistry [3].

1.1.1. Classification of catalysts

Catalysts are in use in the chemical industry for more than 100 years. The numerous catalysts known today can be categorized in various ways. One possibility is to classify them with regard to the state of aggregation in which they act (see Fig. 1.1) [4]. According to this categorization, catalysts can be divided into three groups:

1) Homogeneous catalysts 2) Heterogeneous catalysts, and 3) Hybrid catalysts (biocatalysts and heterogenized homogeneous catalysts) [5]

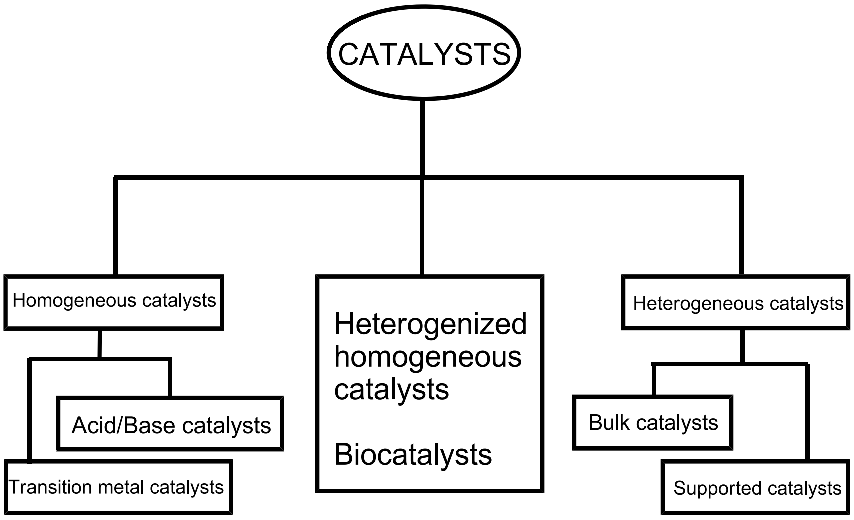


Fig. 1.1: Classification of catalysts

Catalysis plays a key role in the production of a wide variety of products, which have applications in food, clothing, drugs, plastics, agrochemicals, detergents, fuels etc. [6]. In addition to these, it plays an ever-expanding role in the balance of ecology and environment by providing cleaner alternative routes for stoichiometric technologies [7] by conversion of polluting emissions to harmless streams. Thus, the importance of catalysis to society is obviously based on its great economic impact in the production of broad range of commodity products that improve our standards of living and quality of life.

1.1.1.1. Homogeneous catalysis

Catalytic processes that take place in a uniform gas or liquid phase belong to the field of homogeneous catalysis. Homogeneous catalysts are generally well-defined chemical compounds or (transition) metal complexes, which consist of a metal centre surrounded by a set of organic ligands. The ligands impart solubility and stability to the metal complex and can be used to tune the selectivity of a particular catalyst towards the synthesis of a particular desirable product. By varying the size, shape and electronic properties of the ligands, the site at which the substrate binds can be constrained in such a way that only one of a large number of possible products can be produced.

The reactions which are catalyzed by transition metal complexes are hydrogenation, oxidation, carbonylation, hydroformylation, C-C bond formation reactions such as Heck reaction, polymerization, co-polymerization and ring opening metathesis with good selectivity [8]. Despite the selectivity advantage of homogeneous catalysts, most of the industrial catalytic processes use heterogeneous catalysts, because of one major advantage, i.e. ease of separation of catalyst from the reaction product. This aspect has driven the researchers to investigate new, stable and easily separable catalyst systems.

1.1.1.2. Heterogeneous catalysis

Three critical requirements of a catalyst are activity, selectivity and stability. It has been widely demonstrated and generally accepted that homogeneous catalysts are superior to their heterogeneous counterparts in terms of both activity and selectivity. However, the drawbacks that have prevented their use are lack of stability and reusability.

By far the most known catalytic systems are the heterogeneous catalysts, which find broad use in the chemical industry e.g. synthesis of ammonia, Ziegler-Natta polymerization etc. [9]. Since, the present study deals with heterogeneous catalysts; further discussions will be focused on aspects of heterogeneous catalysis. Development of new and novel heterogeneous catalysts for any organic transformation or industrial process is very important as they are easy to separate and hardly pose any problem to handle [10]. But, one of the main disadvantages of heterogeneous catalysts is poor selectivity to the desired product compared to homogeneous counterparts. Hence, heterogenization of the homogeneous catalysts is the need of the hour in order to combine the advantages of both the systems.

Depending on their structure and method of preparation, heterogeneous catalysts can be divided into (i) bulk catalysts and (ii) supported catalysts.

Bulk catalysts are mainly produced from cheap active components. Since the preferred method of production is precipitation, they are also known as precipitated catalysts [4]. Supported catalysts can be divided into (i) impregnated catalysts and (ii) shell catalysts, with the active part only on the surface. The catalysts with expensive active components such as noble metals are employed as supported catalysts.

1.2. Heterogenization of homogeneous catalysts

Though homogeneous catalysts show good activity and selectivity, still there are hurdles when it comes to their industrial use. The difficulties like separation and reuse of high cost metal ligand complexes, could be overcome by heterogenizing the homogenous catalysts. The selectivity and activity of heterogenized catalysts are slightly lower as compared to their homogeneous counterpart, but it combines advantages of both homogeneous and heterogeneous catalysts.

Since the late 1960s, many approaches have been published by academia and industry to “heterogenize”, “immobilize” or “anchor” a homogeneous catalyst [11]. In addition, many excellent reviews were published in recent years describing in detail the synthesis and use of polymer-supported catalysts [12, 13], catalysts on inorganic carriers [14] or both [15]. Hence, heterogenization can be broadly divided into two groups. In the first group, catalyst system is designed in such a way that it could be soluble in a solvent during reaction, but on switching reaction conditions, is immiscible with the reaction products. Generally these types of reactions involve two phases, hence referred to as biphasic systems [16]. The other type is the heterogenization of homogeneous catalysts [17]**,** where the metal complex or nanoparticles of metal are anchored on soluble/ insoluble support and the separation is carried out by simple filtration.

1.2.1. Heterogenization on solid supports

1.2.1.1. Immobilization on polymeric resin

Nearly half a century ago, Merrifield introduced the concept of solid-phase peptide synthesis using heterogeneous chloromethylated polystyrene that was lightly cross-linked by divinylbenzene [18]. Since then the use of polymers in various ways to facilitate synthesis and product purification has become widespread. Heterogeneous polystyrene such as Merrifield resin remains a workhorse in the field of polymer assisted synthesis as a support for not only solid-phase synthesis but also reagent and catalyst immobilization as well. In catalytic applications, the catalyst is anchored to the support and the reagents are passed through a bed of the polymer-supported catalyst. Under appropriate conditions, conversion to product takes place on-stream and elution of product from the supported column of catalyst follows. Other resins like Jandal JEL (polystyrene polymers containing a tetrahydrofuran-derived cross linker) [19] TentaGel (polystyrene-poly (ethyleneglycol-OC_2H_4-$NHCOC_2H_5$)) [20] and PSPEG (polystyrene-polyethylene glycol) resins [21] have been employed successfully for anchoring metal-ligand complexes.

1.2.1.2. Immobilization on inorganic supports

Inorganic materials such as silica, alumina, microporous zeolites, mesoporous silica, macroporous clay type materials, carbon nanotubes and fullerenes etc. are popular as catalyst supports because of their various textural properties. Metals or metal complexes can be immobilized successfully onto them [22]. As compared to polymeric materials, aggregation of active or metal species is low in case of inorganic supports because of their rigid structure. Moreover, they don’t swell or get dissolved in organic solvents. Inorganic supports possess better thermal and mechanical stability under reaction conditions. Other commonly applied supports with a more defined structure are clay minerals, pillared clays and layered double hydroxides (LDH’s). Pillared clays contain stable metal oxide clusters which separate the layers that build the clay. A two dimensional gallery is thus created with an opening that can be larger than 1 nm. LDH’s, often denoted as hydrotalcite-like compounds, belong to the class of synthetic anionic clays. They show a positively charged layered structure with compensating anions between the sheets [23].

Since mid 1990s, zeolites which are crystalline aluminosilicates became more interesting material for support because of their well-defined pores and channels in the micropore range. Different types of zeolites were synthesized and used in industry. Zeolite β is a large pore high-silica zeolite with intersecting channels of 0.55 nm X 0.55 nm and 0.76 nm X 0.64 nm. Similarly zeolite Y consists of almost spherical pore structure with 1.3 nm cavities interconnected through smaller apertures of 0.74 nm [24].

Since the discovery of ordered mesoporous silicates M41S [25-26] and FSM-16 [27-28] in 1992-93, they became popular due to their morphologies, range of framework compositions and pore structures. They have well-defined pore apertures of 20-500 Å and high surface areas. By variation in reaction conditions like using different templates, organic auxiliary and synthesis parameters such as temperature, post synthesis treatment and time etc. the mesoporous materials (MCM-41, MCM-48 and MCM-50) can be synthesized with different pore diameters [29-30].

MCM-41 and MCM-48 possess a uni- and tri-dimensional pore system respectively with pore diameters varying between 1.5 nm to 100 nm [31] along with high surface areas. Initially mesoporous materials had some limitations such as hydrothermal stability, lower reactivity but later they were overcome by carrying out modification in synthetic procedure [32] or by producing materials with thicker walls [33-35]. A large amount of research has been carried out on MCM-41 than MCM-48 because of its comparably easy synthesis. MCM-41 possesses honeycomb arrays of nonintersecting uniformly sized channels with diameters ranging from 15-100 Å.

In 1998, Stucky et.al reported the synthesis of new mesoporous materials SBA-13, SBA-15, SBA-16, which are similar to MCM family of materials [36], using triblock copolymers, such as poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) (PEO–PPO–PEO) in acidic medium. The materials have uniform and large tubular channels of up to 30 nm in diameter [37], thicker pore walls which provides higher hydrothermal stability than MCM-41. Organic modification of the silicates permits precise control over the surface properties and pore sizes of the mesoporous sieves for specific applications, while at the same time stabilizing the materials towards hydrolysis [38]. When the catalyst is supported on inorganic solids, all catalytically active sites are available for the reaction and selectivity is comparable to that obtained with the analogous homogeneous catalysts.

Mesoporous solids have been functionalized at specific sites and were demonstrated to exhibit improved activity, selectivity and stability in a large number of catalytic reactions. In case of impregnation, leaching of metal from the support is a major problem because of weak interaction between metal and ligand during reactions, thus decreasing the reaction rate and activity. Hence, while heterogenizing an active catalyst or organometallic complex, it should be encapsulated or anchored inside or tethered to the pores and walls of the inorganic matrices in such a way that the complex is strongly bound. The important requisite is the stability of the encapsulated complex, so that it does not leach out of the support to the liquid phase in the course of reaction, while retaining high activity, selectivity and the original configuration.

1.3. Techniques of immobilization

In order to easily recover and recycle the catalysts, successful approaches involve the immobilization of molecular precursors either onto a support material or onto an appropriate phase system so that the catalyst can be quantitatively separated from both products and unreacted reagents by filtration or through phase separation. For this purpose, various methodologies and materials have been developed over the years.

Zeolite molecular sieves are crystalline, highly microporous aluminosilicates. The corresponding crystallographic structure is formed by tetrahedra of {AlO_4} and {SiO_4}. These tetrahedra are the basic building blocks for various zeolite structures, such as zeolites A and X. From the first synthetic aluminosilicate (zeolite) prepared by Barrer in the 1940's [39] there has been tremendous progress in the preparation of other classes of materials such as the aluminophosphates [40]. Zeolites possess pores and channels of regular dimensions (> 2nm) within the crystalline lattice. These materials have proven to be highly useful and continue to be exploited for a wide variety of applications e.g., ion exchange, as molecular sieves, gas separation and stereoselective catalysts.

1.3.1. The flexible ligand method

In this method, metal complexes encapsulated in the nano cavities of zeolites and encaged metal complexes combine the advantages of homo and hetero catalytic systems. The ligands (generally Schiff base type) with one to five coordinating atoms are encapsulated into the zeolites pores by mixing well with excessive amounts of ligands ($n_{ligand}/n_{metal} = 3$). Upon complexation with the metal ion after heating at 423 K under high vacuum, the resulting metal complex becomes too large to exit. The ligand should have a sufficiently low melting or sublimation point and should be small enough to enter the zeolite cavities. The atoms within the nano cavities of the inorganic matrix create an electric field that imposes steric constraints on the encapsulated complex, thus modifying properties of the latter like stability, activity and selectivity [41]. The disadvantage of this method is the difficulty in controlling the metal co-ordination with ligand. A wide variety of Co, Fe, Rh, Ru, Mn and Pd complexes have been prepared according to this method within the supercages of faujasites [42-43].

1.3.2. Insitu zeolite synthesis method

This method offers the advantage over above method by encapsulating a well defined metal complex without contamination. During the synthesis of zeolite, metal complex is added to the silica followed by aluminate to the homogenously dispersed gel. The order of addition of material affects the synthesis of encapsulated zeolite. If the metal complex is added to the aluminate solution or aluminophosphate gel, a heterogeneous mixture results and there is practically no encapsulation in the zeolites.

For example metal phthalocyanines and perfluorophthalocyanines are encapsulated in Na-X using this method. In a similar way, metal complexes can also be incorporated in ZSM-5 and mordenite [44]. This method also has some disadvantages. To obtain good encapsulation in zeolites, metal complex has to be stable throughout the zeolite synthesis steps. Also, the complex should be soluble in water. Otherwise, organic solvents in which it is soluble might hinder the crystallization of the zeolite, thus leading to amorphous structures without any encapsulation.

1.3.3. Cationic exchange of inorganic complexes

This method can be applied if the complex is cationic and zeolites have sufficient cationic exchange capacity. The exchange complexation can be directly carried out in aqueous solution; provided that complex is small enough to pass through the pores of the zeolite e.g. copper complex with ethylenediamene ligand $[Cu(ethylenediamene)_2]^{+2}$ can be encapsulated into faujasite zeolites [45].

1.3.4. Ligand adsorption on metal ion exchanged zeolites

Schoonheydt reported preparation of complexes of ammonia and ethylenediamene with CuI in zeolite-A [46]. The only controlling parameter in such synthesis procedures is the pH. Low pH results in the protonation of the ligand, while a high pH may damage the zeolite structure.

1.3.5. Chemical grafting method

This is a post-synthesis modification of mesoporous material by attaching a functional organic molecule with free or germinal silanol group on the surface of mesoporous material by linkage (Fig. 1.2). This can be done usually after removal of surfactant from the inorganic matrix. Mesoporous silicates possess surface silanol (Si-OH) groups like in amorphous silica. They act as convenient anchoring points for organic functionalization [47] surface modification with organic groups is most commonly carried out by silylation, although modification of silanol groups is also possible by esterification, e.g., with ethanol [48].

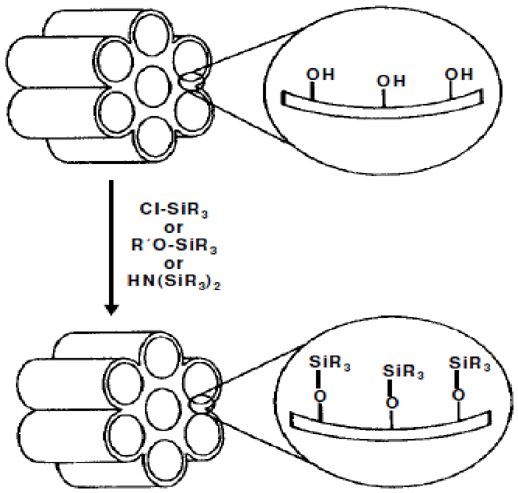


Fig. 1.2: Functionalization of inner walls of mesoporous silicates by grafting

1.3.6. Grafting with passive surface groups

In this method, the properties of the mesoporous materials could be altered by using grafting materials such as organic compounds, e.g. phenols, alkyl chain, trimethyl chlorosilane (Me_3SiCl), trimethyl ethoxysilane ($Me_3Si(OC_2H_5)$) and hexamethyldisilazane [$(Me_3Si)_2NH$]. Resulting material could have pores of definite size, high surface hydrophobicity; passivated silanol groups that help in protecting the framework towards hydrolysis. Further, by varying the quantity or alkyl chain length of the silylating agent the pore diameter of mesoporous materials can be altered [49].

1.3.7. Grafting with reactive surface groups

In this method, grafting is carried out with a reactive functional agent, upon which little modification permits further functionalization with active metal salts or organometallic complexes. For this, reactive functional groups such as olefins, nitriles, cyanide, thiol, alkyl amines, alkyl halides, epoxides and some other surface groups can be used [50]. Only problem with this method is the blocking of the channels by the organic functionalized groups at the external surface or near the pore openings of the material.

1.3.8. Site-selective grafting

While grafting of organic functional groups on mesoporous materials, the external surface of the mesoporous materials is kinetically more accessible than the internal surface. This could be the reason for decreasing product selectivity. In order to minimize involvement of the external surface in reaction processes and to optimize selectivity, it is a need to block or passivate the external surface before functionalizing the internal surface.

The blockage of external silanol groups can be carried out in two ways. In first method, dichlorodiphenylsilane (Ph_2SiCl_2) can be used as passivating agent to block the external surface silanols followed by 3-aminopropyl triethoxy silane to graft inside the channels [51]. In the second method, blockages of external silanol groups on as synthesized mesoporous MCM- 41 material can be done prior to the removal of surfactant. Subsequently, the template is removed by extraction and the internal pore surfaces are functionalized with phenylpropyldimethylchlorosilane [51b].

1.3.9. Co-condensation method

This method, also called as "one pot synthesis", commonly used for preparing functionalized mesoporous silica supported catalysts (inorganic–organic hybrid material). The organoalkoxysilane is introduced to the aqueous solution of CTAB and TEOS during the condensation reaction (Fig. 1.3). To obtained good immobilization of organic functional groups on silica, the organosilanes precursors need to compete with silicate anions to interact favourably with the surfactant micelles by either electrostatic or non covalent interactions during the acid or base catalysed condensation reaction of silicate. Organosilane precursors, which are water soluble, tolerate the extreme pH conditions and have bulky groups usually difficult for incorporation. This method provides good stability to inorganic framework even at relatively higher organic loading, uniform distributions of functional groups. Generally, solvent extraction method is used to remove the template rather than calcination, as organic functional groups inside the channels may decompose [52] in the process.

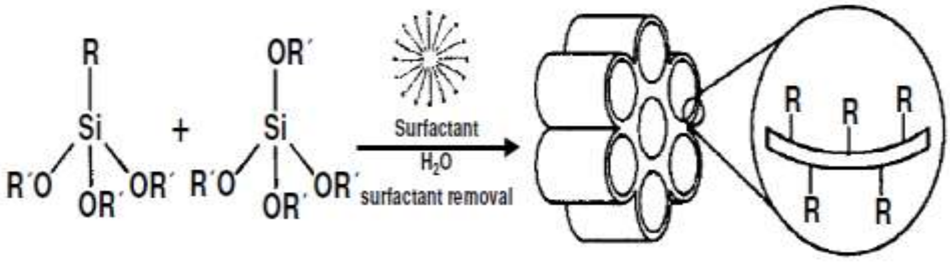


Fig. 1.3: Synthesis of organofunctionalized mesoporous silicates by co-condensation.

1.4. Advantages/ Disadvantages of immobilized catalysts

Table 1.1- Advantages and disadvantages of immobilization

S.No	Advantage	Disadvantage
1	Separation and recovery of the catalyst [53]	Leaching of metal from the support
2	Multifunctional catalysts	Lower catalytic activity compared to corresponding homogeneous catalyst
3	High stability of the catalyst	Poor accessibility of the active sites

The driving force for the introduction of any catalytic processes in the chemical industry is mostly on economic considerations. The classical heterogeneous catalysts find widespread use, in particular for the synthesis of bulk and commodity chemicals. Homogeneous catalysis, especially in the field of asymmetric catalysis, has a considerably smaller significance for industrial production issues, although a large number of important processes have been developed [54].

1.5. Coupling reactions

A coupling reaction in organic chemistry is a catch-all for a variety of reactions, where two hydrocarbon fragments are coupled with the aid of a metal catalyst. Coupling reactions may be divided into two main classes; (i) the reaction in which two different molecules react to form one new molecule, e.g. the nickel chloride catalyzed reaction of aryl magnesium halide with an aryl halide to form a biaryl and (ii) homocoupling reaction such as Ullmann reaction, in which copper metal reacts with two molecule of aryl halide to give a biaryl. The Ullmann reaction often requires high temperatures and has been partly replaced in synthetic chemistry by palladium-catalyzed coupling reaction.

A widely popular metal for this chemistry is Pd, often used in the form of tetrakis(triphenylphosphine) palladium(0). This is an air sensitive compound but is very good for coupling of unsaturated halogen compounds with organometallics such as tributyltin hydride. Most of the coupling reactions involve reagents that are extremely susceptible to the presence of water or oxygen in reaction medium. They disrupt coupling reactions via unsaturated metal complexes that don’t have 18 valence electrons. For example, in Ni and Pd cross coupling reactions, a zerovalent complex with two vacant sites (or labile ligands) reacts with the carbon halogen bond to form a metal halogen and a metal carbon bond. Such a zerovalent complex with labile ligands or empty coordination sites is normally very reactive towards oxygen.

1.5.1. Transition metals in coupling reactions

The formation of bonds such as C-C, C-N, C-O and C-S etc. by the use of group 8-10 metal catalysts, particularly Ni and Pd complexes in cross-coupling reactions of organometallic reagents with organic electrophiles has become attractive [55]. These reactions can occur with a variety of organometallic reagents and electrophiles, commonly referred to as "cross-coupling reactions".

$$\text{R-M} + \text{R'-X} \xrightarrow{\text{Catalyst}} \text{R-R'}$$

Where,

M- Li (Murahashi) Catalysts- Ni, Cu, pd….
Mg (Kumada-Tamao-Corriu) X – I, Br, Cl, OTf…..
B (Suzuki-Miyaura)
Zn (Negishi), Cu (Normant), Sn (Migita-Kosugi, stille)…..

The reaction of Grignard reagent/Ni catalyst was the first example reported in 1972. Since then, many organometallic reagents of Li, Al, B, Zn, Sn and Zr were found to undergo this type of reaction. But prior to that, during the decade of 1960-70, a broad study has been done on reactions of Li/Mg reagents using copper halides in stoichiometric as well as in catalytic amounts [56]. However, this methodology was limited to use of SP^2- or SP- carbons, which was overcome soon after the discovery of the transition metal catalyzed cross coupling reactions of Grignard reagents. In the year 1971, Kochi reported the use of $FeCl_3$ as a catalyst for the coupling of Grignard reagents with 1-alkenyl bromides [57] and Li_2CuCl_4 for the SP^3-SP^3 coupling of RMgX and iodoalkanes [58]. In 1972, Kumada and Tamao [59] as well as Corriu and Masse [60] independently reported the use of Ni as a catalyst in reaction of Grignard reagents with 1-alkenyl or aryl bromides and chlorides.

There were independent extensive reports on development of cross-coupling methodologies. However, the mechanism that follows an oxidative addition-transmetalation-reductive elimination in the reaction of vinyl chlorides with Grignard reagents [59a] has substantially led to the progress of cross coupling methodology. This led to a new strategy for C-C bond formation and had become attractive for researchers in synthetic chemistry.

Table 1.2- Types of coupling reactions

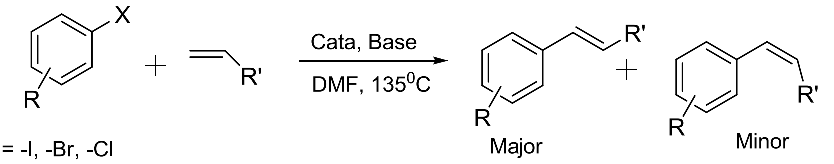
Reaction	Year	Reactant A (hybridization)	Reactant B (hybridization)	Homo/ Cross	Catalyst	Remarks
Wurtz reaction	1855		R-X (SP^3)	homo	Na	
Glaser coupling	1869		R-X (SP)	homo	Cu	
Ullmann reaction	1901		R-X (SP^2)	homo	Cu	
Gomberg-Bachmann reaction	1924		$R-N_2X$ (SP^2)	homo		Requires base
Cadiot-Chodkiewicz coupling	1957	Alkyne (SP)	R-X (SP)	cross	Cu	Requires base
Castro-Stephens coupling	1963	R-Cu (SP)	R-X (SP^2)	cross		
Kumada coupling	1972	RMgBr (SP^2,SP^3)	R-X (SP^2)	cross	Pd or Ni	
Heck reaction	1972	Alkene (SP^2)	R-X (SP^2)	cross	Pd	Requires base
Sonogashira coupling	1973	Alkyne (SP)	R-X (SP^2, SP^3)	cross	Pd and Cu	Requires base
Negishi coupling	1977	R-Zn-X (SP, SP^2,SP^3)	R-X (SP^2, SP^3)	cross	Pd or Ni	
Stille cross coupling	1977	$R-SnR_3$ (SP, SP^2,SP^3)	R-X (SP^2, SP^3)	cross	Pd	
Suzuki reaction	1979	$R-B(OR)_2$ (SP^2)	R-X (SP^2, SP^3)	cross	Pd	Requires base
Hiyama coupling	1988	$R-SiR_3$ (SP^2)	R-X (SP^2, SP^3)	cross	Pd	Requires base
Buchwald-Hartwig reaction	1994	$R_2N-R\ SnR_3$ (SP)	R-X (SP^2)	cross	Pd	N-C coupling
Fukuyama coupling	1998	RCO(SEt) (SP^2)	R-Zn-I (SP^3)	cross	Pd	

Though, the transition metal complexes and organometallic reagents were shown to be highly effective as catalysts or nucleophiles, the use of such highly reactive reagents couldn’t explored because of complication in preparation, lack of functional group compatibility and by competitive halogen-metal exchange leading to homocoupling products.

In 1975, Murahashi first time showed that Pd catalysts are more useful with less reactive organometallic reagents in the reaction of vinyl halides with aryllithiums [61]. The efficiency of Pd catalyzed processes was further demonstrated by Negishi [62] in the reactions of 1-alkenylaluminum [63] and zinc [64], zirconium reagents [65] with vinyl and aryl halides. Many researchers have utilized Pd in cross coupling reactions with different organometallic catalysts. Stille explored the use of organo-stannanes, which were reported first by Migita and Kosugi [66] for C-C cross coupling reaction. The use of organoboron compounds which easily undergo cross-coupling reactions was reported by Suzuki and Miyaura [67]. The versatility of cross-coupling methodologies has found many applications in the synthesis of natural products, fine chemicals and drug intermediates. This is due to the simplicity of their synthesis, isolation, handling and their compatibility with a wide range of functional groups. Table 1.2 gives general idea of different cross coupling reactions reported so far.

1.5.1.1. Heck reaction

Synthesis of arylated and vinylated olefins is of great importance in organic chemistry. The Pd catalyzed Heck coupling reaction (scheme 1.1) between an olefin and an aryl halide provides an efficient way for the synthesis of organic products. The Heck or Mizoroki-Heck [68] reaction, discovered independently by Heck and Mizoroki and improved upon by Heck [69-70] into a general synthetic methodology is associated with the catalytic arylation and alkenylation of olefins.



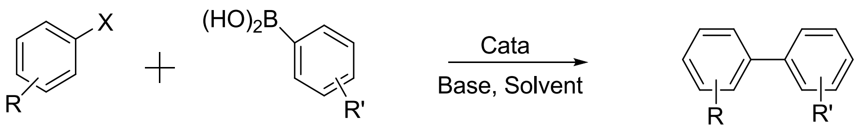
X = -I, -Br, -Cl
R = $-CH_3$, $-NO_2$, -CHO
R' = -Ph, -COOMe, -COOEt

Scheme 1.1. Heck cross coupling reaction

A variety of substituent groups, both on olefin and the aryl halide, are allowed in Heck chemistry, thereby making these reactions versatile and relevant. This does away with the need for protection and deprotection in the case of organic synthesis, thus reducing the number of reaction steps and the cost involved. It also widens the scope of the substrates that can be used for Heck reaction. Complexes of Pd, Cu, Ni, Pt, Co, Rh, Ir and Ru have been used as catalysts in Heck chemistry with varying degrees of success [71]. Pd has been the catalyst of choice for these reactions due to its high activity. Pd catalyzed Heck reaction, with and without ligands, in presence and absence of promoters, under homogeneous and heterogeneous conditions has been reported and found to give good results [72].

1.5.1.2. Suzuki reaction

Suzuki reactions of aryl halides are the most important C-C coupling reactions in organic synthesis [73]. These reactions are generally catalyzed by Pd based catalysts. In 1979, A. Suzuki found that the element boron was a milder activator than zinc and this was especially important to commercial synthesis. Again, it was also carbon activating, so the Suzuki reaction uses boron to move the carbon atoms to the palladium atom. A. Suzuki first time reported the coupling reaction between boronic acids (containing an organic part) and halides. Then in 1981, Akira Suzuki and his colleague, N. Miyaura, developed, generally known as “Suzuki-Miyaura reaction” or "Suzuki coupling", a chemical reaction that employs boronic acids or esters. In the Suzuki–Miyaura coupling (scheme 1.2), aryl or vinyl organoboron compounds are reacted with aryl, alkenyl or alkynyl halides in the presence of a base under mild conditions [74-75].



X = -I, -Br
R = $-NO_2$, -CHO, $-CH_3$
R' = - COOH, $-OCH_3$

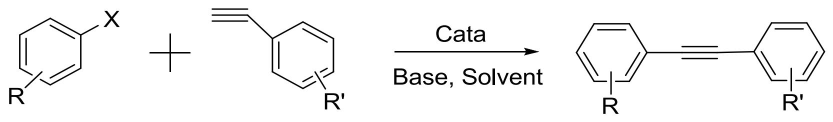
Scheme 1.2. Suzuki cross coupling reaction

Various homogeneous metal complexes are highly effective for this process. The main advantages of this reaction are the safe and commercial availability of the diverse boronic acid derivatives. This method has been applied for the large-scale synthesis of pharmaceutical intermediates and fine chemicals.

1.5.1.3. Sonogashira reaction

Sonogashira reaction (scheme 1.3) is also a C-C cross coupling reaction catalyzed by Pd or Cu catalysts, between aryl halide with terminal alkyne or arylenes. Over the years, the Sonogashira coupling of terminal alkynes with (hetero) aryl halides has become most attractive and powerful tool for the synthesis of alkyl-aryl- and diaryl-substituted acetylenes [76-77]. Functionalised alkynes are important building blocks for the synthesis of biologically active molecules. They have common structural features with natural products derived from plants and the marine organisms and also with synthetic drugs [78].

The Sonogashira reaction proceeds in the presence of a homogeneous palladium/phosphine/copper salt catalyst system, which makes the recovery of the metal tedious. The reaction, in general is carried out with a large excess of secondary or tertiary alkyl amine as a solvent/co-solvent and therefore application of this protocol especially to large-scale preparations can run into environmental issues as a result of the volatile nature of these amines [79]. In addition, many phosphine ligands used for this purpose are air-sensitive and expensive, limiting their applications [80]. Hence, there is a need to simplify the Sonogashira reaction protocol. Several important efforts were made in these directions which were reported in recent years [81]. The most important improvement was the elimination of copper (I) iodide, which was used as the co-catalyst.

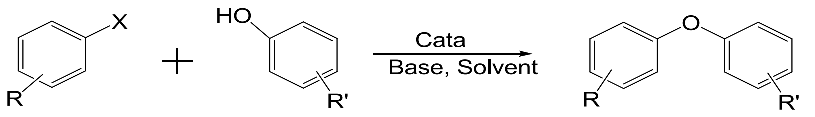


X = -I, -Br
R = -NO_2, -CHO, -CH_3
R' = - CHO, -OCH_3

Scheme 1.3. Sonogashira cross coupling reaction

1.5.1.4. Ullmann reaction

The copper-mediated arylation of amines [82], phenols [83] (Ullmann condensations), amides, carbamates [84] (Ullmann– Goldberg condensations) and activated methylene compounds [85] (Ullmann–Hurtley condensations) are well-documented methods that were discovered several decades before the Pd and Ni catalyzed processes came into existence. For more than a century they were most useful and practical methods for the formation of C(aryl)-N, C(aryl)-C, and C(aryl)-O bonds [86-87]. Such copper-mediated coupling reactions (scheme 1.4) have numerous industrial applications, including the synthesis of intermediates as well as synthetic targets in life science and polymer related industries.

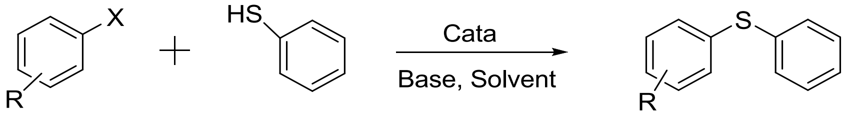


X = -I,-Br
R = $-NO_2$, -CHO, $-CH_3$
R' = - COOH, $-OCH_3$

Scheme 1.4. Ullmann cross coupling reaction

1.5.1.5. Carbon-Sulfur cross coupling

Formation of aryl-sulfur bond (scheme 1.5) is important and a vital tool in synthetic chemistry as the resulting C-S bond containing molecules have many applications in biological, pharmaceutical and materials chemistry [88].



X = -I, -Br
R = $-NO_2$, -CHO, $-CH_3$

Scheme 1.5. C-S cross coupling reaction

Traditional methods for the synthesis of aryl-sulfur bonds often require harsh reactions conditions. For example, coupling of copper thiolates with aryl halides require polar solvents such as HMPA and temperatures around 473 K. In 1980, Migita and co-workers reported the cross-coupling reaction of aryl halides and thiols with $Pd(PPh_3)_4$ as the catalyst for the first time. They used NaO^tBu as the base, in polar solvents such as ethanol or DMSO at 363 K [89]. However, only few reports have appeared in the literature about the formation of aryl-sulfur bonds using transition metal catalysts (Pd or Ni) since Migita's report [90-91].

1.6. Selective Oxidation of hydrocarbons

Selective oxidation of hydrocarbons to prepare chemical building blocks is industrially very important. The process should be highly selective and should not generate any waste that is difficult to dispose. What is important in this respect is that O_2/air should preferably be used as the oxidant and the reaction should not proceed beyond partial oxidation, i.e., combustion.

1.6.1 Oxidation of aromatics

Aromatic hydrocarbons constitute one of the major groups of basic building blocks of the petrochemical industry [92]. The most important source for aromatics is the product obtained from catalytic reforming of naphtha. The hydrocarbon reforming yields a mixture of benzene, toluene, ethylbenzene and xylenes. Oxidation is probably the most widely used unit process in the conversion of aromatic hydrocarbons to industrial chemicals such as phenol, terephthalic acid, cyclohexanone, adipic acid and maleic anhydride.

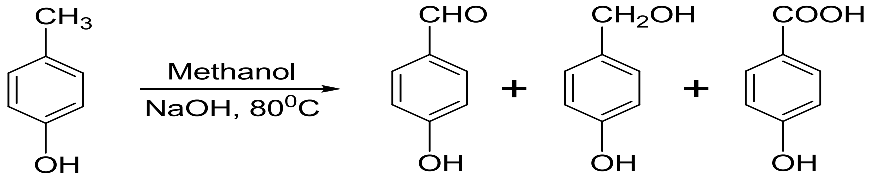
Traditional approaches for oxidation are based on metal-catalyzed activation of hydrocarbons [93]. Organic substrates are oxidized with inorganic oxides such as chromium and manganese oxides, halogen and nitric acid. But, these processes rarely use molecular oxygen for oxidation. In parallel with the development of the petrochemical industry, a wide range of oxygen-containing molecules, including alcohols, aldehydes, ketones, epoxides and carboxylic acids have become necessary as starting materials for the production of plastics, synthetic fibers, polyamides, polyesters, polycarbonates, etc. For instance, ethylene oxide, acrolein, acrylic acid and methacrolein are produced by the vapor-phase partial oxidation of lower alkenes like ethylene, propylene and butenes [94]. Acetic acid, K/A oil (a mixture of cyclohexanone and cyclohexanol), benzoic acid, terephthalic acid and phenol are manufactured by the liquid-phase catalytic oxidation of alkanes like butane, cyclohexane, alkylbenzenes, etc. [95].

Liquid- phase aerobic oxidation, which is generally referred to as autoxidation, is extensively practiced in industry, although the efficiency of this oxidation methodology is not necessarily high [96]. As a result, nitric acid is still widely used as an oxidizing agent for manufacturing carboxylic acids like adipic acid, nicotinic acid and pyromellitic acid etc. [97]. Currently, these environmentally unacceptable traditional oxidation processes, using metal oxides, halogen and nitric acid are being replaced by cleaner oxidation methods. Partial aerobic oxidation of alkanes leading to alcohols and carbonyl compounds has considerable potential from both ecological and economic viewpoints. Current oxidation technology is not fully feasible as it incurs extensive oxidative cleavage or concomitant combustion of alkanes. The most important liquid-phase oxidation methods include the transformation of *p*-xylene to terephthalic acid and cyclohexane to K/A oil. However, the reaction conditions are often harsh, the reagent mixture is corrosive (Cr^- or Br^-) and the reaction often has poor selectivity. Therefore, it is apparent that selective transformation of hydrocarbons, especially saturated hydrocarbons like alkanes, to valuable oxygenated compounds constitutes an extremely important area of contemporary industrial chemistry.

Today, over 90% of organic chemicals are derived from petroleum whose main components are saturated hydrocarbons. Thus, considerable research effort has been made for the development of the selective oxidation of alkanes with molecular oxygen, leading to alcohols, ketones and carboxylic acids [98-100]. A number of catalytic oxidations, particularly oxidation of alkanes with dioxygen by transition metals in the presence of reducing agents such as aldehydes have appeared in the literature. But, these processes were limited to laboratory-scale so far [101]. In recent years, there has been a growing demand for the development of fundamentally new and environmentally benign catalytic systems for hydrocarbons that are operative on an industrial scale under moderate conditions in the liquid-phase with a high degree of selectivity.

1.6.1.1. Oxidation of *p*-cresol

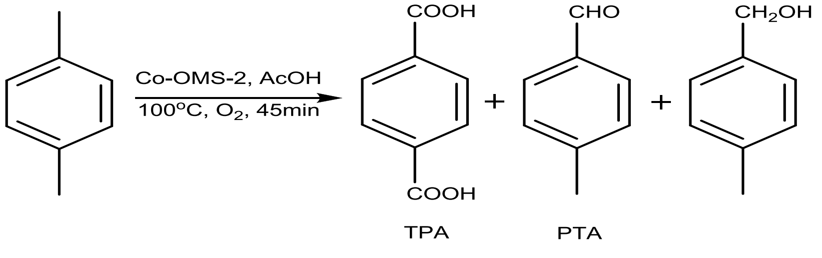
Oxidation of benzylic hydrogen in *p*-cresol (scheme 1.6) selectively to *p*-hydroxy benzaldehyde is important as the resulting product has applications in the field of pharmaceuticals such as semi-synthetic penicillin, amoxicillin and the antiemetic drug trimethobenzamide [102]. It is also used as building block for several key organic products [103]. Old processes for the synthesis of *p*-hydroxy benzaldehyde such as Reimer Tiemann reaction using sodium hydroxide, Gattermann reaction, Saligenin process and oxidation of alkylbenzenes using strong oxidizing agent such as chromic acid or potassium permanganate and side chain chlorination of *p*-cresol [104] use toxic reagents in stoichiometric amounts, involve tedious work up procedure, low yield of product in addition to generation of harmful chemicals. Nishizawa et.al [105] reported the use of cobalt based catalyst in oxidation of *p*-cresol to *p*-hydroxy benzaldehyde for the first time.



Scheme 1.6. Oxidation of p-cresol

1.6.1.2. Oxidation of *p*-xylene

The oxidation of *p*-xylene (scheme 1.7) is an industrially important process as the product terephthalic acid (TPA) is the main raw material for the synthesis of polyesters [106]. The manganese–cobalt based catalyst used for *p*-xylene oxidation process, developed by Amoco Chemicals [107], is carried out using $Co(OAc)_2$-$Mn(OAc)_2$-HBr as the catalyst. The oxidation conducted using acetic acid as solvent and bromide as promoter leads to nearly quantitative yield. The problem with this process is separation of by product 4-formylbenzoic acid, which is required to be separated through hydrogenation of a hot aqueous solution. The solution is then cooled in a stepwise manner to crystallize highly pure terephthalic acid. Hence, there is a need for an alternate process that is free of Br promoter and selectively yields terephthalic acid.



Scheme 1.7 Oxidation of p-xylene

1.7. Objective of the present investigation

It is well recognized that carbon-carbon and carbon-heteroatom coupling reactions are very important in organic chemistry, as two hydrocarbon fragments are coupled with the aid of a metal catalyst. Transition metal catalysts from groups 8-10 (Ni, Cu and Pd complexes) are the most suitable to catalyze these cross-coupling reactions involving organometallic reagents with organic electrophiles. Generally, coupling reactions involve reagents that are extremely susceptible to the presence of water or air/oxygen in reaction medium. There were many reports on development of novel catalysts that can withstand presence of water or air/oxygen, but leaching of metal was a major handicap, at least with some of those catalyst systems. Moreover, majority of the heterogeneous catalysts reported either used neutral or acidic supports for heterogenizing the metal, affecting the product selectivity. Hence, one of the objectives of the present investigation is to overcome these problems by heterogenizing the metal on supports with basic character. Literature reports suggests that OMS-2 is one such support with basic character which can be prepared using simple chemical methods, with reasonably good surface area. Hence, it was planned to use this for supporting Pd.

Generally, transition metal oxides have very good redox properties that help in achieving better catalytic activity in selective oxidation reactions. In this connection, selective oxidation of *p*-cresol and *p*-xylene are important reactions for preparing pharmaceutical intermediates and to manufacture monomers for polymer industry. In principle, these oxidations can be driven by using oxidizing agents such as nitric acid and chromic acid in stoichiometric quantities. But, a major drawback of these reagents is generation of toxic waste with accompanying disposal problems. Numerous reports can be seen in the literature related to development of novel homogeneous as well as heterogeneous catalysts for oxidation reactions with good conversion and selectivity to the desired product. It has been reported that Co with Mn as promoter is a promising catalyst system for these oxidation reactions. Hence, one of the objectives is to prepare materials containing these metals and apply them for selective oxidation of hydrocarbons. Another aim is also to develop catalysts that offer superior performance in terms of catalyst life and recyclability.

Keeping the above background in mind and based on the up-to-date literature, we commenced our study with the following objectives:

- ✓ To develop Pd-KOMS-2 catalyst materials by exchanging Pd into KOMS-2 (octahedral molecular sieve) with an aim to get heterogenized Pd catalyst;
- ✓ Preparation of Cu-SBA-15 catalysts through immobilization of copper complexes on mesoporous SBA-15;
- ✓ Preparation of Co substituted KOMS-2 materials with different Co content and characterize them for obtaining structural and textural information;
- ✓ Evaluation of Pd-KOMS-2 and Cu-SBA-15 catalysts for their activity, stability and durability in carbon-carbon, carbon-heteroatom bond formation reactions;
- ✓ Testing and evaluation of Co-OMS-2 catalysts for selective oxidation of hydrocarbons such as *p*-cresol and *p*-xylene in a Br- ion free reaction system.
- ✓ Study of the influence of various variables like metal content of the catalysts, reaction temperature, time, presence of base and solvent for the above reactions and
- ✓ Correlation of catalytic activity with the characterization results to understand the structure-activity relationship.

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Chapter-II

Synthesis and characterization of catalysts

2.1. Introduction

In general, heterogeneous catalysts are considered to be more useful over the homogenous catalysts in terms of their commercial utility. To prepare a successful catalyst in accordance with the requirement of a particular reaction; one has to understand the nature and properties of the catalytic material that gives the exact role of the catalyst in a particular reaction. The characterization techniques have played a major role in the process of catalyst development. If the structure, composition and surface properties of a catalyst can be correlated with its activity and selectivity, the working of the catalyst can be understood better.

The theoretical and experimental procedures of various characterization techniques used for this dissertation are briefly described in the following sections. Commonly used physico-characterization techniques in catalysis are:

1. Atomic absorption spectrophotometry (AAS)
2. Surface area, pore size distribution by N_2 adsorption (BET method)
3. Powder X-ray diffraction (PXRD)
4. Scanning electron microscopy (SEM)
5. Transmission electron microscopy (TEM)
6. Thermal analysis
7. Infra-Red spectroscopy
8. X-ray photoelectron spectroscopy (XPS)

2.2. Catalyst preparation

2.2.1. Preparation of K-OMS-2

A particular class of oxide materials that have tunnel structures are called octahedral molecular sieves (OMS). K-OMS-2 is one such material that belongs to this class. It was prepared by precipitation using reported methods [1]. Potassium permanganate 5.89g in 100 mL of water was added to a solution containing 8.8g of manganese sulfate in 30 mL of water and 3mL concentrated nitric acid. The resulting mixture was stirred and refluxed at 373 K for 24h. The precipitate formed was filtered and washed with de-ionized water until the pH of the filtrate is neutral. Subsequently, the precipitate was dried for 12h at 393 K, calcined at 623K for 4h to finally yield KOMS-2.

2.2.2. Preparation of mesoporous SBA-15

Mesoporous siliceous SBA-15 was synthesized according to a reported procedure [2]. In a typical synthesis, 2g of amphiphilic tri-block copolymer, poly (ethylene glycol)-block-poly (propylene glycol)-block-(poly ethylene glycol) with average molecular weight of 5800 (Aldrich), was dispersed in 15g of water and 60g of 2M HCl solution under vigorous stirring for 4h. This was followed by the addition of 4.3g of tetraethyl orthosilicate (Aldrich) to the homogeneous solution. The gel obtained was continuously stirred at 313 K for 24h and finally crystallized in a teflon-lined autoclave at 373 K for 48h. After crystallization, the solid product was filtered, washed with de-ionized water and dried in air at room temperature. The material was calcined in air at 823 K for 24h to decompose the tri-block copolymer to yield white crystalline powder (SBA-15).

2.3. Characterization of catalysts

2.3.1. Atomic absorption spectrophotometry

Atomic absorption spectrophotometry is the study of absorption of radiant energy by atoms. The principle of atomic absorption is based on energy absorbed during transitions between electronic energy levels of an atom. When energy is absorbed, an electron of the absorbing atom moves from one orbital to an orbital of higher energy level. These levels have well defined energies and electrons moving between them must absorb or emit energy equal to the difference between them. When the energy is provided by a source such as a flame (temperatures between 2373–3073 K), outer-shell electrons are excited to higher energy level. During this transition, energy is absorbed that can be measured. As a result, it can be used for analysis and estimation of metals present in solution. The basis of quantitative analysis is the measurement of amount of energy absorbed; which is used for quantitative determination of the amount of analyte element present [3].

2.3.2. Surface area determination by BET method

Irving Langmuir in 1916 reported Langmuir equation which relates to the coverage or adsorption of molecules on a solid surface relative to gas pressure at the solid surface at a known temperature. In 1938, Stephen Brunauer, Paul Hugh Emmett and Edward Teller extended the Langmuir work and reported the BET theory, which is for the physical adsorption of gas molecule on a solid surface. This serves as the basis for an important analysis technique for the measurement of the specific surface area of a material [4].

The isotherm points are transformed into the linear version of BET equation

$$P/V (P_o-P) = 1/V_mC + [(C-1)/V_mC] (P/P_0)$$

Where, P is the adsorption equilibrium pressure, P_0 is the saturation vapor pressure of the adsorbate at the experimental temperature, V is the volume of gas adsorbed at pressure P, V_m is the volume of adsorbate required for monolayer coverage and C is a constant that is related to the heat of adsorption (E_I) and liquefaction (E_L), which is expressed by

$$C = \exp \{(E_I-E_L)/ RT\}$$

For the present study, specific surface areas of the catalysts were measured by N_2 physisorption at liquid nitrogen temperature using a Quanta chrome Nova-1200 surface area analyzer. Samples were dried at 573 K in vacuum (10^{-3} Torr) for 2h before N_2 physisorption measurements. The specific surface area was determined by using standard BET method on the basis of adsorption data. The pore size distributions were calculated from both adsorption and desorption branches of the isotherms using BJH method [5] and the corrected Kelvin equation. Pore volume values were determined by using the t-plot method of De Boer.

2.3.3. Powder X-ray diffraction

Powder x-ray diffraction (XRD) is a versatile, non-destructive technique that gives detailed information about the chemical composition, atomic spacing and phase identification of a crystalline material and can provide information on unit cell dimensions of crystalline materials. X-ray diffraction is based on constructive interference of monochromatic X-rays in a crystalline sample. In catalyst characterization, diffraction patterns are mainly used to identify the crystallographic phases that are present in the catalyst [6]. When a monochromatic X-ray beam (e.g. CuKα or MoKα) with wavelength λ is projected onto a crystalline material at an angle theta (θ), diffraction occurs only when the distance travelled by the X-rays reflected from successive planes differ by an integer *n* of wavelengths.

$$n\lambda = 2\, d \sin\theta; \;\; n = 1, 2, 3\ldots$$

Where,

λ- Wavelength of the X-rays used,

d- The distance between two lattice planes,

θ- The angle between the incoming X-rays and the normal to the reflecting lattice plane and

n- Integer, called order of the reflection.

This Bragg's law [7] relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. The width of the diffraction peaks can be used to estimate the crystal size by applying Debye-Scherrer formula [8]

$$D_{hkl} = 0.9\, \lambda / \beta \cos \theta$$

Where,

D_{hkl} is the volume averaged particle size, λ is the wavelength of X-rays, β is full width at half maximum (FWHM) and θ is the diffraction angle of peak respectively.

Low angle X-ray diffraction patterns of mesoporous samples were collected on a PANalytical Philips X'Pert Pro diffractometer using Cu Kα radiation (λ = 1.5418 Å) equipped with nickel filter and an X'celerator as detector. XRD patterns were collected in the range of 2θ = 0.5-10. For the XRD studies of octahedral molecular sieve catalysts, same instrument was used, to collect data in wide angle region at a scan speed of 2°/min in the 2θ range 10-80°.

2.3.4. Electron microscopy

The electron microscopy has many variants. In this section, we deal only with scanning electron microscopy and transmission electron microscopy. The former is useful for the examination of physical features of the sample, like size and shape of crystals in the material. On the other hand TEM is much more useful to study the nano structure of the material alongwith metal dispersion.

2.3.4.1. Transmission electron microscopy

A high voltage electron beam is used to create an image in transmission electron microscopy (TEM). In this technique, a beam of electrons interact with the sample when it passes through the sample and form the image of sample. This image is further magnified and focused onto a fluorescent screen, or recorded on film or detected by CCD digital camera. Use of smaller wavelength of electron, TEM instrument is capable of imaging at a significantly higher resolution than light microscopes [9, 10]. Thus one can study details of the material even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. High Resolution TEM (HRTEM) allows the production of images with resolution of 1Å [11] at magnifications above 50 million. The information obtained from TEM can be used for structural characterization and identification of various phases of mesoporous materials. TEM technique also can be used in cancer research, nanotechnology and semiconductor research.

Materials used in this study were analyzed using a high-resolution transmission electron microscope (HRTEM) Tecnai-T30 model at an accelerated voltage of 300 kV. Samples were prepared by placing droplet of a sample suspension in isopropyl alcohol on a carbon coated Cu grid for TEM measurements.

2.3.4.2 Scanning electron microscopy

The scanning electron microscopy (SEM) is a variant of electron microscopy that produces magnified image of a sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. SEM scans over a sample surface with a probe of electrons (5-50 eV) and detects the yield of either secondary or back-scattered electrons as a function of the position of the primary beam [12, 13]. The electrons from electron beam interact with the atoms of the sample, producing signals that contain information about the sample's surface structure and morphology of the sample. SEM can produce very high-resolution images of a sample, revealing morphology of the sample in nm range. Generally, the image resolution of an SEM is about an order of magnitude poorer than that of a TEM. However, because the SEM image relies on surface processes rather than transmission, it is able to image bulk samples up to many centimetres in size (depending on instrument design and settings) and has a great depth of field and so can produce images that are good representations of the three-dimensional shape of the sample. For the present study, Leica stereoscan, Cambridge 440 Microscope (UK) was employed to characterize the morphology of the samples.

2.3.5. Thermal analysis

Thermal analysis is a branch of materials science where the properties of materials are studied as they change with temperature. There are several techniques which are distinguished from one another that use change in thermal property e.g.

1) Differential thermal analysis (DTA): temperature difference between sample and reference
2) Differential scanning calorimetry (DSC): heat difference
3) Thermogravimetric analysis (TGA): mass etc.

Thermogravimetry (TG) is a technique to determine change in weight with temperature. It relies on a high degree of precision in two measurements: weight and temperature in a controlled atmosphere. The variation in mass can be either a loss (water removal) or a gain of mass (gas fixation). Differential thermal analysis (TGA) is a technique measuring the difference in temperature between sample and a reference (a thermally inert material such as α-alumina) as a function of temperature. The DTA curve is a plot of differential temperature against time or against temperature. Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred in the sample, such as glass transitions, crystallization, melting, sublimation and redox or solid state reactions. The area under a DTA peak can be proportional to the enthalpy change and is not affected by the heat capacity of the sample [14].

For the current studies, PerkinElmer’s Diamond model instrument was used to perform the thermogravimetric and differential thermal analysis (TG-DTA) of the samples in air flow (ca. 50 mL min^{-1}). The samples were heated at a heating rate of 283 K min^{-1} in the temperature range 298- 1273K using α- Al_2O_3 as reference.

2.3.6. Solid-state nuclear magnetic resonance spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy gives information on the interaction of a nucleus having a nuclear spin quantum number, I, greater than zero with an external magnetic field. The interaction of nuclear spins with the externally applied magnetic field, B_0 and their environment can be described by the spin Hamiltonian H:

$$H = H_Z + H_{CS} + H_Q + H_D + H_J$$

H_Z is a Hamiltonian, which describes the interaction of the nuclear spin with the external field B_0 (Zeeman interaction). The chemical shift Hamiltonian H_{CS} gives the information on the local environment of a nucleus. The chemical shift is measured relative to that of a reference compound and is expressed in Hertz or in ppm with respect to the resonance frequency of the reference compound. H_Q describes the quadrupolar interaction of the nucleus with the surrounding electric field gradient. H_D describes the dipolar interaction with other nuclei, while H_J describes the interaction with other nuclei through J coupling.

In solid-state NMR, the line shape is determined by dipolar and quadrupolar interactions. The lines are usually broader because the rigid structure of the solid phase prevents the averaging of the dipolar interaction (H_D) by motions. Since the first order quadrupolar and dipolar interactions are proportional to ($3\cos^2\theta - 1$), where θ is the angle between an internuclear vector and the magnetic field, these interactions can be removed, to a first order approximation, by spinning the sample around the so-called magic angle β with respect to the external magnetic field, for which $3\cos^2 \beta - 1 = 0$, i.e. $\beta = 54.740$. This technique is known as Magic Angle Spinning (MAS) [15]. As the chemical shift depends upon the local environment of the nucleus, different shifts are observed depending on whether a particular silicon atom has 0, 1, 2, 3 or 4 silicon atoms in the four surrounding tetrahedral sites, which also can be explained in the terms of 'Q' units, the structural units in the silicate anions.

2.3.7. Infra-red spectroscopy

Infrared spectroscopy is one of the most important analytical techniques, as any sample virtually in any physical state can be studied. Liquids, solutions, pastes, powders, films, fibres, gases and surfaces can be examined with a judicious choice of sampling techniques. IR spectroscopy technique is based on the vibrations of the atoms of a molecule on absorptions of energy. Absorption of an infrared photon occurs only if dipole moment changes during the vibration.

An IR spectrum is a plot of percentage transmittance versus wave number, commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular frequency. The wave number at which the peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. The intensity of the infrared band is proportional to the change in the dipole moment. In-situ type of analysis can be done by using special IR cells designed for the purpose. The IR analysis of catalysts of this study was performed on Perkin-Elmer Spectrum GX spectrophotometer.

2.3.8. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a spectroscopic technique that measures the elemental composition, chemical state and electronic state of the elements of a material. It is a surface analysis technique with a sampling volume that extends from the surface to a depth of approximately 50-70 Å. XPS, generally use either a highly focused 20-200 mm beam of monochromatic AlKα X-rays or a broad 10–30 mm beam of non-monochromatic polychromatic MgKα X-rays. Some modified XPS instruments can analyze volatile liquids or gases, materials at low or high temperatures or materials at roughly 1torr vacuum.

The basic experimental technique in photoelectron spectroscopy involves exposing the sample to a flux of nearly mono energetic radiation with mean energy hν and then observing the resultant emission of photoelectrons. X-ray with known wavelength, the binding energy of emitted electrons can be determined by using Ernest Rutherford equation

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi)$$

Where,

$E_{binding}$ - the binding energy (BE) of the electron,

E_{photon} - the energy of the X-ray photons,

$E_{kinetic}$ - the kinetic energy of the electron and

ϕ - the work function of the spectrometer.

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 [16]. Each element produces a characteristic set of XPS peaks at different binding energy values that directly identify each element that exist in or on the surface of the material being analyzed. These characteristic peaks correspond to the electronic configuration of the atoms, e.g., 1s, 2s, 2p, 3s, etc. To account for the multiplet splitting and satellites accompanying the photoemission peaks, the photoelectron spectra have to 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 [17].

X-ray Photoelectron Spectroscopy analyses were performed on a VG Micro Tech ESCA 3000 instrument at a pressure of $> 1\times10^{-9}$ Torr (pass energy of 50 eV, electron take-off angle of 60° with overall resolution was ~0.1 eV) using a non-monochromatized MgKα (1253.6 eV) or AlKα radiation (1486.6 eV) operated at an accelerating voltage of 12.5 kV. The powder sample was pressed into thin discs and mounted on a sample rod to be placed a pre-treatment chamber. After the pre-treatment, sample was transferred into the analysis chamber where the spectra of required binding energy range recorded. Charging effects were corrected by adjusting the binding energy of C^{1s} peak to a known position of 285 eV.

2.4 References

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Chapter-III

C-C cross coupling reactions on Pd-K-OMS-2 catalysts

Palladium supported on octahedral molecular sieves (OMS-2) for C-C cross coupling reactions

3.1. Introduction

Reactions that involve new carbon–carbon bond formation are important in building complex molecules that can lead to development of new drugs and agrochemicals. Kolbe, for the first time in 1845, reported the synthesis of acetic acid using new methodology of carbon –carbon bond formation. Since then carbon–carbon bond-forming reactions have played extremely crucial and important role in shaping chemical synthesis. The reactions such as Aldol, Grignard-type, Diels– Alder, pericyclic processes, Wittig and related reactions have led to advancing the ability of chemists to construct increasingly complex carbon containing molecules, thus enabling the syntheses of a myriad of organic compounds. These reactions are also vital in developing new generation of ingeniously designed organic materials with novel electronic, optical or mechanical properties.

Professor Heck is generally considered to be the father of Pd-catalysed coupling chemistry, as his work in this area became widely known and has found varied applications. Generally, the C-C cross coupling reactions uses Pd complexes or Pd salts as the catalyst, while employing a base and a polar/non polar solvent. The formation of a new C-C bond under these experimental conditions is not only important but also can be applied widely, as a broad range of functional groups can be used. Moreover, these starting reagents are easily available.

The original studies on Pd-catalysed reactions, reported for the first time, mostly used aryl bromides and iodides, while for a number of years there were no effective catalysts for the less active aryl chlorides. The activity is related to the strength of the Ar-X bond, which increases from iodine to chlorine. (65, 81 and 96 kcal mol^{-1} for I, Br, Cl respectively). This makes the oxidative addition step increasingly difficult [1]. As compared to aryl bromides or iodides, using aryl chlorides as substrates offer greater commercial scope as the substrates are much cheaper. Palladium catalyzed C-C coupling reactions e.g. Heck, Suzuki and Sonogashira reactions are versatile and practiced in various chemical syntheses both for academic research and industrial applications [2-4]. The Heck [5], Suzuki [6] and Sonogashira [7] reaction are well established, excellent tools for C –C bond formation. They have found wide-spread applications as a wide variety of reactants with different functional groups can be used and also availability of wide aryl bromides/chlorides for stereo selective synthesis of various coupling products. These reactions have found applications in the production of fine chemicals, including the manufacture of Novartis' Prosulfuron™—as herbicide [8], octyl-*p*-methoxycinnamate-a sun-screen agent, Albemarle's Naproxen—an antibiotic [9] and Singulair—an anti-asthma drug [10].

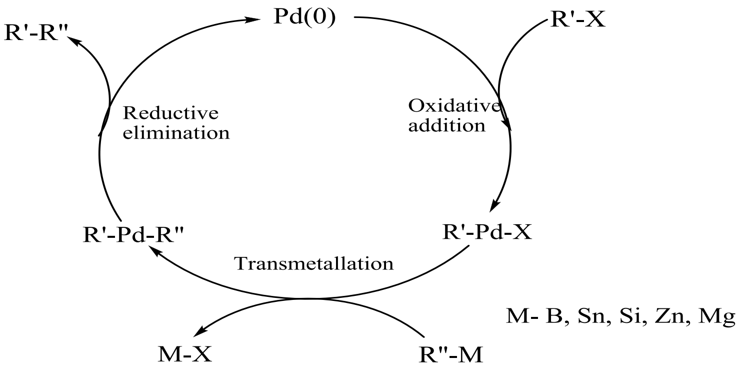
3.1.1. Heck reaction

The carbopalladation of an alkene by an organopalladium halide is the essential step in one of the contemporary metal catalyzed C-C coupling reactions. In the year 1971-72, Japanese and American groups reported, almost simultaneously, Pd catalyzed coupling reactions of aryl and alkenyl halide with alkenes [11]. In mid 1980, power of C-C bond forming reaction got more attention and many started to utilize this technique. By now an impressive number of publications have been reported and it is widely known as "Heck reaction", a vital and versatile process in organic synthesis [12]. Using catalytic amount of a Pd catalyst, the heck reaction can bring about desired structural changes, particularly when the reaction is conducted intramolecularly.

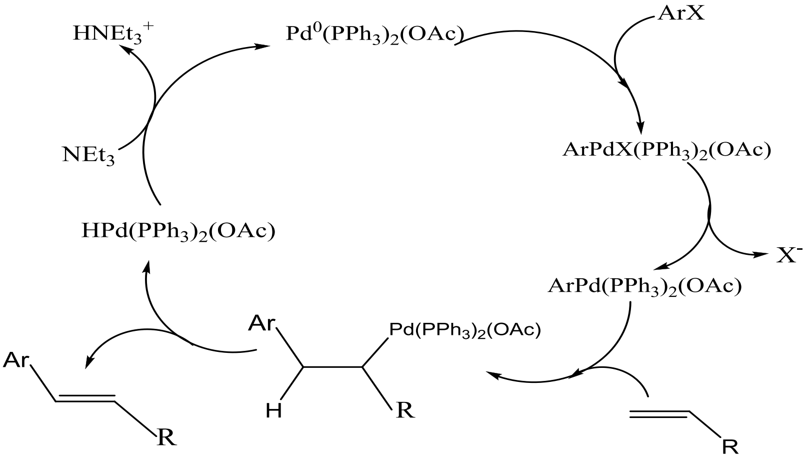
Understanding of the mechanism and the ways to enhance the rate determining step could provide opportunities to use even less reactive substrates for this reaction. Understanding the properties of the Pd intermediates in the catalytic cycle has allowed the reactions to be applied to a wider range of substrates with improved selectivity under milder conditions.

3.1.1.2. Reaction mechanism

In general, C-C coupling reactions catalyzed by solid-supported Pd catalysts follow the usual reaction mechanism, as shown for coupling of organometallics with organohalides or -triflates in Scheme 3.1a. Amatore and Jutand [13] provided evidence for an anionic version of the catalytic cycle in Heck and other Pd-catalyzed coupling reactions under homogeneous conditions (Scheme 3.1b). Probably this mechanism is more prominent than the textbook cycle shown in Scheme 3.1a unless aryl triflates or arenes with non-halide leaving groups are used [14]. This mechanism has not been proved in all details; especially the rate determining step has not been identified unequivocally in all cases. Frequently, the oxidative addition has been assumed to be rate determining, however, in certain cases it has been doubted or even disproved experimentally e.g. in case of tetra substituted alkenes [15].



a.- Catalytic cycle found in textbooks



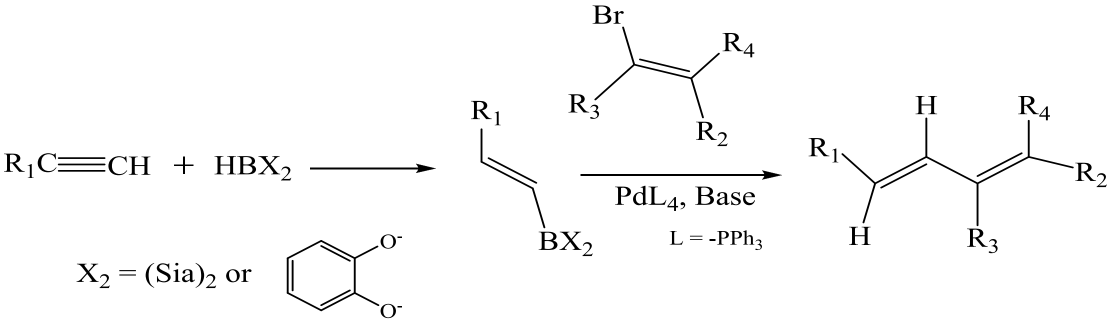
b.- Heck reaction cycle proposed by Amatore and Jutand

Scheme 3.1: Reaction mechanism of Heck reaction

Considering several mechanisms [14], the reaction can take place either at the surface of Pd [16] as a truly heterogeneous reaction or a quasi-homogeneous mechanism can occur, where Pd gets dissolved as colloids [17] or as complexes that have been leached out from the support [18]. The dissolved Pd can catalyze cross-coupling reactions, which makes it difficult to find out the true nature of the catalytic species [19]. There were reports that the dissolved Pd that is leached out of the catalyst is active for the Heck reaction, whereas solid Pd particles lead to side reactions such as dehalogenation, reductive coupling of haloarenes etc [20].

3.1.2. Suzuki reaction

The Suzuki cross coupling reaction is a highly versatile methodology for generation of C-C bonds as substituted biaryls are important building blocks for the syntheses of many pharmaceutically important compounds, herbicides, polymers, polyolefins, liquid crystals and ligands [21]. Among the various methods known to synthesize biaryls, the transition-metal-catalyzed Suzuki-Miyaura cross-coupling of aryl halides with arylboronic acids or esters has emerged as a powerful tool in organic synthesis for the formation of C_{sp2} - C_{sp2} bonds under mild conditions [22]. Further, in recent times, the Suzuki coupling has been extended to C_{sp3} - C_{sp2} and C_{sp3} - C_{sp3} couplings [23].



Scheme 3.2: Suzuki reaction

Suzuki group for the first time reported the Pd catalyzed reaction between boronic acids (containing an organic part) and halides. This reaction is extended to an aryl- or vinyl-boronic acid with an aryl- , vinyl- or an alkyl-halide. They reported that in presence of base such as sodium methoxide, ethoxide, acetate and hydroxide, reaction of an equimolar amount of (E) - 1-hexenyldisiamyl borane in THF with (E) -1-bromo-2-phenylethene with 1mol% of *tetrakis*(triphenylphosphine) palladium gave (E,E)-1-phenyl-1,3-octadiene in decent yields [24] (Scheme 3.2).

3.1.2.1. Reaction mechanism

By analogy to the other cross coupling reactions, the catalytic cycle of Suzuki coupling reaction involves three basic steps: (i) Oxidative addition (ii) Transmetallation and (iii) Reductive elimination. A general catalytic cycle for the Suzuki coupling reaction is given in scheme 3.1a [25].

The advantage of the Suzuki reaction is, it has high tolerance to most functional groups, the milder reaction conditions, the relative stability of boronic acids/esters to heat, oxygen, water, the ease of handling and separation of boron-containing by-products and their abundant commercial availability. These are all important and desirable features for the construction of diverse aryl and heteroaryl compounds which are essential in medicinal chemistry.

3.1.3. Sonogashira reaction

The Sonogashira reaction has emerged in recent years as one of the most general, reliable and effective methods for the synthesis of substituted alkynes [26]. The Pd-catalyzed coupling of organic electrophiles with number of different metal acetylides e.g. Zn, Mg, Sn, B, Al and Sn [27], also provide a useful access to alkynes or its derivatives. However, the Sonogashira protocol by Pd-catalyzed alkynylation in presence of co-catalyst CuI is the most widely used, particularly in the context of total synthesis and largely owing to its broad applicability and convenience.

Stephans-Castro reported Sonogashira reaction, for the first time, for synthesis of acetylenes by coupling of copper (I) aryl acetylenes with iodoarenes [28] or iodoalkenes [29]. The scope of the reaction sometimes is limited by the reaction conditions and due to difficulties in the preparation of cuprous acetylides.

In 1975, Cassar [30] and Heck [31] independently reported the substitution of acetylenic hydrogen by iodoarenes, bromoalkenes or bromopyridines in the presence of catalytic amount of bis (triphenylphosphine) palladium dichloride. Both methods generally require higher temperature (upto 373 K). In the same year, Sonogashira and Hagihara [32] reported this reaction, but in presence of cuprous iodide and triethylamine under very mild conditions. Addition of a cocatalyst, cuprous iodide, to reaction gives more satisfactory results for the direct synthesis of symmetrically disubstituted acetylenes. Therefore, the Sonogashira-Hagihara protocol (more often known as Sonogashira coupling) became the most popular procedure for the alkynylation of aryl or alkenyl halides. The alkynylation of primary alkyl bromide or iodides [33] and secondary alkyl bromides [34] have also been reported using sonogashira protocol. This type of sp^3-sp coupling is very recent and remains almost unexplored. It is believed that the reaction goes through formation of copper acetylide and then this group is subsequently transferred to Pd by a transmetallation step. Use of catalytic amount of cuprous salt as cocatalyst increases rate and yield of reaction, but the formation of copper acetylides can also lead to homocoupling products. In addition, it has drawbacks such as less environmental friendliness and difficulty in recovering reagents. Hence, there is need to modify the reaction conditions, in particular copper-free conditions.

Many methodologies have been reported on Sonogashira reaction without use of Cu as cocatalyst and all these Cu-free methodologies are usually called Cu-free Sonogashira couplings. Generally, these Cu-free processes involve the use of excess amine (often even acting as solvent), something that diminishes to some extent the environmental and economic advantages of the methodology. Hence, the development of methods that allow the elimination of both Cu and amine in the Sonogashira cross-coupling has been pursued for the past few years.

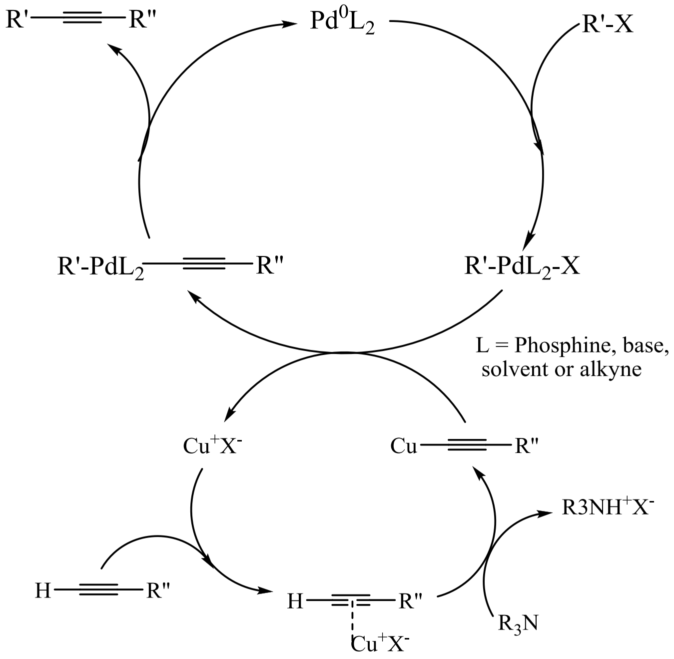
The Pd catalyzed coupling reaction between aryl or alkenyl halides or triflates (sp^2) and terminal alkynes (sp), with or without the presence of a Cu is a more important process to prepare arylalkynes and conjugated enynes. The products are useful as intermediates in the synthesis of natural products [35], pharmaceuticals [36] and molecular organic materials [37].

3.1.3.1. Mechanism of Sonogashira reaction

The exact mechanism of the homogeneous copper-co-catalyzed Sonogashira reaction is unclear with some doubtful points and proof for the intermediates. Though the possible mechanistic paths of particular reaction are based on the identification of some of the transient species formed in the reactions, but it is very difficult to isolate and characterize the intermediates to confirm a mechanism beyond doubt.

3.1.3.2. The copper-co-catalyzed Sonogashira reaction

The Cu-co-catalyzed Sonogashira reaction mechanism is included in two independent catalytic cycles as shown in Scheme 3.3. The generally accepted catalytic cycle for the Pd catalyst in coupling reaction is based on a usually fast oxidative addition of R^1-X to the Pd catalyst. For the crucial oxidative addition of R^1-X to the Pd catalyst, R^1-X bond must be broken. This step is facilitated if the leaving group is iodide; -OTf or electron-withdrawing groups are attached to R^1, which can decrease the electron density between the R^1 group and the leaving group (halide, OTf).



Scheme 3.3: Mechanism of copper catalyzed Sonogashira reaction

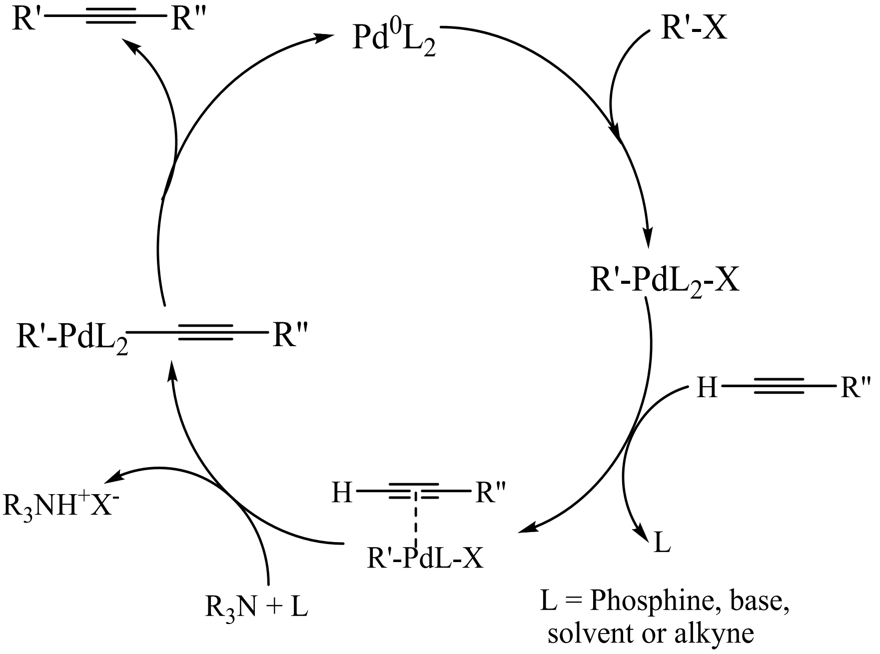
The next step, transmetalation, which is believed to be rate determining step, takes place in the Pd-cycle along with the Cu cycle. Copper acetylide is formed in the Cu cycle by reacting Cu and acetylene followed by deprotonation with the help of base. This copper acetylide undergoes transmetalation with Pd to give $R^1Pd(-C\equiv CR^2)L_2$ intermediate. The final coupled alkyne product obtained after reductive elimination step with regeneration of the catalyst.

The second Cu-cycle is still not clearly understood. The formation of copper acetylide in the presence of copper salt and acetylene is the result of abstraction of acetylenic proton of the terminal alkyne by base. The used tertiary amine is not a strong base to deprotonate the alkyne in order to generate the anionic nucleophile. Hence, as shown in Fig 3.1, π-alkyne- Cu complex which could be involved in the cycle, has no direct evidence available for its existence [38]. This π-alkyne- Cu complex makes the alkyne proton more acidic for easier abstraction. NMR studies have shown that π -alkyne-Ag complexes in place of Cu are formed in Sonogashira reaction [39].

3.1.3.3. The copper-free Sonogashira reaction

The mechanism of the copper-free Sonogashira reaction (Scheme 3.4) is also not well-understood and has similar problems, when deprotonating the palladium acetylide. Therefore, in this cycle, complexation of the alkyne with Pd catalyst is supposed to proceed with dissociation of one of the original Pd ligands to give intermediate complex (ή^2-R C≡CH)-PdXL^2 [40] and could weaken the terminal alkyne hydrogen bond.

This eases deprotonation of acetylide by the amine, forming the intermediate R^1Pd-(-C≡CR^2)L_2, which results in the coupling product R^1-C≡C-R^2 by reductive elimination.



Scheme 3.4 Mechanism of copper free catalyzed Sonogashira reaction

3.1.4. Homogeneous catalysts in coupling reactions

Various reports on cross coupling reactions pertain to homogeneous Pd catalysts with use of highly air sensitive and expensive ligands. These new catalysts contain palladacycle, N-heterocyclic carbene palladium catalysts and thiourea Pd(0) type of complexes [41]. These homogenous transition metal catalyzed cross-coupling reactions are generally performed in organic phase, which doesn’t have the immiscibility problem, because of efficient mass transfer between the substrate and the catalyst. The reaction catalyzed by homogenous catalysts has broad acceptability for aryl bromides and chlorides and the tolerance of the reaction for a wide variety of functional groups. Over the decades, many researchers were successful in developing novel highly active Pd complexes that can allow the activation and conversion of even some aryl chlorides [42], which are less reactive than bromides and iodides. The catalysts used in homogeneous reactions are palladium complexes with expensive ligands systems e.g. phosphines. It has been reported that these groups add functionality and selectivity to the metal, but the problem is recovery of the catalyst from the homogeneous reaction medium.

Very few reactions were reported about their separation from the reaction and reuse. With major problems, such as decomposition of the catalytically active component, metal leaching, insufficient catalyst activity, difficulties in regard to recovery and recycling properties, it is highly desirable to develop a ligand free, recyclable novel heterogeneous catalysts to carryout reaction without the use of expensive and air-sensitive phosphine ligands for C-C cross coupling reactions catalyzed by Pd catalyst.

3.1.5. Heterogeneous catalysts in coupling reactions

In order to overcome the problems associated with the homogeneous catalysts, more attention has been focused on heterogenization of homogeneous catalysts or immobilization of metal complexes, to yield catalysts that have functionality of both homogeneous and heterogeneous catalysts. A variety of heterogeneous metal catalysts have been investigated for their easy recovery and recyclability [43-47]. During reaction, Pd switches between its two oxidation states Pd^0 to Pd^{+2}, so it is important to make a good choice of support, which can retain these two oxidation states of Pd. Studies have also been reported on Pd nanoparticles [17a], use of Cu, Ni, Co, and Mn heterogeneous catalysts for the Heck reaction [48]. Polymer supported Pd-complexes have been used for activation of aryl iodides and bromides by many researchers [49]. The use of microwave irradiation in coupling reactions has also been reported by Wali *et al* [50]. Efforts are also made in search of new, efficient and recyclable heterogeneous catalysts or complexes supported on a variety of solid supports such as activated carbon, mesoporous silica, inorganic oxides, molecular sieves and hydrotalcites for Heck [51], Suzuki [52] and Sonogashira reactions [53]. There are also reports on Pd supported on mesoporous material such as MCM-41, SBA-15 etc. There was great interest in these materials, as their large and uniform pore sizes (20-100 Å) allow easy diffusion of sterically hindered molecules to react at their internal active sites [54]. Though above catalysts were able to activate even less reactive substrates such as chlorobenzene, the activity of the catalyst was lower on reuse. Also leaching of Pd was reported by Djakovitch and Koehler [51] with zeolite as support.

The reported supports so far, except hydrotalcite and MgO, were acidic in nature. But, it has been observed that metals on basic supports showed better catalytic activity as compared to acidic supports. Choudhary *et al* reported nanopalldium supported layered double hydroxide as a basic catalyst, which facilitated the transfer of electron from basic support to the metal. This would make the metal surface more readily oxidizable and therefore more reactive towards the halide [55]. However, only a few reports are available on the use of metals supported basic substrates for the C- C coupling reaction [56].

3.1.6. Octahedral molecular sieves as catalyst supports

Microporous molecular sieves have pore dimensions close to molecular size. They have been widely used in many chemical processes because of their porous structure, acidity and ion-exchange properties. The most common molecular sieve materials are zeolites. These are aluminosilicates with well-defined three-dimensional framework structures with pores having diameter less than 2 nm.

Similar to zeolites, manganese oxides with tunnel structures exhibit molecular sieving properties [57]. These are referred to as manganese oxide octahedral molecular sieves (OMS) [58]. They include synthetic todorokite (OMS-1) and cryptomelane (OMS-2). Manganese oxide octahedra (MnO_6) are the basic structural units of OMS materials that combine to form tunnels in the range of 4.6 to 6.9 Å by linkages at their edges and vertexes. OMS-1 utilizes three MnO_6 octahedra on each side to form a 3x3 square tunnel with a pore size of about 6.9 Å. Similarly, OMS-2 has a 2x2 square tunnels with pore size of about 4.6 Å. The main origin of later material, KOMS-2, is manganese nodules (available in the deep-sea region) and some of the soil sediments. Naturally occurring manganese nodules contain large number of manganese oxide minerals [59]. The main phases present in the manganese nodules are birnessite type layer structures, cryptomelane and todorokite type tunneled manganese oxide phases.

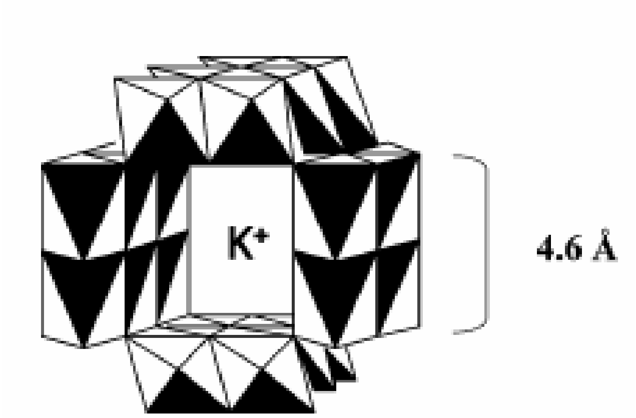


Fig. 3.1: Structure of OMS-2 (Cryptomelane)

Less crystallinity and poor in homogeneity are the principal drawback of these naturally occurring manganese oxide materials Manganese is the tenth most abundant element in the earth's crust. Due to the easy availability of the manganese precursors; synthesis of OMS-2 is inexpensive and simple. OMS-2 is microporous tunnel – structured manganese oxide material and basic in nature. Inside the tunnel of these OMS structures, K (cryptomelane) or Mg (todorokite) ions are present as exchangeable cations. Potassium containing cryptomelane type manganese oxide OMS-2 material (Fig.3.1) has a composition of $KMn_8O_{16}.nH_2O$ [58]. The structure contains units of 4.6x4.6 A^0 tunnels because of the 2x2 arrangement of octahedral MnO_6 and K^+ ion with a small amount of water present in the tunnel. The average oxidation state of manganese in OMS-2 is 3.8 due to the presence of a mixture of Mn^{4+}, Mn^{3+} and Mn^{2+} ions [60]. The smaller pore opening is probably the reason for its higher stability. In addition, counter cations (e.g., K^+, Na^+, Ba^{2+}, and other alkali and alkaline earth metal ions) and water are present in the tunnels of OMS-2 materials to provide charge balance and stability to the structure.

In recent years, KOMS has been used in catalytic oxidation reactions [61]. OMS-2 produced by reflux method has advantages such as higher surface area, smaller particle size and more defects in manganese oxide octahedral lattice that could serve as redox sites compared to OMS-2 material produced by other methods e.g. sol-gel etc. Doping or incorporation of foreign metal particularly divalent or trivalent cations in OMS-2 changes its electronic, catalytic and structural properties [62]. The K-OMS-2 is basic in character and no reports were found in the literature that used this material as a support for transition metals such as Pd in order to apply it as a catalyst for C-C coupling reactions. Hence, we chose to prepare and investigate the Pd loaded OMS-2 for C-C coupling reactions.

The present study reports the synthesis of KOMS-2 material, incorporation of Pd through exchange and their characterization. It reports the stability study of Pd-K-OMS-2 investigated through thermal analysis and dispersion of Pd and its nano structured nature through electron microscopy techniques. Interesting results were obtained when Pd-K-OMS-2 was used for Heck, Suzuki and Sonogashira coupling reactions. Effectiveness of this material as a novel catalyst for these reactions was demonstrated. The study also covers the influence of Pd content, the nature of the base used, solvent effects and the reactivity of the different substrates and reactants on the coupling reaction in this chapter.

3.2. Experimental procedures

Synthesis of K-OMS-2 was carried out using potassium permanganate and manganese sulphate monohydrate (Loba Chemie, India). Tetraammine Pd (II) nitrate and substrates used for C-C coupling reactions were purchased from Sigma-Aldrich. The solvents, acetonitrile, dimethylactamide (DMA), dimethylformaide (DMF) and N-methylpyrrolidinone (NMP) were obtained from LOBA India, were dried using standard procedures before use [63].

3.2.1. Preparation of catalysts

As described earlier, OMS-2 belongs to a class of oxide materials that have tunnel structures. The synthetic OMS-2 has one-dimensional tunnel structure formed by 2X2 edge shaped MnO_6 octahedral chains.

It was prepared by reflux method [58]. A solution of $KMnO_4$ (5.89g in 100 mL of water) was added drop-wise to a solution containing mixture of manganese sulfate (8.8g in 30 mL water) and concentrated nitric acid (3 mL). This resulted in the formation of a black precipitate, which was stirred and refluxed at 373 K for 24h. Subsequently, the precipitate was filtered and washed with distilled deionized water until the pH of the filtrate was close neutral. Followed by this, the material was dried for 12h at 383 K before calcined in air at 623 K for 4h.

The palladium OMS-2 catalysts were prepared by ion exchange method. K-OMS-2 (1g) was ion exchanged with $Pd(NH_3)_4NO_3$, 0.056g in 20 mL of distilled water, by refluxing for 3h at 353 K to obtain Pd^{+2}-K-OMS-2. The residue was filtered, washed with deionized water and dried overnight at 373 K. The solid material was then calcinated in air at 623 K for 4h.

Pd^0-OMS-2 catalyst was obtained on reduction of Pd^{+2}-OMS catalysts with sodium borohydride solution. $NaBH_4$ in ethanol solution was added to the Pd^{+2}–OMS dispersed in ethanol. The stirring was continued for 3h at room temperature under inert atmosphere. The black solid was filtered, washed with absolute ethanol followed by dry ether. The catalysts were stored in dry atmosphere. Similar procedure was adopted to prepare catalysts with different Pd contents (1 to 3 wt %), by varying the concentration of $Pd(NH_3)_4(NO_3)_2$ solution. These samples were designated based on the Pd loading as Pdcat-I (0.98%), Pdcat-II (1.8%), Pdcat-III (2.8%). The Pd content of the samples was determined by dissolving them in concentrated HCl and estimated using ICP-OES (Spectro Arcos).

3.2.2. Characterization of catalysts

Powder XRD measurements of the as synthesized and final catalysts were carried out using PANalytical Philips X'Pert Pro diffractometer equipped with Ni filtered Cu Kα radiation (λ = 1.5418 Å). The data were collected at a scan speed of 2 ^{o}/min. Specific surface areas of the catalysts was measured by N_2 sorption at liquid N_2 temperature using a Quanta chrome Nova-1200 surface area analyzer employing multi point BET method. The catalyst samples were evacuated at 473 K for 3h at a residual pressure of $2x10^{-3}$ Torr prior to N_2 sorption. The isotherms were analyzed in a conventional manner in the relative pressure range of p/p^0 = 0.05 to 0.30.

Transmission electron micrographs (TEM) of the catalysts were recorded on a high-resolution microscope (HR-TEM) Tecnai-T30 model at an accelerated voltage of 300 kV. Samples were prepared by placing isopropyl alcohol solution of the catalyst on carbon coated grids, followed by evaporation of the solvent at room temperature.

Scanning electron micrographs of the samples were recorded using JEOL-JSM-5200 SEM to study the morphology and particle size. Thermal analysis of the samples was performed using a PerkinElmer Diamond TG/DTA instrument in the flow of air (ca. 50 mL min^{-1}). The samples were heated at a heating rate of 283 K min^{-1} in the temperature range 298-1273 K, using α-Al_2O_3 as reference. For each analysis, about 10-15 mg of the sample was used. X-ray photoemission spectra (XPS) of Pd-K-OMS-2 samples were acquired on VG Microtech Multilab ESCA 3000 spectrometer using non monochromatized MgKα X-ray source (hν = 1253.6 eV), at a pass energy of 50 eV and electron take off angle of 60^0. Correction to the binding energy (B.E.) values was made by using the C_{1s} peak of carbon at 285 eV.

3.2.3. General experimental Procedure for coupling reactions

3.2.3.1. Heck reaction

In a dry two-neck Schlenk flask fitted with a reflux condenser, Pd- K-OMS-2 catalyst (50mg), aryl halide (1 mmol), styrene (1.2 mmol), base (1.2 mmol) and DMF (4 mL) were added. The flask and condenser were evacuated 2 to 3 times and flushed with argon gas. Subsequently, the flask with reaction mixture was placed in a preheated oil bath at 408 K and heated under vigorous stirring. To monitor the progress of reaction, aliquots of reaction mixture were drawn at different intervals and analyzed by GC (Varian CP-3800) using FID and HP-1 capillary column (50m, 0.35mm id). Confirmation of the products was done using GC-MS (Varian Saturn 2200).

3.2.3.2. Suzuki reaction

In a dry two-necked Schlenk flask, Pd- K-OMS-2 catalyst (50mg), base (2 mmol), aryl halide (1 mmol), phenylboronic acid (1.2 mmol) and 4 mL of DMF+H_2O (1:1) were introduced and stirred at 303 K temperature. The progress of the reaction was monitored by removal of the reaction mixture at different intervals of time and analyzed by a GC, as described above. After completion of reaction organic layer was extracted with DCM and product identification was done using GC-MS (Varian Saturn 2200) equipped with BPX-5 capillary column. Substrate conversion and product selectivity's were calculated based on GC analysis.

3.2.3.3. Sonogashira reaction

To a dry two-necked Schlenk flask equipped with a reflux condenser, Pd-K-OMS-2 catalyst (50mg), aryl halide (1mmol), phenyl acetylene (1.2 mmol), base (1.4 mmol) and 4 mL of IPA : H_2O (3:1) were added. The flask and condenser were evacuated 2 to 3 times and flushed with argon gas. Subsequently, the flask with reaction mixture was placed in a preheated oil bath at 353 K and heated under vigorous stirring. To monitor the progress of the reaction, aliquots of reaction mixture were drawn at different intervals and analyzed by GC. The product identification was done using GC-MS.

3.2.3.4. Test for heterogeneous nature of reaction

In order to find whether the reaction is purely heterogeneous catalyzed or homogeneous with the help of leached Pd from catalyst, the reaction containing catalyst, 1mmol of iodobenzene, 1.2 mmol of styrene (Heck reaction) or phenylboronic acid (Suzuki reaction) or phenyl acetylene (Sonogashira reaction), 1.2 mmol base in 4 mL of solvent was carried out in 50 mL of flask under desired reaction conditions. At half the time of the reaction, the catalyst was filtered off and reaction was continued without the catalyst. Aliquots of reaction mixture were drawn at different intervals of time and analyzed by GC.

3.3. Results and Discussion

3.3.1. Characterization

The Pd content (wt %) of the catalysts was determined by AAS after dissolving known amount of catalyst in dilute HCl. They were found to be 0.98, 1.98 and 2.78 wt% for the catalysts named as Pdcat-I, Pdcat-II and Pdcat-III respectively.

3.3.1.1. X-ray diffraction

Powder XRD pattern of various Pd-K-OMS-2 samples is shown in Fig.3.2. All peaks are clearly resolved and pertain to parent K-OMS-2. The prominent *d*-spacing values are given against corresponding (h k l) values; 12.7 (1 0 1), 18.0 (0 0 2), 28.7 (3 0 1), 37.4 (2 1 1), 41.8 (3 1 0), 50.0 (1 1 4) and 55.3 (6 0 0). All these values match with the reported data for cryptomelane structure of OMS-2 (JCPDS- 05-0681). It appears that cryptomelane type structure is intact during the reflux treatment for Pd^{+2} exchange.

No peaks attributed to Pd^0 were seen in the spectra, even for samples with high Pd content (2.78 wt %). Metallic Pd (cubic) is expected to give three major peaks at $2\theta = 40.11$, 46.66 and 68.08 (JCPDS 05-0681). But none of these peaks were seen in our XRD spectra. This could be attributed to either very fine dispersion of Pd as nano-particles or the Pd particles are below detection by XRD. The probability of Pd peaks being masked by K-OMS-2 peaks is discounted as they are expected to appear at different positions than K-OMS-2 peaks. No changes were observed for the XRD of spent catalyst (Fig. 3.2e), which indicates that the catalyst is stable under the reaction conditions as it retains its cryptomelane structure.

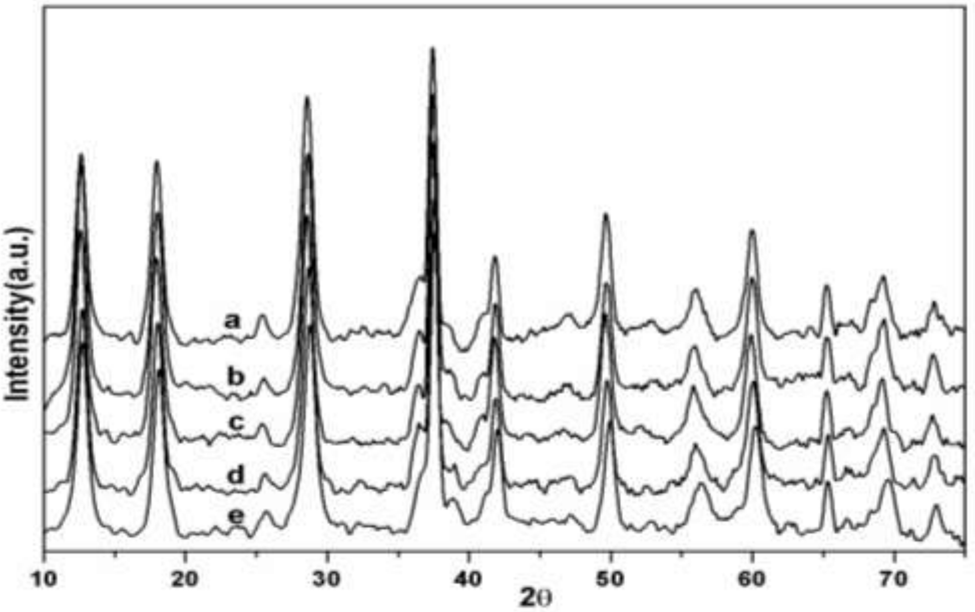


Fig.3.2: XRD pattern of (a) KOMS-2; (b) Pdcat-I; (c) Pdcat-II; (d) Pdcat-III and (e) spent Pdcat-II

3.3.1.2. Scanning electron microscopy

Scanning electron microscopy was used for studying the morphology of the catalysts. The SEM photograph in Fig. 3.3a clearly shows that the material is fibrous in nature, a characteristic of the K-OMS-2 [61]. No visible changes in morphology or crystallinity were observed on Pd loading and reduction (Fig.3.3b, c, d).

3.3.1.3. Transmission electron microscopy

Transmission electron microscopy is quite useful technique to understand nature of the sample and also to understand the metal dispersion. The TEM photograph clearly shows fine, sharp needle type nature of KOMS-2 material. The length of the fiber is in the range of 50-200 nm [60] (Fig.3.4a). Similar images were obtained for Pd exchanged KOMS-2 material (Fig. 3.4b, c, d). This indicates that the structure of original material is retained even after loading of palladium. The sizes of Pd particles on all three catalysts were found to be about 5nm, which is finely dispersed in a uniform manner on fibrous OMS-2 material.

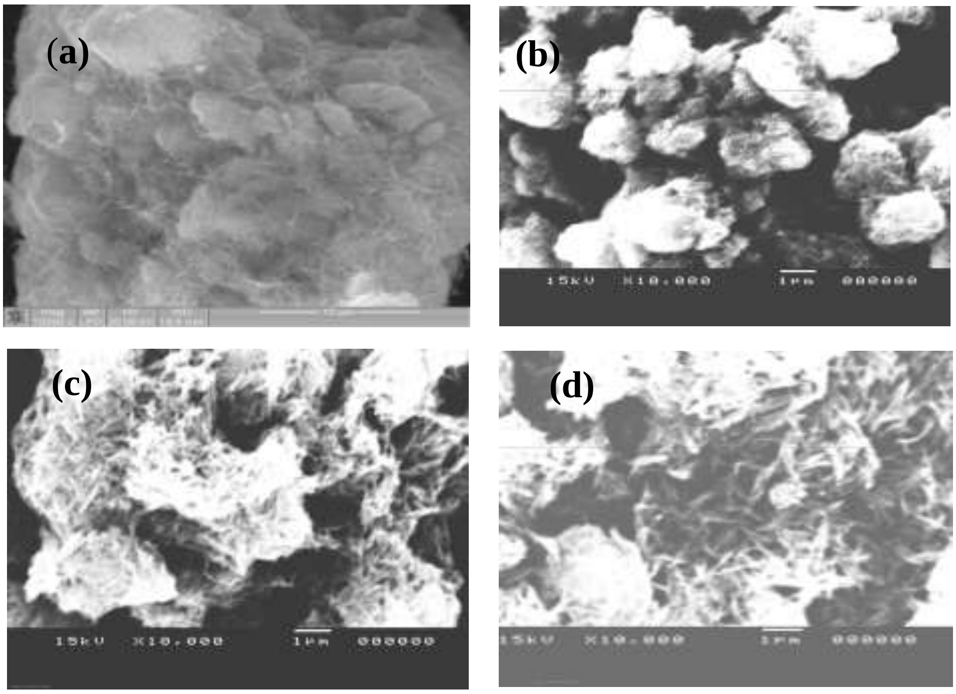


Fig 3.3: SEM images of (a) KOMS-2; (b) Pdcat-I; (c) Pdcat-II and (d) Pdcat-III

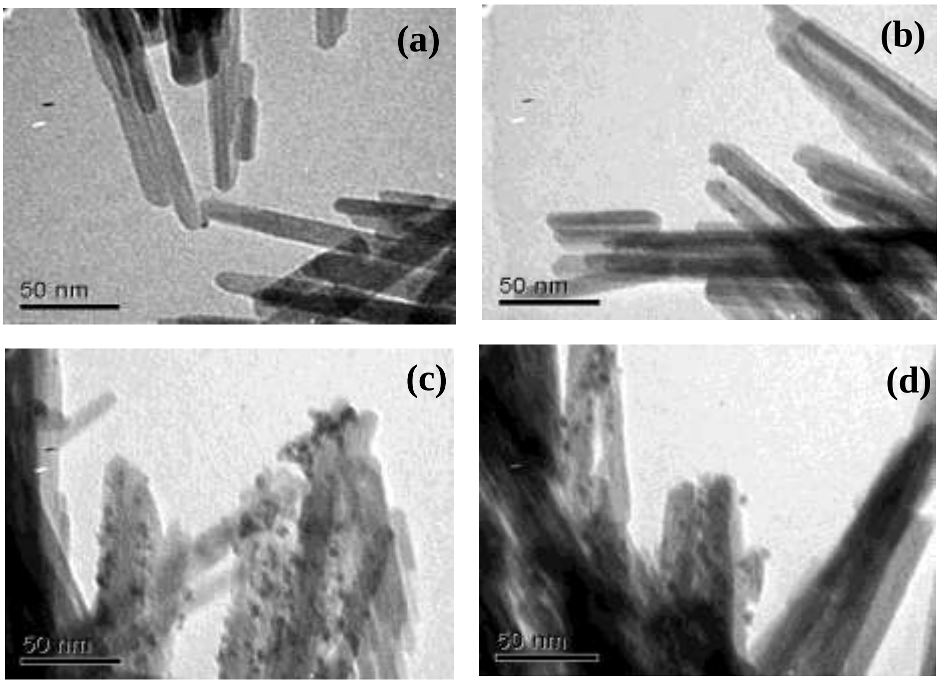


Fig. 3.4: TEM image of (a) K-OMS-2; (b) Pdcat-I; (c) Pdcat-II and (d) Pdcat-III

3.3.1.4. BET surface area by N_2 sorption

N_2 sorption measurements were carried out for the pure support as well as for the Pd supported catalysts. Table 3.1 shows textural characteristics of pure and prepared catalyst samples.

Surface area of the parent K-OMS-2 used for supporting Pd was 96 m^2g^{-1} with a pore volume of 0.3 ccg^{-1}. Both the surface area and pore volume decreased with increasing Pd content in the sample. The surface area fell to 65m^2g^{-1} for Pdcat-III and this trend may be attributed to the partial blockage of the micropores of OMS-2 with Pd, as no changes in XRD intensity was observed to show that there is any loss in crystallinity. A similar pattern was observed in case of micropore volume.

Table 3.1- Physiochemical properties of different catalysts

S. No.	Catalyst	S.A. (m^2g^{-1})	Pore volume ($cc.g^{-1}$)	Micropore Vol. ($cc.g^{-1}$)
1	K-OMS-2	96	0.30	0.0059
2	(0.98%) Pdcat-I	80	0.18	0.0049
3	(1.80%) Pdcat-II	71	0.12	0.0044
4	(2.78%) Pdcat-III	65	0.11	0.0039

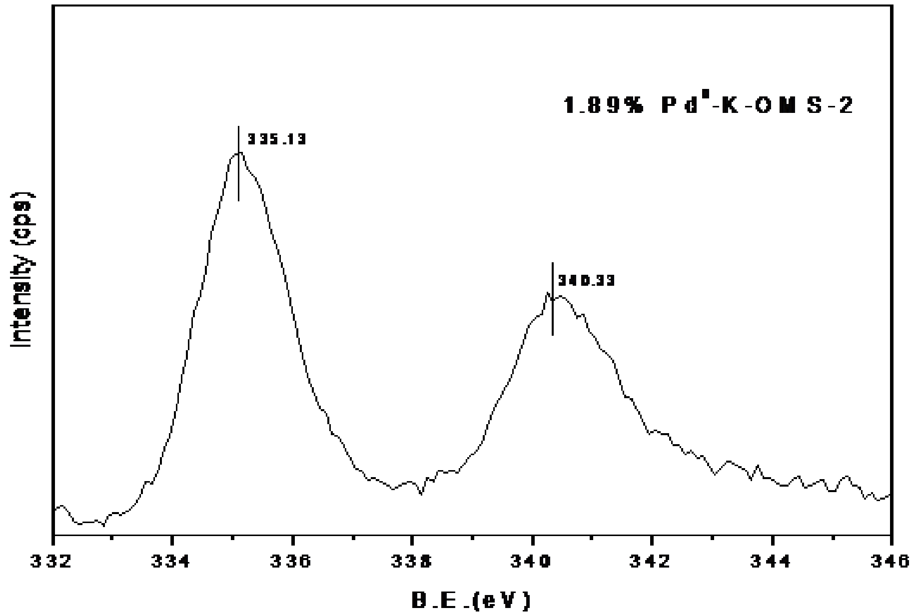


Fig. 3.5: XPS graph of Pdcat-II catalyst

3.3.1.5. X-ray photoelectron spectroscopy

The Pd-K-OMS-2 catalysts were investigated by X-ray photoelectron spectroscopy (XPS). Fig. 3.5 shows the Pd_{3d} spectra of 1.89 wt % Pd-K-OMS-2 catalyst (Pdcat-II). The results show that peaks for $Pd_{3d5/2}$ and $Pd_{3d3/2}$ appear at 335.13 eV, 340.33 eV respectively. These B.E values are very close to that of metallic Pd, which clearly shows that the Pd is in its metallic state (Pd^0), in agreement with literature reports [64].

3.3.1.6. Thermal analysis

Thermo gravimetric analysis of K-OMS- 2 and Pd-K-OMS- 2 materials was carried out in N_2 flow in the temperature range of 303-1273 K, while heating the sample at a rate of 283 K min^{-1}. Thermal gravimetric (TGA/ DTA) curve for KOMS-2 (Fig. 3.6) shows weight loss in three temperature zones; 323-550 K, 653-963 K and 963-1073 K. The low temperature weight loss of ~2.3% is attributed to the loss of water in the sample. The second weight loss of about 7.2% in the 653-963 K temperature zone is due to loss of lattice oxygen, as the manganese cations reduce to lower oxidation state leading to formation manganese oxide such as bixbyite (Mn_2O_3) [65].

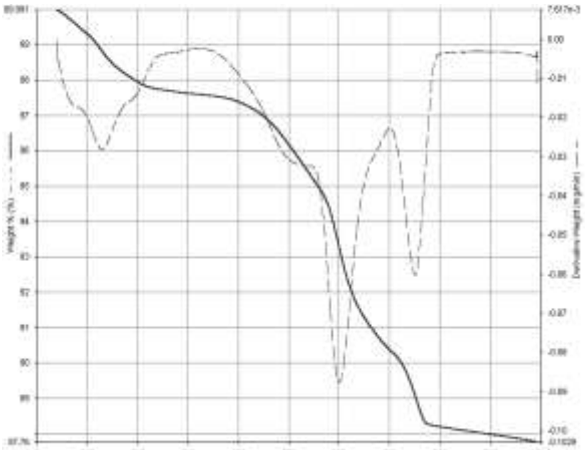


Fig 3.6: TGA/ DTA plot of KOMS-2

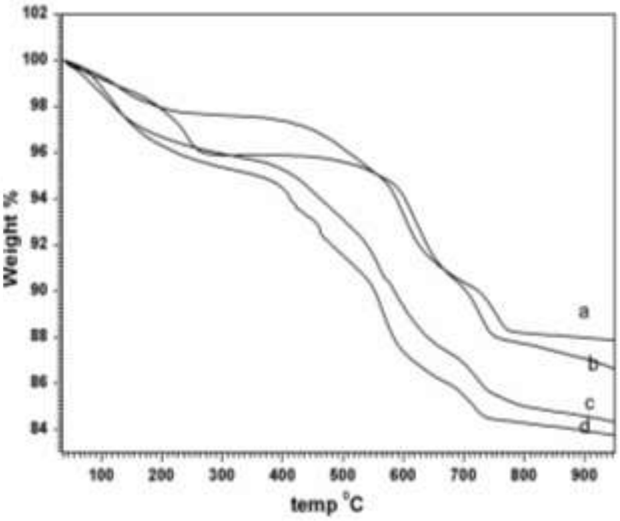


Fig. 3.7: TGA plot of (a) KOMS-2; (b) Pdcat-II; (c) Pdcat-I and (d) Pdcat-III

The third weight loss of about 2.8%, observed in the temperature zone 963 - 1073 K is attributed to a further loss of oxygen from bixbyite leading to the formation of more stable spinel hausmanite (Mn_3O_4) [66]. The general trend remained similar for

Pd-K-OMS-2 catalysts (Fig. 3.7b, c, d), but the weight loss in the low temperature region (323-550 K) increased substantially to 4.4% (Pdcat-II), 4.2% (Pdcat-I) and 6.0 % (Pdcat-III) at increased Pd loadings, suggesting that there was more water occluded in these samples compared to parent K-OMS-2. Moreover, the weight loss in the 423-550 K was very sharp.

The weight loss in the middle temperature zone (653-963 K) has considerably reduced to 5.3% (Pdcat-II) and 6.0% (Pdcat-I), while in case of Pdcat-III (7.0 %), the weight loss was similar (7.2%) to that of K-OMS-2. There was a small shift in the third temperature zone to higher temperature, though the weight loss almost remained same as that of KOMS-2.The study shows that there was no noticeable change in thermal stability of Pd catalysts as compared to K-OMS-2.

3.4. Evaluation of catalyst activity

Palladium containing Pd-K-OMS-2 materials were tested for Heck, Suzuki and Sonogashira C-C coupling reactions. For Heck reaction, halobenzene(s) and styrene were used as substrates (scheme 1.1), for Suzuki coupling (scheme 1.2) phenylboronic acid(s) and aryl halides were used and phenylacetylene and aryl halides were used for Sonogashira reaction (scheme 1.3). The catalytic activity of Pd-K-OMS-2 for all these reactions was found to be very good, as even 0.0046 mole of Pd in the catalyst gave good yield of products in Heck as well Suzuki reactions.

3.4.1. Heck reaction

Heck C-C coupling reaction was carried out with bromobenzene and styrene in presence of alkali carbonate as base with DMF as solvent using various Pd containing octahedral molecular sieves catalysts (Pd-K-OMS-2).

3.4.1.1. Effect of base

Influence of different bases on Heck reaction, using Pd-K-OMS-2 catalysts was studied (Table 3.2). The base is expected to play a major role in the arylation of alkene as it helps to neutralize the acid (HCl/HBr/HI) generated as a byproduct during the reaction, which in turn helps to increase the rate of reaction. A report by Wolfson *et al* shows that use of stronger base improves the product yield [67]. Carbonate type of bases gave good conversion of bromobenzene, leading to higher yield of product.

Among the bases used, Rb_2CO_3 gave the highest conversion of substrate (95.7%) with 88.7% product yield. The next best in terms of conversion is Cs_2CO_3, which gave 90% conversion with 85.5% yield. On the other hand, with K_2CO_3, only 62% conversion was observed, though better (99%) product selectivity was observed. Taking the cost, stability and good selectivity into consideration, we have used K_2CO_3 as a base for further investigations.

Table 3.2- Effect of bases on conversion of bromobenzene

S. No.	Base	Conversion of Bromobenzene (mol %)	Selectivity (mol %)	Yield (mol %)
1	NaOAc	44.7	95.1	42.5
2	Na_2CO_3	32.0	91.0	29.1
3	K_2CO_3	62.0	99.0	61.7
4	Cs_2CO_3	90.0	95.0	85.5
5	Rb_2CO_3	95.7	92.7	88.7

<u>Reaction conditions</u>: Pdcat-II (50mg), Bromobenzene (1mmol), Styrene (1.2 mmol), Base (1.2 mmol), DMF (4 mL), Ar atmosphere, 408 K, 24h.

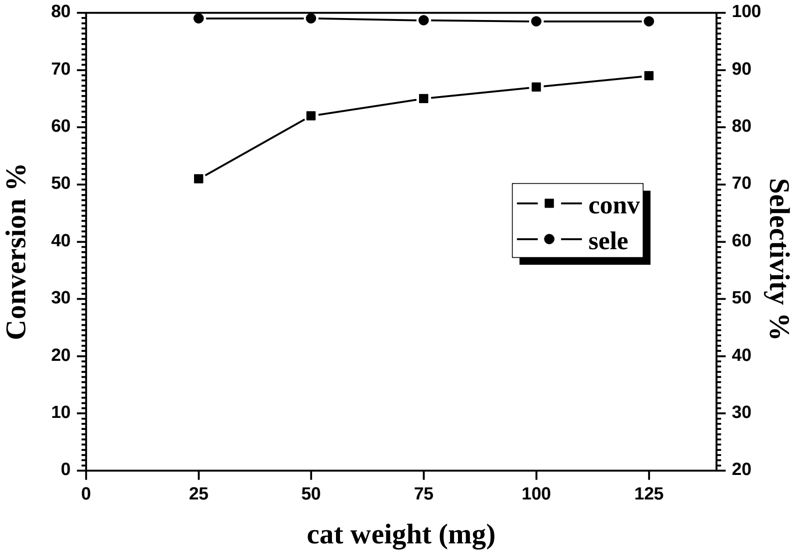


Fig. 3.8: Conversion of the bromobenzene over Pd-OMS with different catalyst weight

<u>Reaction conditions</u>: Pdcat-II (50 mg, 0.0093 mmole), Bromobenzene (1 mmol), Styrene (1.2 mmol), K_2CO_3 (1.2 mmol), DMF (4 mL), 408 K, 24h, Ar atmosphere.

3.4.1.2. Effect of catalyst weight

Fig 3.8 shows the influence of catalyst weight on conversion of bromobenzene and selectivity to the desired product. Results show that as the catalyst weight increases, conversion increases rapidly in the beginning, till the catalyst weight reaches to around 75mg, beyond which the change was not significant. However, selectivity to the desired product does not change on similar lines. Maximum desired product selectivity was obtained, around 99%, when the catalyst was about 25mg, which slightly decreased when the amount of catalyst increased, which flattened beyond 100mg catalyst weight.

3.4.1.3. Effect of temperature and Pd metal content in the catalyst

Influence of temperature on substrate conversion, selectivity and yield of the product is given in Table 3.3 (rows 1-3). No product was observed, when the reaction was carried out at 373 K using styrene and bromobenzene as reactants. However, on increasing the temperature further, the conversion increased. The bromobenzene conversion was 62 % at 408 K which was raised to 98.9%, when the reaction temperature increased to 423 K. As a result, stilbene yield also increased from 61.7% at 408 K to 90.1% at 423 K.

Table 3.3- Effect of temperature and Pd loading in Pd-K-OMS-2 on Heck reaction

S. No.	-R	-X	[a]Conversion of Bromobenzene (mol %)	Selectivity (mol %)	Yield (mol %)
1	-H	-Br	--	--	-- [b]
2	-H	-Br	62.0	99.0	61.7
3	-H	-Br	98.9	91.0	90.1[c]
4	-H	-Br	50.7	90.0	37.0 [d]
5	-H	-Br	58.3	95.0	55.4 [e]
6	-H	-Br	-	-	- [f]

Reaction conditions: Pdcat-II (50 mg, 0.0093 mmole), Aryl halide (1 mmol), Styrene (1.2 mmol), K_2CO_3 (1.2 mmol), DMF (4 mL), Reaction temp. 408 K, 24h, Ar atm, [a] Conversion and yields based on GC analysis, [b]Temp 373 K; [c]Temp 423K; [d] Pdcat-I; [e] Pdcat-III; [f] with Parent K-OMS-2.

The influence of Pd wt% in the catalyst was also studied, results of which are compared in Table 3.3 (rows 2, 4 & 5). The reaction was carried out efficiently with very small amount of the catalyst (0.0049 mmole of Pd) under optimized reaction conditions with 37 % yield and 90% product selectivity. As increasing the amount of the catalyst, the yield of the product enhanced. Catalysts, Pdcat-II with 1.89 wt% Pd showed relatively higher (62%) conversion as well as selectivity for product [68]. But on higher Pd loading (Pdcat-III catalyst), the conversions of bromobenzene was slightly dropped to 58.3% with slight decrease in stilbene selectivity (95%). No bromobenzene conversion was observed, when the reaction was carried out in the absence of metal KOMS-2 as catalyst, showing the role of Pd in the catalyst.

3.4.1.4. Heck reaction of different arylhalides with styrene over Pdcat-II

The reaction results of different aryl halides with styrene on Pd supported KOMS-2 catalysts is given in Table 3.4. Reaction results were compared at 408 K with DMF as solvent and K_2CO_3 as base. A slight excess (20%) of styrene was used for all the experimental runs. Results show that Pd-K-OMS-2 catalysts not only give good conversion of the substrates, even the product selectivity was very high. The reactivities of the different halobenzenes expectedly follow the order: iodobenzene > bromobenzene > chlorobenzene. When iodobenzene was the substrate; conversion was in the range of 97% with 95% stilbene yield. For bromobenzene, conversion was lower at 62% with 99% selectivity to stilbene. However, no reaction was observed, under the given reaction conditions, when chlorobenzene was used.

Table 3.4- Heck reaction of different arylhalide with styrene over Pd-OMS

S. No.	-R	-X	^{a}Conversion of arylhalide (mol %)	Selectivity (mol %)	Yield (mol %)
1	-H	-I	97.0	97.9	94.9
2	-H	-Br	62.0	99.0	61.7
3	-H	-Cl	--	--	--
4	$-OCH_3$	-Br	40.0	93.3	35.5
5	$-COCH_3$	-Br	90.0	100	90.0
6	-F	-Br	96.0	100	96.0

Reaction conditions: Pdcat-II (50 mg), Aryl halide (1 mmol), Styrene (1.2 mmol), K_2CO_3 (1.2 mmol), DMF (4 mL), 408 K, 24h, Ar atm. ^{a}Conversion and yields based on GC analysis.

There was strong influence of substituent groups on the bromobenzene, as the presence of electron withdrawing groups at p-position helps to activate the bromobenzene, while reverse effect was observed with electron donating groups [69]. The electron withdrawing $–COCH_3$ group at p-position helped to improve the conversion to 90% with 100% selectivity to the desired product by activating bromobenzene. Whereas, presence of $-OCH_3$ group on the ring led to substantial fall in conversion to 40% as compare to the non activated bromobenzene. These results are in good agreement with the reported results [70].

3.4.1.5. Effect of solvent on Heck reaction

Table 3.5- Heck reaction with different solvent

S. No.	Solvent	Conversion of Bromobenzene (mol %)	Selectivity (mol %)	Yield (mol %)
1	DMF	62.0	99.0	61.7
2	DMA	64.9	96.0	62.3
3	NMP	59.1	93.9	55.5
4	Toluene	--	--	--
5	p-xylene	--	--	--

Reaction conditions: Pdcat-II (50 mg), Bromobenzene (1 mmol), Styrene (1.2 mmol), K_2CO_3 (1.2 mmol), Solvent (4 mL), 408 K, 24h, Ar atm.

Generally, the organic transformations are performed in solution, which brings the reactants and catalysts in one phase and delivers the thermal energy needed for the reaction [71]. The choice of solvent may affect the reaction activity and selectivity. So, in Pd catalyzed C-C coupling reactions choice of the solvent is important and it must dissolve both non-polar and polar organic reactants, inorganic bases and catalyst if it is organometallic complexes [72]. Different polar aprotic and non polar solvents were used as shown in Table 3.5. Among polar aprotic solvents, DMF gives good results when bromobenzene was reacted with styrene; the substrate conversion was 62% with 61.7 % yield of product. When reaction was carried out in DMA, marginally higher yield of product (62.3%) was achieved, inspite of a small drop in selectivity (96%), using NMP as solvent lower substrate conversion (59.1%) and 93.9% product selectivity was observed. No substrate conversion was observed, when reaction is carried out in non-polar solvents such as toluene and p-xylene.

3.4.1.6 Heck reaction of different olefins with bromobenzene over Pdcat-II

The reactivity's of different olefins with bromobenzene are compared in Table 3.6. The results show that there were only slight differences in terms of activity and selectivity when different olefins are used. Styrene was found to be slightly better in terms of activity and selectivity among the olefins tested, with 62% conversion of bromobenzene and 99% selectivity to the desired product. The next best conversion of 60.9% and product yield of 59.7% was obtained for ethyl acrylate.

Table 3.6- Heck reaction of different olefins with bromobenzene

S. No.	Olefin	Conversion of Bromobenzene (mol %)	Selectivity (mol %)	Yield (mol %)
1	Styrene	62.0	99.0	61.7
2	Methyl acrylate	58.6	98.1	57.4
3	Ethyl acrylate	60.9	98.0	59.7

Reaction conditions: Pdcat-II (50 mg), Bromobenzene (1 mmol), Olefin (1.2 mmol), K_2CO_3 (1.2 mmol), DMF (4 mL), 408 K, 24 h, Ar atm.

3.4.1.7 Recycle study

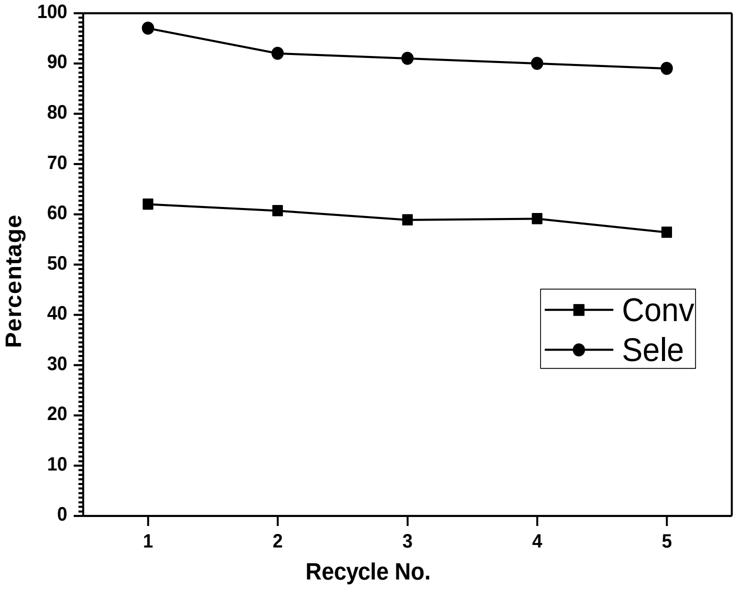


Fig 3.9: Recycle study of catalyst for Heck reaction

To study the recyclability of the catalyst for the heck reaction, Pdcat-II was separated by filtration after the reaction, washed with dichloromethane till it is free from organic substrate and dried in air. This catalyst was re-used for the reaction with fresh reactants and base. The ratio of catalyst to substrate and base was maintained in all subsequent runs. Thus we have conducted reaction up to 5 cycles. The results are shown in Fig. 3.9. The activity slightly dropped with each consecutive cycle, with minor change in selectivity for all the consecutive runs. However, we did not observe any leached Pd in the reaction mixture. The results show that slight drop in conversion could be due to small reduction in activity with each cycle. The results show that it is possible to recycle the catalyst after a thorough wash of the used catalyst.

3.4.2. Suzuki reaction

Suzuki coupling reaction is another Pd-catalyzed important methodology for the C-C cross bond formation to yield diaryl as the main product. The diaryl containing compounds are more useful in biological active complexes, drug molecules. Suzuki reaction was carried out on Pd-K-OMS-2 catalysts at room temperature, by reacting bromobenzene with boronic acid in presence of a base. Reactions were carried out in 1:1 (volume) mixture of water and organic solvent using 50mg of Pdcat-II.

3.4.2.1. Effect of Pd content in Catalyst

Table 3.7- Effect of Pd loading in Pd-K-OMS-2 on Suzuki reaction

S. No.	Catalyst	Conversion of Bromobenzene (mol %)	Selectivity (mol %)	Yield (mol %)
1	Pdcat-I	92.3	69.4	64.1
2	Pdcat-II	93.1	99.2	92.9
3	Pdcat-III	92.8	81.8	75.9
4	KOMS-2	--	--	--[a]
5	Pdcat-II	--	--	--[b]

Reaction conditions: Catalyst (50 mg), Bromobenzene (0.5 mmol), Phenylboronic acid (0.7 mmol), K_2CO_3, (2 mmol), (1:1) DMF: H_2O (4 mL), 303 K, Time 2h. [a]K-OMS-2 as catalyst, [b]without bromobenzene.

The influence of Pd wt% in the catalysts was studied and reported in Table 3.7. The Pdcat-II catalyst with Pd content of 1.89 wt. % gave 92.9% yield with 100% selectivity for diaryl product as compared to Pdcat-I (64.1%) and Pdcat-III (75.9%) with Pd wt% of 0.98 and 2.78 respectively. Though the bromobenzene conversion was nearly same on all the three catalysts, the diaryl product selectivity was lower on Pdcat-I at 69.4% and Pdcat-III at 81.8% as compared to catalyst Pdcat-II (99.2%).

No reaction occurred when bromobenzene was reacted with phenylboronic acid using K-OMS-2 as catalyst, demonstrating the importance of Pd as a catalyst component. No homo coupling product of phenylboronic acid was observed when the reaction was carried out in absence of aryl halide. This indicates that the product was obtained by cross coupling reaction and not by homocoupling.

Table 3.8- Effect of base on conversion of bromobenzene

S. No.	Base	Conversion of Bromobenzene (mol %)	Diaryl product (mol %)	
			Selectivity	Yield
1	NaOAc	40.9	72.9	29.8 [a]
2	KOH	17.8	60.7	10.8 [a]
3	$NaHCO_3$	65.1	89.6	61.8
4	Na_2CO_3	88.4	99.1	87.6
5	K_2CO_3	93.1	99.2	92.9
6	Cs_2CO_3	90.0	100	90.0
7	Rb_2CO_3	91.7	100	91.7

Reaction conditions: Pdcat-II (50 mg) Bromobenzene (0.5 mmol), Phenylboronic acid (0.7 mmol), Base (2 mmol), 4 mL of (1:1) DMF: H_2O, 303 K, 2h, [a]5h.

3.4.2.2. Effect of base

The results of Suzuki coupling reaction, carried out on Pdcat-II catalyst, using different bases is given in Table 3.8. Results show that among the bases used in this study, carbonate bases gave better yields (rows 3-7) under the optimized reaction conditions.

In Pd-catalyzed C-C cross coupling reaction requires an addition of a base to maintain the catalytic cycle and as expected stronger base gives the higher conversion of substrate [67]. The Cs_2CO_3 and Rb_2CO_3 showed 100% selectivity to coupling product, though conversions were slightly lower as compared to the run with K_2CO_3 as the base. The product yield was slightly higher due to marginally higher conversion of bromobenzene. These results are similar to the results reported in the literatures [67, 73]. When NaOAc and KOH were used both the conversion and yield of product decreased substantially as compared to carbonate bases.

3.4.2.3. Effect of solvent

Influence of organic solvent on product yields, during Suzuki coupling are shown in Table 3.9. The reaction rates are expected to be enhanced if polar solvents are used [74].

Table 3.9- Effect of solvent in Suzuki reaction on Pdcat-Ii catalyst

S. No.	Organic Solvent (H_2O: X)	Conversion of Bromobenzene (mol %)	Diaryl product (mol %) Selectivity	Diaryl product (mol %) Yield
1	DMF	93.1	99.2	92.4
2	DMA	71.0	100	71.0
3	Ethanol	48.2	81.0	39.3[a]
4	CH_3CN	18.5	96.0	17.8[a]
5	Dioxane	13.0	40.0	5.2

Reaction conditions: Pdcat-II (50 mg), Bromobenzene (0.5 mmol), Phenylboronic acid (0.7 mmol), K_2CO_3 (2 mmol), (1:1) Solvent (4 mL), 303 K, 2h, [a]Reaction time 5h.

It was found that reaction proceeded when ethanol, CH_3CN, DMA, dioxane and DMF were used as co-solvents. Dimethyl formamide, a polar aprotic solvent was found to be the best with 93.1% conversion of bromobenzene and 99.2% product selectivity (row 1). The other polar protic solvent DMA is the next best with 72% conversion and 71% yield. On the other hand, protic solvent such as ethanol, acetonitrile and dioxane gave poor yield of products (rows 3, 4 & 5).

3.4.2.4. Effect of water to co-solvent ratio

The organic to water solvent volumetric ratio has considerable influence on product yields during Suzuki cross-coupling, as shown in Table 3.10. The higher or lower water content in the solvent mixture had an adverse effect. The best volumetric ratio of this mixture was found to be 1:1, wherein the product yield was 92.4% with 93.1% conversion. The product yield decreased to 70%, when the reaction was carried out in DMA alone, while it is still lower at 15%, when water was exclusively used as solvent. However, the second best yield (78.3%) was obtained when 2:1 water to DMF was used. On the other hand, when a 1:2 mixture rich in DMF was used, the product yield was only 64.2%.

Table 3.10- Effect of water to co-solvent ratio on Suzuki reaction

S. No.	Solvent ratio (H_2O: DMF)	Conversion of Bromobenzene (mol %)	Diaryl product (mol %)	
			Selectivity	Yield
1	2:1	78.3	100	78.3
2	1:0	47.0	32.3	15.2
3	1:1	93.1	99.2	92.4
4	0:1	70.8	100	70.8
5	1:2	64.2	100	64.2

Reaction conditions: Pdcat-II (50mg), Bromobenzene (0.5mmol), Phenylboronic acid (0.7mmol), K_2CO_3 (2mmol), (1:1) DMF: H_2O solvent (4 mL), 303 K, 2h.

3.4.2.5. Recycle study

To confirm, whether the reaction is purely heterogeneous or the leached Pd metal is contributing for the reaction, the catalyst was separated by filtration after reaction and the filtrate was analyzed for presence of Pd. We did not find any Pd in the filtrate, confirming the reaction as truly heterogeneous.

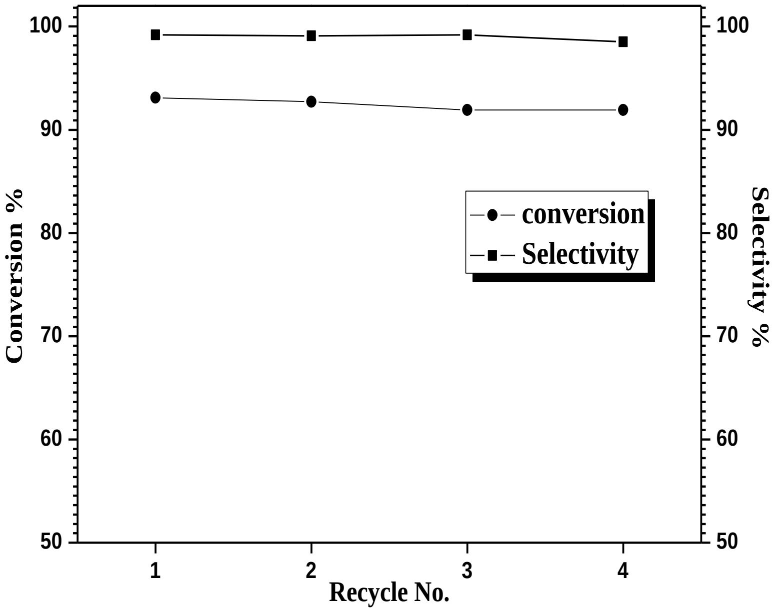


Fig. 3.10: Recycle study of catalyst

Catalytic activity in Suzuki reaction, after each repeated use is plotted as shown in Fig.3.10. As described for Heck reaction, the catalyst after filtration was washed with DCM before its use for its next run of the reaction. The results show that the activity of the catalyst remained more or less similar, showing that the catalyst can be re-cycled without any loss of activity. Even the yields of product are expected to remain same, as no change in product selectivity was observed.

3.4.3. Sonogashira reaction

The Sonogashira reaction presents one of the most powerful technique and simplest ways to obtain various substituted acetylenes. This is more useful in the preparation of drug and biologically active compounds. Sonogashira coupling reaction was carried out on Pd-K-OMS-2 catalysts at 353 K temperature in IPA+ H_2O mix solvent. Iodobenzene and phenyl acetylene were used as starting substrates with base.

3.4.3.1. Effect of catalyst concentration

Pd exchanged octahedral molecular sieve catalysts with three different Pd contents (0.98, 1.89 and 2.78 wt %) were used in this study. Reaction of iodobenzene with phenylacetylene was chosen as the model reaction to test the catalytic activity of the samples to start with. The catalytic activities of these catalysts are given in Table 3.11. All the catalysts gave moderate conversion of iodobenzene with better selectivity for coupling product-diphenyl acetylene (above 95%).

Table 3.11- Effect of Pd content of conversion of iodobenzene

S. No.	Catalyst	Conversion of Iodobenzene (mol %)	Selectivity (mol %)	Yield (mol %)
1	Pdcat-I	36.9	96.1	35.5
2	Pdcat-II	39.3	97.8	38.4
3	Pdcat-III	37.8	95.8	36.3

Reaction conditions: Catalyst (50 mg), Iodobenzene (1 mmol), Phenyl acetylene (1.2 mmol), K_2CO_3 (1.4 mmol), 4 mL of iPrOH:H_2O (3:1), 353 K, 24h.

The catalytic activity of the catalyst with 1.89 wt % (Pdcat-II) loading was relatively higher among all three catalysts. Conversion and selectivity has increased initially with Pd content, however, the variation was very small. Pdcat-II gave maximum conversion of iodobenzene at 38.4% yield and > 97% for product selectivity with potassium carbonate as base. However, both the conversion and selectivity decreased at higher loading of Pd. Pdcat-I with palladium 0.98 wt % gave 36.9% and Pdcat-III with palladium 2.98 wt % gave 37.8% conversion with iodobenzene as substrate.

3.4.3.2. Effect of base

Influence of different bases for the Sonogashira reaction was studied using Pd-cat-II catalyst; the results are shown in Table 3.12. Various bases such as Na_2CO_3, K_2CO_3, NaOAc, Et_3N, Cs_2CO_3 and Rb_2CO_3 were examined for the reaction.

Table 3.12- Effect of different base on conversion

S. No.	Base	Conversion of Iodobenzene (mol %)	Selectivity (mol %)	Yield (mol %)
1	NaOAc	2.8	75.8	2.1
2	Na_2CO_3	13.1	95.2	12.5
3	K_2CO_3	39.3	97.8	38.4
4	Cs_2CO_3	41.2	98.5	40.5
5	Rb_2CO_3	45.8	98.9	45.3
6	NEt_3	35.9	96.6	34.7

Reaction conditions: Pdcat-II (50 mg), Iodobenzene (1 mmol), Phenyl acetylene (1.2 mmol), Base (1.4 mmol), 4 mL of iPrOH:H_2O (3:1), 353 K, 24h.

The results show that when inorganic bases are used, the conversion of substrate and selectivity to desired product was higher compared to organic bases like Et_3N. Among the inorganic bases used stronger base such as Rb_2CO_3 gave the highest conversion of 45.8% with 98.9% selectivity to the product. When K_2CO_3 was used as base in place of Rb_2CO_3, conversion of iodobenzene has decreased to 39.3% with slightly lower yield of product. Slightly lower conversion of iodobenzene (35.9%) and 96.6 % selectivity of product was obtained for organic base (NEt_3).

3.4.3.3. Effect of solvent

Different solvents were investigated in Sonogashira reaction to study the influence of solvent on conversion and product yields of aryl halide. The results are shown Table 3.13. It was reported that the use of polar solvents, usually have a beneficial effect on Sonogashira coupling [75]. Among the protic polar solvent used, isopropanol with water as co-solvent in 3:1 ratio was found to be good with 39.3% conversion of iodobenzene and 97.8% product selectivity. Whereas decrease in conversion and yield were observed, when more polar ethanol and methanol solvents were used instead of IPA.

Table 3.13- Effect of different solvent on Sonogashira reaction

S. No.	Organic Solvent (H_2O: X)	Conversion[a] of Iodobenzene (mol %)	Selectivity (mol %)	Yield (mol %)
1	iPrOH:H_2O	39.3	97.8	38.4
2	EtOH:H_2O	29.5	98.0	28.9
3	MeOH:H_2O	23.5	95.6	22.5
4	DMF:H_2O	21.0	96.3	20.2
5	DMA: H_2O	19.9	97.0	19.3
6	NMP: H_2O	20.2	94.1	19.0

Reaction conditions: Pdcat-II (50 mg), Iodobenzene (1 mmol), Phenyl acetylene (1.2 mmol), K_2CO_3 (1.4 mmol), 4 mL of solvent (3:1), 353 K, 24h.

The reaction was also carried out with polar aprotic solvents. As compared to polar protic solvents they resulted in lower yield of iodobenzene. Among the polar aprotic solvents, DMF with water as co-solvent gives 21 % conversion of iodobenzene with 96.3% product selectivity, whereas slight decrease in conversion was observed for DMA and NMP solvent with 97 and 94.1% product selectivity respectively.

3.4.3.4. Sonogashira reaction of different aryl halides with phenylacetylene on Pdcat-II

Table 3.14- Effect of different aryl halide on sonogashira reaction

S. No.	Type of halo aryl	Conversion of arylhalide (mol %)	Selectivity (mol %)	Yield (mol %)
1	Iodobenzene	39.3	97.8	38.4
2	Bromobenzene	32.2	94.0	30.3
3	Chlorobenzene	--	--	--
4	p-bromo toluene	26.1	93.2	24.3
5	p-bromo nitrobenzene	36.0	94.5	34.1

Reaction conditions: Pdcat-II (50 mg), Arylhalide (1 mmol), Phenyl acetylene (1.2 mmol), K_2CO_3 (1.4 mmol), 4 mL of iPrOH: H_2O (3:1), 353 K, 24h.

The reaction results of different aryl halides with phenylacetylene on Pd exchanged KOMS- 2 are given in Table 3.14. Reaction was carried out at 353 K with IPA:H_2O (3:1) as solvent using K_2CO_3 as base. The reactivities of the different halobenzenes were found in the order of iodobenzene > bromobenzene > chlorobenzene. When iodobenzene was the substrate; conversion was around 39.3% with 38.4% product yield. Whereas, when reaction was carried out with bromobenzene as substrate, conversion decreased to 32.2% with 94.0% product selectivity and 30.3 % yield.

No reaction took place under the used reaction conditions, when chlorobenzene was the substrate, even after increasing reaction temperature to 373K. Electron withdrawing group on bromobenzene at p- position increased the yield of product (34.1%) with 36% conversion of substrate; whereas reverse effect was observed with electron donating group resulting into 24.3% yield of product and 26.1% conversion.

3.4.3.5. Recycle study

To confirm, whether the reaction is purely heterogeneous or the leached Pd metal is contributing for the reaction under used reaction conditions, the catalyst was separated after each reaction and the filtrate was analyzed for presence of Pd. The filtrate doesn't contain any Pd species, which confirms the reaction as truly heterogeneous. Catalytic activity in Sonogashira reaction, after each repeated use is plotted and shown in Fig. 3.11.

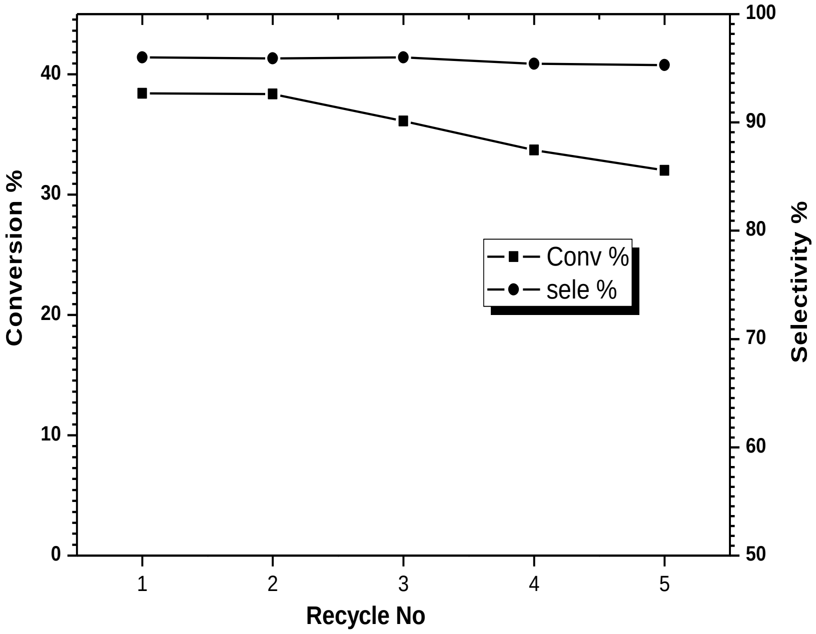


Fig. 3.11: Recycle study of catalyst Pd-cat-II

As described for Heck reactions, the catalyst was separated by hot filtration and washed with DCM before its use for its next run of the reaction. The results show that the catalyst for sonogashira reaction was recycled at least five times with more or less similar activity of the catalyst, showing that the catalyst can be re-cycled with any marginal loss of activity. The slightly decrease in conversion may be due to loss in weight of catalyst during recycling of catalysts, as no change in product selectivity was observed.

3.5. Conclusions

In conclusion, palladium containing octahedral molecular sieves with different palladium concentrations as catalysts was prepared successfully by reflux method followed by exchange and reduction of palladium with potassium ion of OMS-2 material and characterized by many physicochemical techniques. X- ray diffraction patterns showed that, in all cases the presence of well sharp peaks even after exchanging of palladium ion. The XRD of spent catalyst didn’t show any change confirms the stability of catalyst under used reaction conditions. SEM images show fibrous nature of OMS-2 and all catalysts and it also confirmed with TEM images which results in needle type along with the formation and fine dispersion of nano palladium particle on OMS material, which is useful to enhance the activity of catalyst.

The versatility and efficiency of the Pd-OMS catalyst for carbon-carbon bond formation reaction is thus demonstrated. This ligand free heterogeneous catalyst can be more advantageous to use than the other reported Pd-based catalysts for the reaction due to ease of separation and reuse besides good yields of the products. The reaction is found to proceed mainly by the heterogeneous route. The easy recoverability of the catalyst with efficient recyclability makes it a good catalyst for C-C bond formation reactions.

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Chapter-IV

C-O & C-S cross coupling reactions

Immobilized copper imine on mesoporous SBA-15 as catalyst for C-O and C-S cross coupling reactions

4.1. Introduction

Transition-metal catalysts are powerful tools for cross-coupling reactions, particularly for the formation of carbon‒heteroatom bonds [1]. Among these, C-O and C-S bond formations have received great attention due to the requirement of these bonds in many important chemical intermediate that include biological, pharmaceutical and other materials of interest [2]. Since, the discovery of the Ni catalyzed reaction of Grignard reagent with alkenyl or aryl halide in 1972 [3], there have been numerous reports of organometallic reagents, that are useful in various cross coupling reactions. But during the last few decades, cross coupling reactions were more closely identified with Pd catalysts, because of remarkable developments that have happened in case of Pd-catalyzed C-C and C-heteroatom bond formations. Organometallic Pd complexes show a range of activity e.g., transmetallation, β-hydride elimination and reductive elimination [4]. Pd based catalysts have ability to accept different functional groups e.g., heteroatom, acidic, basic and carbonyl groups. Hence, with proper choice of ligands and nucleophiles; C-C, C-H, C-N, C-O and C-P bonds can be formed.

Prior to Pd being used as a catalyst for coupling reactions, Cu was in use for cross-coupling reactions. Cu-catalyzed arylation of nucleophiles (Ullmann, Ullmann-Goldberg and Ullmann- Hurtley condensations) is known for more than a century as one of the most useful and practical methods in the formation of C-N, C-C and C-O bonds [5]. These reactions have many important industrial applications e.g. synthesis of intermediates as well as synthetic targets, which are useful in life science and polymer applications. Though Cu was used for coupling reactions over a century, it has several drawbacks e.g. harsh reaction conditions, limited substrate range and moderate yields. These reactions were traditionally operated at temperatures as high as 483 K, in the presence of stoichiometric amounts of copper reagents and preferentially with activated aryl halides [5].

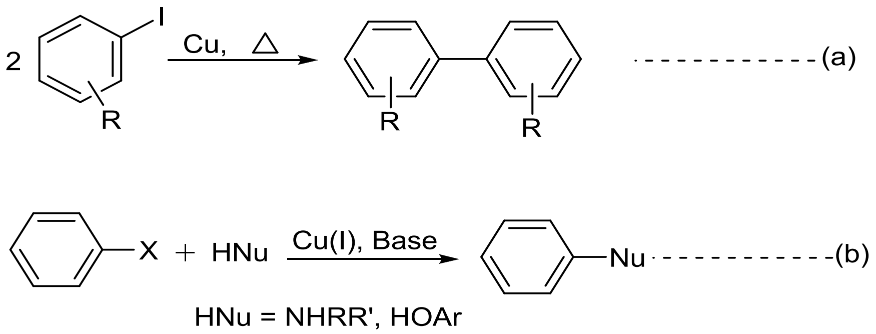
During the last few years, a lot of interest was generated in Cu catalyzed C-O, C-S and C-N bond formations with modified procedure e.g. addition of additive [6], which was reported to increase catalyst solubility and stability. In 2001, Taillefer and

Buchwald independently [7] reported new methodologies using copper/ligand complexes, which became versatile and very efficient for C-C, C-N or C-O coupling reactions. The important aspect of this methodology was the use of catalytic amount of copper under very mild reaction conditions (263-383 K). Since then, many researchers showed greater interest in Cu catalyzed Ullmann-type reactions and in the development of new Cu/Ligand systems to improve variety and efficiency of the coupling reactions. Cu-catalyzed heteroatom cross-coupling reactions are expected to be good to complement those organic transformations that are catalyzed by Pd, because of its low cost and functional group compatibility.

4.1.1. C-O cross coupling

As discussed in the introduction, the transition–metal catalyzed aryl carbon-carbon and carbon–heteroatom bond forming reaction are important basic transformations in synthetic chemistry [8]. The C-O cross coupling for diaryl ether bond formation, is a straightforward method in organic synthesis [9]. Diaryl ethers are not only useful for drug intermediates synthesis but also useful for biologically important compounds [10] and industrial polymers [11]. Professor Fritz Ullmann [12], in 1903, for the first time reported Cu-catalyzed reactions of aryl halide with salts of phenols to give diaryl ether and aryl halide with aryl amine/N-acyl aryl amines to give N-aryl aryl amine.

The Cu-catalyzed "Ullmann-type" reactions are classified into two different categories. The first one, known as "classic" Ullmann Reaction, is the synthesis of symmetric biaryls from aryl halide (Scheme 4.1a). The second type is Cu-catalyzed nucleophilic aromatic substitution between various nucleophiles (e.g. substituted phenoxides) with aryl halides (Scheme 4.1b). The most common of these is the Ullmann Ether Synthesis (C-O coupling). Synthetic chemists have devoted considerable attention to develop and modify methodologies for the preparation of diaryl ethers [13] using Ullmann’s method. The increased attention for this reaction might have arisen due to the need of ‘ether’ functional group in vancomycin and other important antibiotics.



Scheme 4.1: Ullmann cross coupling

Though classical 'Ullmann' reaction proves to be a good method, it requires harsh reaction conditions as a result of poor nucleophilicity of the phenoxide and low reactivity of aryl halide [14]. Required conditions for this reaction are temperature in the range 393-523 K, high boiling strong polar and often toxic solvents [15] or neat reagents and an extended period of reaction time. These reaction conditions probably lead to additional problems, i.e., the formation of isomeric biaryl compound via substitution through an elimination-addition mechanism and reductive homocoupling of aryl halide [16]. In addition, these reactions often require the use of stoichiometric amounts of copper reagent, which leads to the generation of waste that need to be disposed-off.

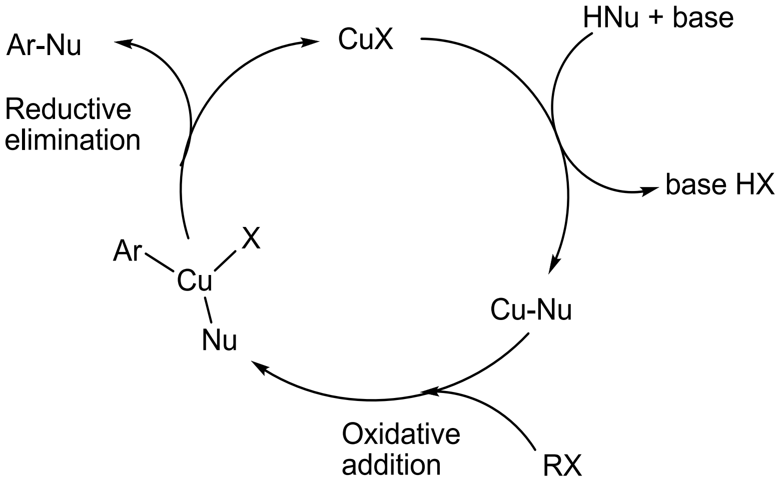
Mann and Hartwig [17] reported a Pd-catalyzed coupling reaction between sodium phenoxide and electron deficient aryl bromide based on an in-situ ligand exchange of dibezylideneacetone (dba) with 1, 1, diphenylphosphannyl-ferrocene. Later, Buchwald reported C-O coupling of aryl halide and phenol using Pd catalyst in the presence of electron rich 2-(di-tert-butyl phosphino) biphenyl as a ligand [18]. The ability of Pd based catalysts to efficiently promote coupling reaction of phenol with arylhalide has been reported [19]. However, the use of expensive Pd and moisture sensitive phosphine ligands limit the attractiveness of this method for industrial application. Critical requirements for development of an industrial process are reliability, ease with which experiment can be carried out and most importantly low catalyst cost. Similar to Pd, Ni and Cu catalysts also mediate nucleophilic aromatic substitution with aryl halides and have attracted more interest [20]. In view of the cost and industrial utility, Cu-based catalyst systems make the cut for large-scale industrial applications. There are reports on use of copper (II) triflate and simple Copper (II) acetate in C-O coupling reaction [21] as well as Cu catalyst with use of microwave [22], ultrasonic irradiation [23] and ionic liquids [24] as reaction conditions.

However, the reagents used are in stoichiometric quantities, air sensitive ligands, high cost and low atom efficiency. Since then, considerable efforts have been made to have more efficient and simple Cu-catalyzed Ullmann O-arylation methods e.g. the use of additives, such as Chxn–Py–Al, N,N-dimethylglycine, 2,2,6,6-tetramethylheptane-3,5-dione, 1,10-phenanthroline or neocuproine and phosphazene P4–^{t}Bu. Probably they act as ligands, enhance reaction rates and facilitate the couplings at milder temperatures while using only catalytic amounts of copper [25]. The high cost of transition metals and their toxicity led to an increased interest in immobilization of catalysts onto a support. These supports not only help in facilitating the isolation of metal sites, but also help in recycling the catalysts through simple filtration. This helps in achieving environmentally cleaner [26-27] and green alternative processes, instead of homogenous catalyzed processes. In recent years, more interest in this area has led to the development of better heterogenized catalysts using different supports with high surface area. Also for immobilization or grafting of metal/metal complexes, polymeric materials were used as supports [28]. Chiang and group have reported immobilization of Cu onto modified Wang resin, a polymer, which improves the workup procedure associated with preparation of polymer supported Pd catalyst [29].

There are also reports on the use of carbon black and charcoal for immobilization of CuO hollow nanospheres for N-arylation of heterocycles with aryl halides [30], in addition to, sol gel immobilization of copper [31]. In recent years, mesoporous silica materials e.g. MCM- 48, SBA-15, silica gel etc., were used as support for the immobilization. They have good stability, high surface area and larger pores [32], leading to high dispersion of active sites, diffusion of reactant molecules. This is also useful in view of the industry seeking more environmental friendly chemical manufacturing processes [33].

4.1.1.1. Reaction mechanism

Similar to the other cross coupling reactions, as discussed in chapter–III, the reaction mechanism of C-O bond formation also goes through oxidative addition and reductive elimination. A general catalytic cycle for the Ullmann (C-O) coupling reaction is given in Scheme 4.2



Scheme 4.2: Catalytic cycle

4.1.2. C-S cross coupling

Cross-coupling reactions of aryl halides with various nucleophilic compounds using transition metal catalysts are the most prominent synthetic methods for the formation of carbon-heteroatom bonds [34]. Among these, the formation of C-S bond has received much attention for the synthesis of molecules with biological, pharmaceutical and materials applications [35].

A large variety of aryl sulfides are in use for diverse clinical applications such as the treatment of Alzheimer's and Parkinson's diseases, treatment of cancer and also for treatment of HIV. Traditional methods of diaryl sulfide synthesis involve the use of (i) Grignard reagents, (ii) organo-cuprates; (iii) Friedel crafts catalysts (iv) diazonium salts and (v) polar solvents. The above methods have certain drawbacks such as the need for activating the reagents (i, ii), lack of regioselectivity (iii, iv, vi), lower yields (v) and formation of side products.

The synthetic reaction involving sulfur-containing compounds need special attention as the sulfur functionality is known to be more reactive and may act as a poison for metal-based catalysts because of its strong coordinative properties to the metal, making the catalysts ineffective [36]. In 1980, Migita and co-workers reported the cross coupling of aryl halides with thiophenols in the presence of $[Pd(PPh_3)_4]$ as the catalyst and NaO^tBu as a base in polar solvents, such as ethanol under reflux conditions or dimethyl sulfoxide (DMSO) at 363 K [37]. Some research groups reported efficient catalysts containing Pd with bidentate or organophosphane for C-S coupling reactions. But they suffer from limitations, as the ligand used need to be prepared, involving a tedious procedure, while it is environmental unfriendly, restricting their applications in large-scale processes.

Recently, other metals like cobalt [38], nickel [39] etc. were studied for the catalytic carbon-sulfur bond formation. But, these systems too face similar common problems such as metal toxicity, low turnover numbers and reagents in excess. In recent years, ionic liquids also have become good solvent for organic transformations. Researchers have successfully used ionic liquids such as methylimidazolium {[Bmim]PF_6/H_2O} [40] and molten tetrabutylammonium bromide [41] for the addition of thiol to unsaturated ketones (C-S coupling). However, the cost of the ionic liquids and sometimes their toxicity limited their utility as the reaction medium [41]. Hence, there is interest to develop further, the classical Ullmann's coupling reaction, using cheaper metals (e.g. copper) for the preparation of the diaryl thioethers.

To overcome the drawbacks encountered for the C-S bond formation, such as requirement of large quantities of metal catalyst, short lifetime (and hence low turnover numbers) and harsh reaction conditions, various approaches were developed to come with a general and more efficient system for the preparation of diaryl thioethers. Cu catalysts mediate the C-S bond formation and this approach is attractive from an industrial perspective as Cu is cheap and less toxic than Pd or Ni [42]. The traditional Cu-catalyzed coupling between thiols and aryl halides requires the use of copper salts in more than stoichiometric amounts, high polar solvents and high temperatures (473 K) [43]. Examples of attractiveness of Cu-catalysts for C-S coupling reaction have recently been reported by Palomo [44], Venkataraman [45], Buchwald [46] and others [47]. More recently, simple copper halide salts with suitable ligands were used successfully by Domı´nquez [48] and Verma [49]. There are also reports of use of microwave irradiation in C-S coupling reactions catalyzed by homogeneous catalysts (Cu or Pd) with ligands [50]. However, reports of ligand-free copper catalyzed C–S coupling reactions are minimum e.g., Ranu *et al* reported ligand free copper nano particles as a catalyst in presence of microwave irradiation for C-S bond formation with base and DMF as solvent [51]. Some other groups also used same methodology using different reaction conditions [52]. Reddy *et al* reported use of indium oxide nanoparticles to catalyze C-S coupling reaction in presence of KOH as a base and

DMSO as solvent [53]. There were hardly any reports wherein heterogeneous copper catalysts were used for C-S cross coupling reactions [54].

In the next sections, we report copper immobilized on mesoporous SBA-15 as heterogeneous catalyst. Its characterization and catalytic activity in C-O and C-S cross coupling reactions have been reported.

4.2. Experimental procedures

4.2.1. Materials

P123 triblock co-polymer, aryl halide with different substituent groups, phenolic compounds and thiophenol were purchased from Sigma-Aldrich Corporation, USA. Copper acetate, phenol, potassium carbonate and dimethyl sulfoxide, toluene and other solvents were purchased from Loba Chemie Pvt. Ltd., India. The commercial solvents were dried using standard procedures before their use [55].

4.2.2. Preparation of catalysts

The Schematic representation of catalyst preparation is shown in scheme 4.3.

4.2.2.1 Preparation of mesoporous SBA-15

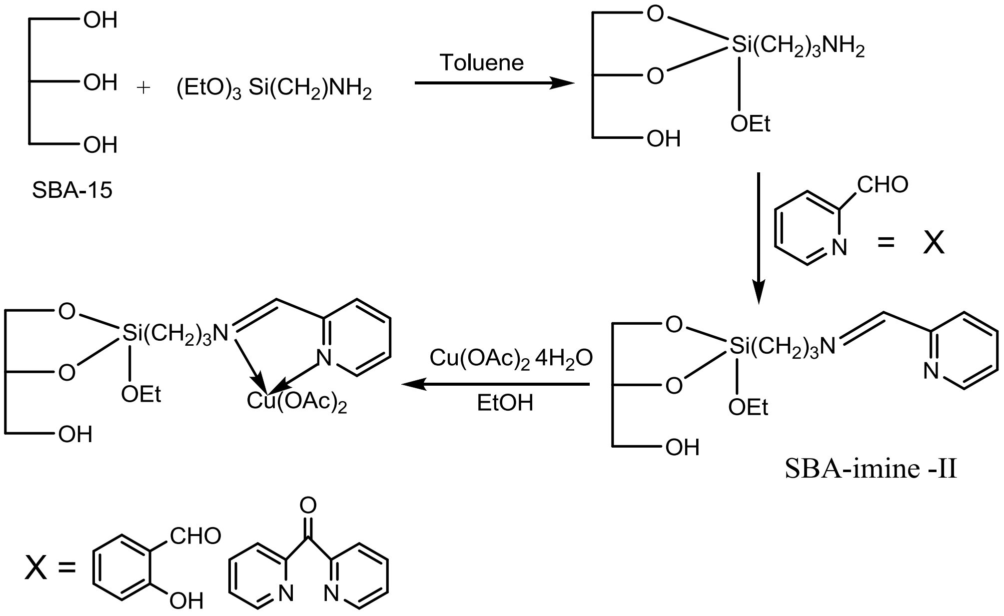
Mesoporous SBA-15 was synthesized according to a reported procedure by Zhao *et al* [56]. In a typical synthesis, 2g of amphiphilic tri-block copolymer, P123 [average molecular weight 5800, Aldrich], was dispersed in 15g of water plus 60g of 2M HCl solution with stirring. To this, 4.3g of tetraethyl orthosilicate (Aldrich) was added to get homogeneous mixture. This was continuously stirred at 313 K for 24h and subsequently loaded in a Teflon-lined autoclave at 373 K for 48h. After crystallization, the solid product was centrifuged, filtered, washed with deionized water and dried in air at 373K temperature. The product was calcined in air at 823 K for 24h to remove the tri-block copolymer to white crystalline powder (SBA-15).

4.2.2.2 Immobilization of Cu on modified SBA-15

A suspension of APTES (4.56g, 20.63 mmol) in 90 mL of toluene and 10g of calcined SBA-15 was refluxed under stirring in inert atmosphere for 24h. The resulting crystalline mass was cooled to room temperature and filtered. The solid was filtered and washed successively with dry toluene and diethyl ether with subsequent drying under vacuum at ambient. The dried material was subjected to soxhlet extraction with dry dichloromethane for 24h. Finally; the solid was dried at 323 K under vacuum for 8h.

In a round bottom flask, 3-aminopropyl functionalized SBA-15 (1g) and 2-carboxaldehyde pyridine (2 mmol) was added to ethanol and refluxed for 12h. After cooling the mixture, it was filtered and washed with sufficient ethanol and finally with acetone followed by drying at 333 K in oven. In a similar fashion, two more samples were prepared using salicyaldehyde and dipyridyl ketone in the place of 2-carboxaldehyde pyridine.

Immobilization of Cu was accomplished by stirring imine modified SBA-15 (1g) and copper acetate (1 mmol) in acetone at room temperature for 24h. The solid obtained was filtered and dried at 323 K in air. Two more catalysts were prepared using salicyaldehyde and dipyridyl ketone functionalized SBA-15 samples.



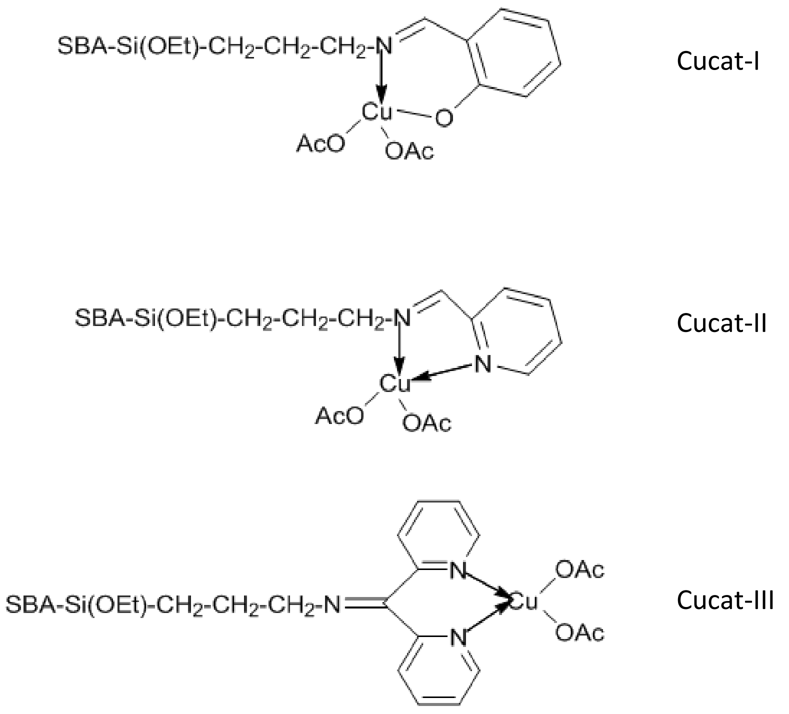
Scheme 4.3: Schematic representation of catalyst preparation

All the samples were dried and used for reaction as well as characterization. The sample prepared with salicyaldehyde, 2-carboxaldehyde pyridine and dipyridyl ketone as ligand was named as catalyst Cucat-I, Cucat-II and Cucat-III respectively (Scheme 4.4).

4.2.3. Characterization of catalysts

Powder XRD pattern of the samples was obtained using PANalytical X’Pert Pro diffractometer using Cu Kα radiation. The data was collected in the low angle region 0.5-5.0 θ. The atomic absorption spectrophotometric (AAS) analysis of the samples was carried out using Varian Spectra FS 220 instrument. The solution for AAS analysis was made by dissolving known amount of the catalyst in aq.HF and diluted with distilled water to 100 mL HDPE volumetric flask.

Specific surface areas of the catalysts were obtained by N_2 sorption at liquid N_2 temperature using a Quanta chrome Nova-1200 surface area analyzer employing multi point BET method. The catalyst samples were evacuated at 333 K for 3h at a residual pressure of $2x10^{-3}$ Torr prior to N_2 sorption. The isotherms were analyzed in conventional manner in the relative pressure region of $p/p^0 = 0.05$ to 0.30.



Scheme 4.4: Catalysts prepared with different imines

Transmission electron micrographs (TEM) of the catalysts were recorded on high-resolution transmission electron microscope (HR-TEM) Tecnai-T30 model at an accelerated voltage of 300 kV. Samples were prepared by placing isopropyl alcohol solution of the catalyst on carbon coated grids, followed by evaporation of the solvent at room temperature. Scanning electron micrographs of the samples were recorded using JEOL-JSM-5200 SEM to study the surface morphology. Thermal analysis of the samples was performed using a PerkinElmer Diamond TG/DTA instrument in air flow (ca. 50 mL min^{-1}). The samples were heated at a heating rate of 283 K min^{-1} in the temperature range 298-1273 K, while using α-Al_2O_3 as reference. For each analysis, about 10-20 mg of the sample was used. The IR analysis of catalysts was performed on Perkin-Elmer Spectrum GX spectrophotometer.

The reactions were monitored by GC (Varian CP-3800, capillary column, BP-5, 50m x 0.3 mm, FID detector). The temperature program used was initial 273 K, hold for one minute and heat to final temperature of 523 K at a heating rate of 293 K/min. The identification of product was done using GC-MS (Varian Saturn 2200).

4.3. General Procedure for testing catalysts in coupling reactions

4.3.1. C-O cross coupling reactions

In an oven-dried two-necked Schlenk flask equipped with a reflux condenser, 50mg of catalyst (0.020 mmole of Cu), 1.4 mmol of base, 1 mmol of aryl halide, 1.2 mmol of phenol and 4 mL of DMSO were introduced. Flask was de-aerated 2-3 times under vacuum and flushed with Argon. The flask with above reaction mixture was placed in a pre-heated oil bath at 393 K while stirring the mixture vigorously. Aliquots of sample were withdrawn at different intervals of time and analyzed using a GC. The products were also confirmed by GC-MS.

4.3.2. C-S cross coupling reactions

C-S cross coupling reaction was carried out in 25 mL of two neck Schlenk flask. The flask was charged with 50mg of catalyst (0.020 mmole of Cu), 1 mmol of aryl halide, 1.2 mmol of thiophenol, 1.2 mmole of base and 4mL of (DMA) solvent. The flask was de-aerated 2-3 times under vacuum and flushed with Argon. The flask with above reaction mixture was then placed in a preheated oil bath at 383 K with vigorous stirring. Aliquots of sample were withdrawn at different intervals of time and analyzed using a GC. The products were confirmed by GC-MS.

4.4. Results and Discussion

4.4.1. Characterization of catalysts

The as synthesized as well as modified catalysts were characterized to understand their texture and composition. Copper content of the catalysts was estimated using AAS, the results of which are given in Table 4.1.

Table 4.1- Physico-chemical and textural properties of materials and catalysts

S.No	Catalyst/Material	S.A. by BET (m^2/g)	Pore vol. cc/g	Pore diameter (Å)	Cu (mmol/g)
1	SBA-15	645	0.940	78.3	---
2	SBA-NH_2	409	0.670	70.3	---
3	SBA-imine-I	221	0.380	68.6	---
4	SBA- imine-II	226	0.383	68.0	---
5	SBA- imine-III	139	0.260	63.1	---
6	Cucat-I	214	0.339	63.4	0. 36
7	Cucat-II	174	0.313	61.9	0.41
8	Cucat-III	099	0.170	60.7	0.38

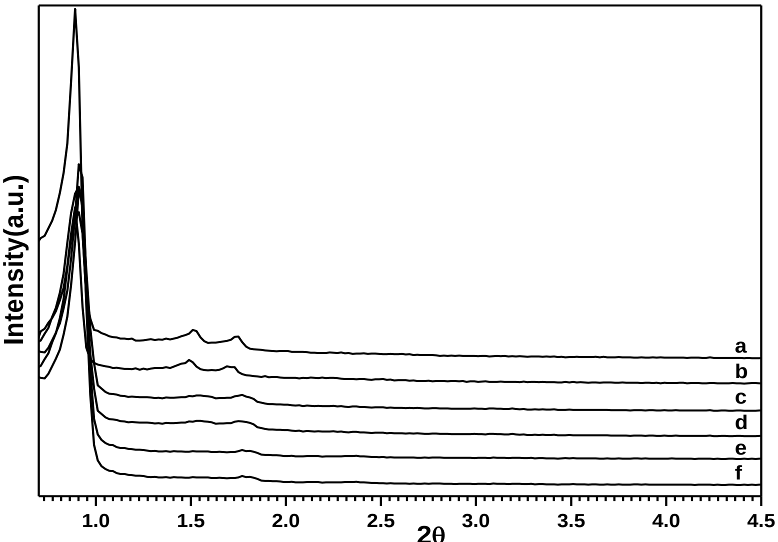


Fig. 4.1: XRD of (a) SBA-15 ; (b) SBA-NH_2 ; (c) Cucat-I ; (d) Cucat-II ; (e) Cucat-III and (f) Spent catalyst

4.4.1.1. X-ray diffraction

The powder XRD pattern of parent SBA-15 and the three supported Cu catalysts were shown in Fig. 4.1 The powder XRD pattern show well-resolved diffraction peaks at 0.93 (2θ) and less intense peaks at 1.5 and 1.8 (2θ) assigned to 100, 110 and 200 Bragg reflections respectively. The present data is in agreement with the reported results [57]. The modified SBA-15, prepared using immobilization of silane followed by ligand and copper incorporation gave similar type of pattern.

It shows that the material has retained its mesoporosity even after the incorporation of organic functional groups and copper. However, there was significant decrease in the intensity of the peaks for modified SBA-15 samples, which may be due to some loss in crystallinity on linkage between silicate framework and organic moieties [58]. However, the XRD of spent catalyst didn't show any reduction in peak intensities, confirming that the catalyst is stable under reaction conditions.

4.4.1.2. Scanning electron microscopy

Scanning electron microscopy study of the samples was carried out on JEOL-JSM- 5200 to study the surface morphology of the Cu supported catalysts and the parent SBA-15 sample.

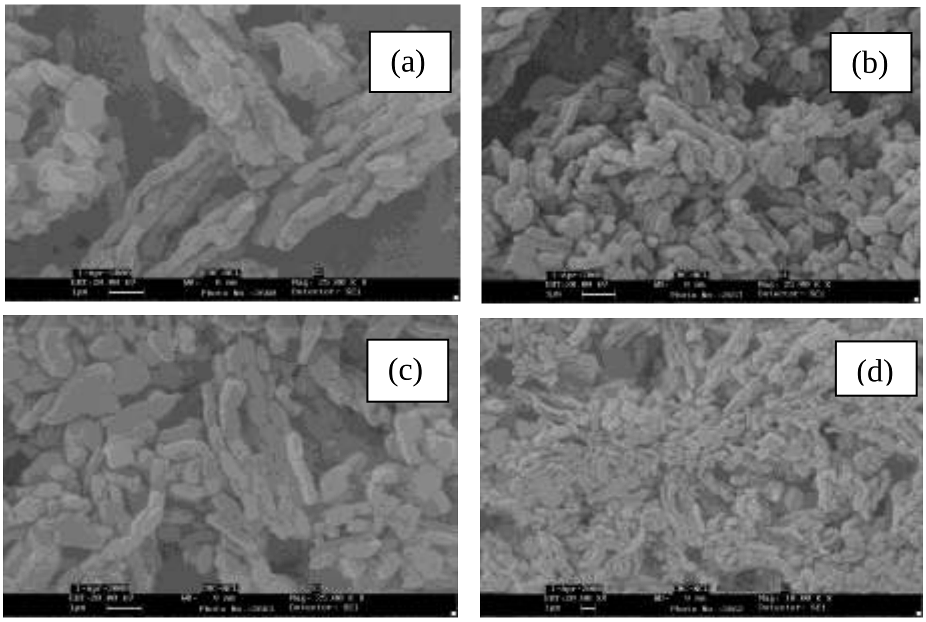


Fig. 4.2: SEM images (a) SBA-15; (b) Cucat-I; (c) Cucat-II and (d) Cucat-III

In Fig. 4.2a, SEM picture shows a worm-like morphology for mesoporous material arranged into rope-like chains of SBA-15 crystals, which is characteristic of SBA-15 [57]. The same morphology was observed for immobilized copper catalysts. These observations show that the mesoporous SBA-15 retained its morphological integrity even after functionalization.

4.4.1.3. Transmission electron microscopy

Transmission electron microscopy of the samples (Fig. 4.3), recorded on Tecnai-T30, helps to understand channels and crystal nature of the sample.

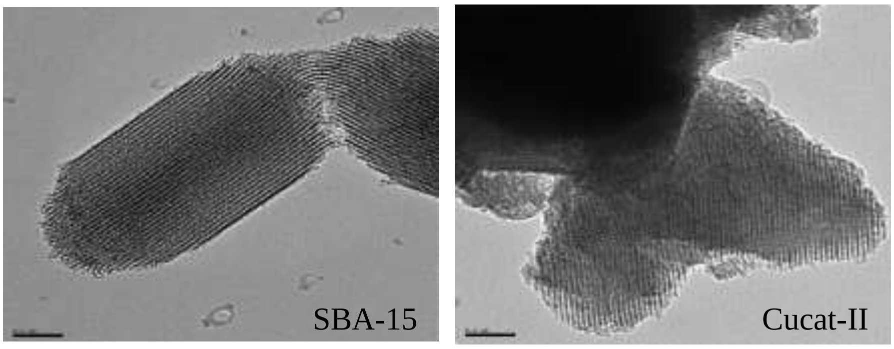


Fig. 4.3: TEM images of (a) SBA-15 and (b) Cucat-II

TEM studies of pure SBA-15 as well as Cu loaded catalysts reveal hexagonally arranged pore structure. The presence of equidistant parallel fringes demonstrates the nature of separation between layers and the unique well-packed arrangement of such monolayers. The study indicates the characteristic features of SBA-15 material and how it retained its features even after modification.

4.4.1.4. BET surface area by N_2 sorption

All the N_2 sorption isotherm of the materials (Fig. 4.4) shows H1 hysteresis with type IV isotherms. Sharp increase in adsorbed N_2 at relative pressure of (p/p^o = 0.7) [59] shows characteristic properties of highly ordered mesoporous materials having pore diameters in the range of 6-8 nm. The sharpness of the adsorption step in these isotherms suggest the relative order in mesopore size and the characteristic hysteresis loop account for the large-tubular pores of SBA-15 with uniform size distribution [60]. Textural data of all these mesoporous materials (surface area, total pore volume and pore diameter etc.) are given in Table 4.1.

The SBA-15 has good BET surface area (645 m^2/g), large pore volume (0.94 cm^3/g) and pore diameter (78.3 Å). After immobilization of organic moieties, changes in textural properties were observed for modified SBA-15 samples. Surface area as well as pore volumes dropped considerably as compared to pure SBA-15. This may be attributed to occlusion of organic moieties inside the channels of SBA-15. The average pore diameter reduced on loading of organic moieties as well as copper [61].

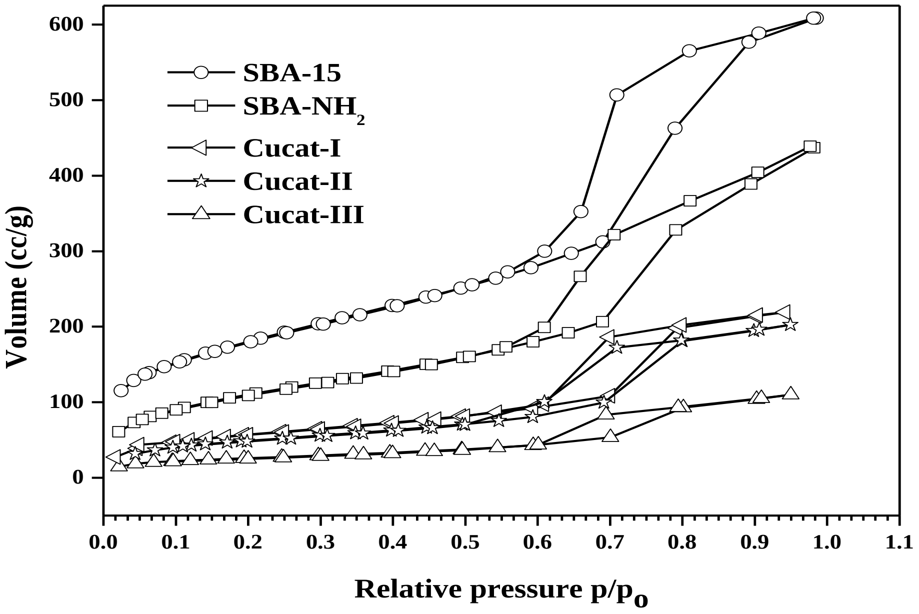


Fig. 4.4: N_2 sorption isotherms

4.4.1.5. Thermal analysis

Thermo gravimetric analysis of SBA-15 and Cu loaded materials was carried out in N_2 flow in the 303-1273K temperature range, while heating the sample at the rate of 283 K min^{-1}.

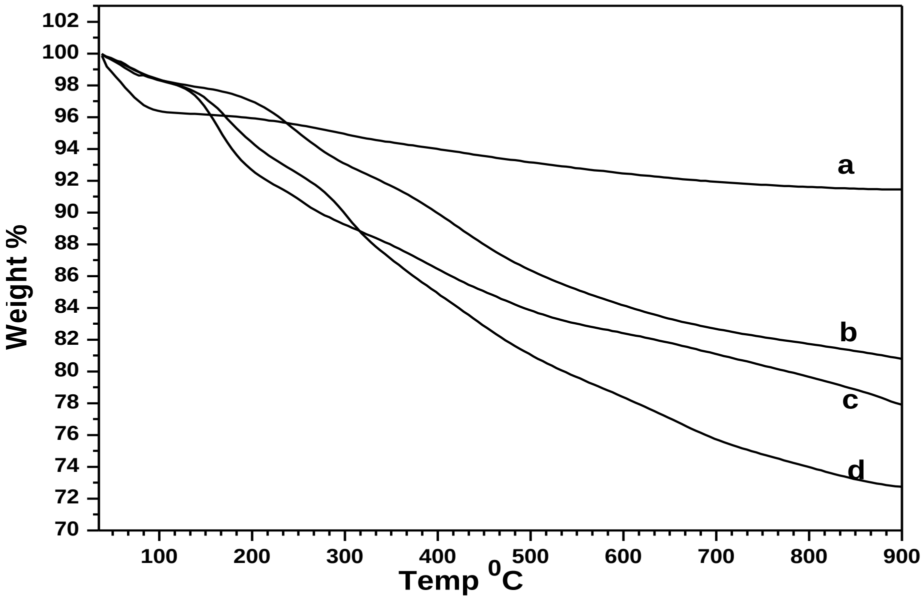


Fig. 4.5: TGA of (a) SBA-15; (b) Cucat-II; (c) Cucat-III and (d) Cucat-I

Fig. 4.5 shows the weight loss of pure SBA-15 and copper immobilized on SBA-15 catalysts. Thermal analysis of the immobilized catalyst shows considerable weight loss in the temperature range 323-773 K. The SBA-15 shows only one sharp weight loss at 363 K assigned to sorbed water. Thereafter, the weight loss was shallow, showing high thermal stability of SBA-15. The catalyst samples show slightly lower weight loss compared to SBA-15 upto 363 K, while the weight loss increased in the temperature region 473- 873K. The first weight loss for catalysts around 2-4 weight % upto 363K is due to physically adsorbed water in the pores of the material. The second weight loss, observed in the temperature range 373-773 K is attributed to the decomposition of the linker groups (aminopropyl group), confirming the anchoring of the APTES. Weight losses of about 6.9, 5.8 and 5.5 wt % were observed for Cucat-I, Cucat-II and Cucat-III respectively. This weight loss which was continuous upto 873K may be attributed to the combustion of organic species and loss of unincorporated ethoxy group of silane.

4.4.1.6. ^{13}C & ^{1} H MASNMR studies

^{13}C MASNMR was used for studying the functionalization of organic moiety (APTES) and structural integrity of the support. As shown in Fig. 4.6a, the ^{13}C NMR spectrum of functionalized SBA-15, clearly shows resonance peaks at chemical shifts δ= 9.23, 21.66 and 42.32 ppm, respectively. These peaks were attributed to different carbon environments in the linker APTES, assigned to C1, C2 and C3 carbons of APTES [62]. These results confirm the incorporation of APTES group into pure SBA-15.

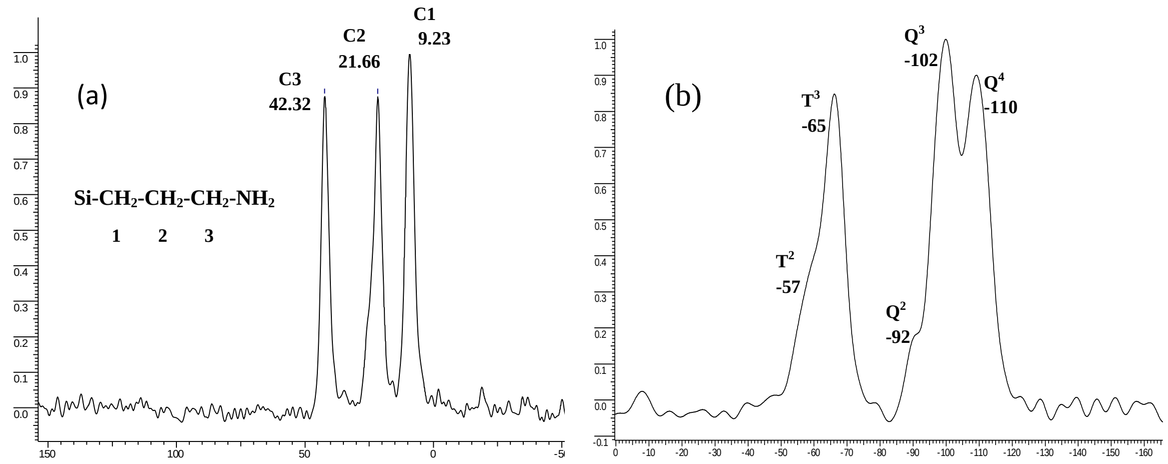


Fig. 4.6: (a) ^{13}C MAS NMR spectrum and (b) ^{29}Si NMR spectra of SBA-APTES

Fig.4.6b shows the MAS NMR spectra of ^{29}Si of amine immobilized SBA. Three resonance peaks at -110, -102 and -92 ppm clearly indicate the different environments of silicon in SBA-15. These three peaks correspond to different Q-type (Q^4, Q^3 and Q^2 respectively) environments in the SBA-15. Along with these three peaks, spectra also shows two more resonances at δ= -65 and at -57 ppm, assigned to T^3 and T^2 respectively. These peaks are attributed to the Si atoms of different environments in the organosilane APTES and confirm the immobilized APTES in the SBA-15 pores.

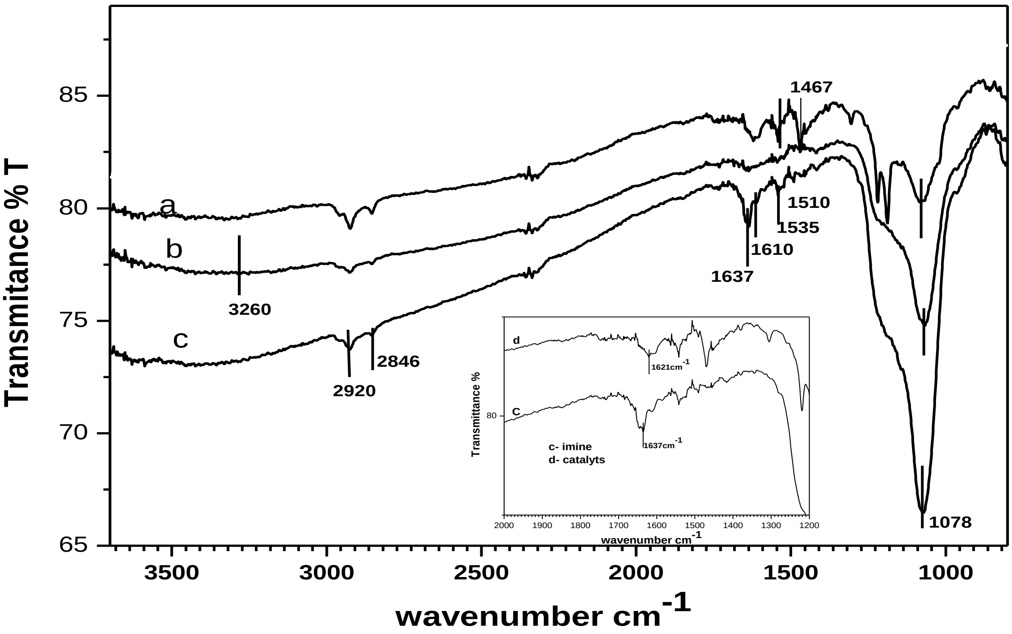


Fig. 4.7: FT-IR spectra of (a) SBA-$(CH_2)_3$-NH_2; (b) SBA-N-Sal and (c) SBA-N-Sal Cu $(OAc)_2$ (Cucat-I)

4.4.1.7. FT-IR spectroscopy

The IR spectra of SBA-APTES and Cucat-I is shown in Fig. 4.7. The peaks around 3260 cm^{-1} and 1510 cm^{-1} may be assigned to symmetrical N–H stretching and symmetrical $-NH_2$ bending of the primary amine of aminopropyl groups. A broad strong peak appears in the range 1000-1200 cm^{-1} is attributed to siloxane, $-(SiO)_n-$. The absorbance peak of the C–N stretching vibration in the wave number range of 1000–1200 $cm^{-1}$is generally not resolved due to overlap with the absorbance of Si–O–Si stretch in the range 1000–1130 $cm^{-1}$and that of Si–CH2–R stretch in the range 1200–1250 cm^{-1} [62].

The peaks at 2990–2840 cm^{-1} and 1467 cm^{-1} could be assigned to stretching vibration of the $–CH_2–$ groups of the aminopropyl moieties [63]; again confirming the immobilization of APTES on SBA-15. The peaks at 1637, 1610 and 1535 cm^{-1} correspond to stretching frequency of $C=N_{imine}$, aromatic C=C and phenolic C–O respectively [64], which confirms the formation of imine bond between carbonyl and amine group. The reduction in stretching frequency of C=N- (1621 cm^{-1}) in IR spectra of catalyst samples confirm the complexation of copper with imine immobilized SBA-15. The IR stretching frequencies of other catalyst samples is given in Table 4.2.

Table 4.2- IR peak value of the catalysts

S.No	Compound	Frequency (vibration) cm^{-1}
1	SBA-$(CH_2)_3$-NH_2	3260 (ν_{N-H}), 2990-2840 (ν_{-CH2})
2	Cucat-I	1621 ($\nu_{C=N}$), 1610 ($\nu_{C=C}$), 1535 (ν_{C-O}), 2990-2840 (ν_{-CH2})
3	Cucat-II	1624 ($\nu_{C=N}$), 2990-2845 (ν_{-CH2}), 1582 ($\nu_{C=N,}$ Pyridine ring)
4	Cucat-III	1615 ($\nu_{C=N}$), 2990-2840 (ν_{-CH2}), 1573 (($\nu_{C=N,}$ Pyridine ring)

4.5. Catalytic activity of CuSBA-15 catalysts in cross coupling reactions

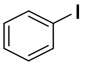
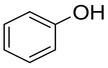
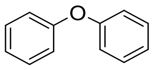
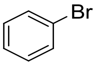
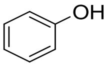
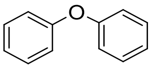
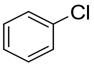
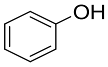
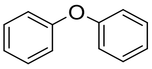
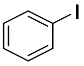
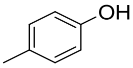
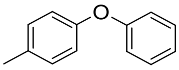
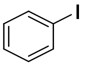
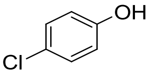
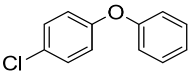
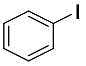
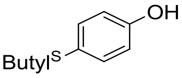
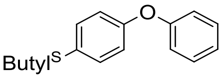
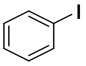
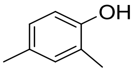
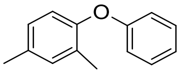
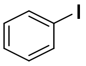
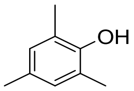
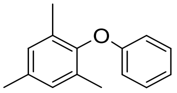
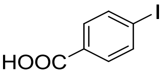
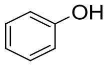
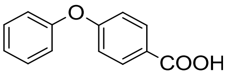
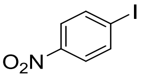
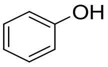
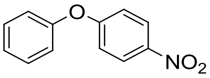
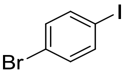
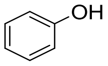
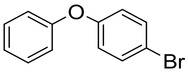
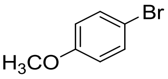
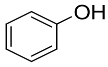
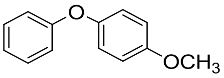
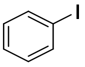
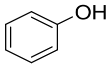
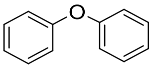
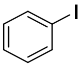
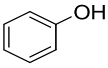
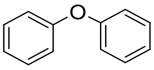
4.5.1. Ullmann reaction

Ullmann reaction is one of the most powerful techniques to obtain substituted diaryl ethers. Hence, it is useful in the preparation of drug intermediates and biologically active compounds. We report below Cu catalyzed cross coupling reactions of aryl halide with phenol in presence of a base.

4.5.1.1. Activity of various copper catalysts

Copper loaded SBA-15 catalysts were used as catalysts for reaction of iodobenzene with phenol, which was chosen as a model reaction to test the catalytic activity. The catalytic activities of the different Cu-SBA-15 catalysts are given in Table 4.3 (rows 1, 13 and 14). The results show that the catalyst Cucat-II, which was prepared from 2-carboxaldehyde pyridine, gave relatively higher conversion of aryl halide and yielded more product when compared to other catalysts. The yield over this catalyst was as high as 78% with almost 100% selectivity to diaryl product. On the other hand, Cucat-I and Cucat-III gave 60.5% and 75.5% conversion respectively.

Table 4.3- Activity of Cu catalysts in C-O cross coupling reaction

S.No.	Aryl halide	Phenol	Product	Conv %	Sele %	Yield %
1				78.5	99.4	78.0
2				62.9	89.7	56.4
3				--	--	--
4				78.8	98.6	77.7
5				70.1	93.3	65.4
6				84.4	98.1	82.8
7				80.2	98.4	78.9
8				73.7	98.3	72.4
9				97.0	100	97.0[a]
10				98.0	100	98.0[a]
11				83.5	99.0	82.6
12				66.9	90.1	60.3
13				60.5	99.1	60.0[b]
14				75.5	99.3	75.0[c]

Reaction Conditions: Cucat-II (50mg, 0.020 mmol of Cu), Aryl halide (1 mmol), Phenol (1 mmol), K_2CO_3 (1.2 mmol), DMSO (4 mL), 393K, 24h, [a]Time 12h, [b]with Cucat-I, [c]with Cucat-III.

These differences in activity may be attributed to electronic environment present around copper. When bromobenzene was used instead of iodobenzene with Cucat-II as catalyst, the product yield decreased from 78 to 56.4%. However, with chlorobenzene as the reactant, reaction did not proceed (Table 4.3, rows 1-3) to yield any product. These observations are in line with the reported results, as C-Cl bond is stronger than C-I and C-Br bond.

For phenols with electron-donating group at *p*-position of the ring, the yield of product has increased up to 82.8 %. Whereas, when electron-withdrawing groups are present, yield of product decreased (Table 4.3, rows 4-7). On the other hand, presence of electron withdrawing groups on arylhalide at *p*-position gave higher yield of product as compared to electron donating groups (Table 4.3, rows 9-12). As a result good yield products were obtained within 12h. These results are in good agreement with those reported by Buck *et al* [65].

4.5.1.2. Effect of base

The influence of different bases on aryl halide conversion and selectivity to the desired product was investigated. The base plays a major role in arylation of phenol, as the HBr/HI generated during the reaction is neutralized by the base, leading to an increase in the rate of reaction.

Table 4.4- Effect of different base on conversion

S.No	Base	Conversion of Iodobenzene (mol %)	Diaryl ether (mol %)	
			Selectivity	Yield
1	Na_2CO_3	53.1	96.6	51.3
2	K_2CO_3	78.5	99.4	78.0
3	Rb_2CO_3	79.9	98.8	79.0
4	Cs_2CO_3	79.5	99.1	78.8
5	K_3PO_4	76.8	94.3	72.5

Reaction Conditions: Cucat- II (50mg), Iodobenzene (1 mmol), Phenol (1 mmol), base (1.2 mmol), DMSO (4 mL), 393 K, 24h.

Table 4.4 gives results of different bases studied for this reaction. Carbonate type of bases were found to be good for this reaction. Among the carbonates, Na_2CO_3 gave lowest conversion and yield (51.3%). Among K_2CO_3, Rb_2CO_3 and Cs_2CO_3, no particular trend was observed, as these three bases gives almost 100% product selectivity with around 79% conversion of iodobenzene. On the other hand, slight decrease in conversion (76.8%) and selectivity (94.3%) were observed when potassium phosphate was used as a base instead of K_2CO_3.

4.5.1.3. Effect of solvent

To study the effect of solvent on conversion of iodobenzene, different polar and non polar solvents were used for the Ullmann reaction.

Table 4.5- Effect of Solvent on conversion

S.No	Solvents	Conversion of Iodobenzene (mol %)	Diaryl ether (mol %)	
			Selectivity	Yield
1	DMSO	78.5	99.4	78.0
2	DMF	47.3	89.7	42.4
3	DMA	53.4	91.3	48.7
4	Toluene	--	--	--
5	Dioxane	--	--	--

<u>Reaction Conditions</u>: Cucat-II (50mg), Iodobenzene (1 mmol), Phenol (1 mmol), K_2CO_3 (1 mmol), solvent (4 mL), 393 K, 24h.

The results show polar aprotic solvent show good activity compared to non polar, as polar aprotic solvents in Ullmann reaction generally promotes the dehalogenation [66]. The reaction was carried out with DMSO, DMF and DMA etc., results of which are given in Table 4.5. The conversion of substrate in DMSO (78%) was higher as compared to other solvents such as DMF (42.4%) and DMA (48.7%). Even the selectivity (99.4%) to diaryl product was highest with DMSO as solvent. However, when non polar solvents such as toluene and dioxane are used, no reaction was observed under the experimental conditions studied.

4.5.1.4. Catalyst recycle study

To confirm, whether the reaction is purely heterogeneous or the leached Cu metal is contributing to the catalytic activity under the reaction conditions, the catalyst was separated after each reaction run and the filtrate was analyzed for the presence of Cu. But, filtrate did not show any Cu, confirming that the reaction is truly heterogeneous. Conversion and selectivity obtained for the each run of the Ullmann reaction are plotted as shown in Fig. 4.8.

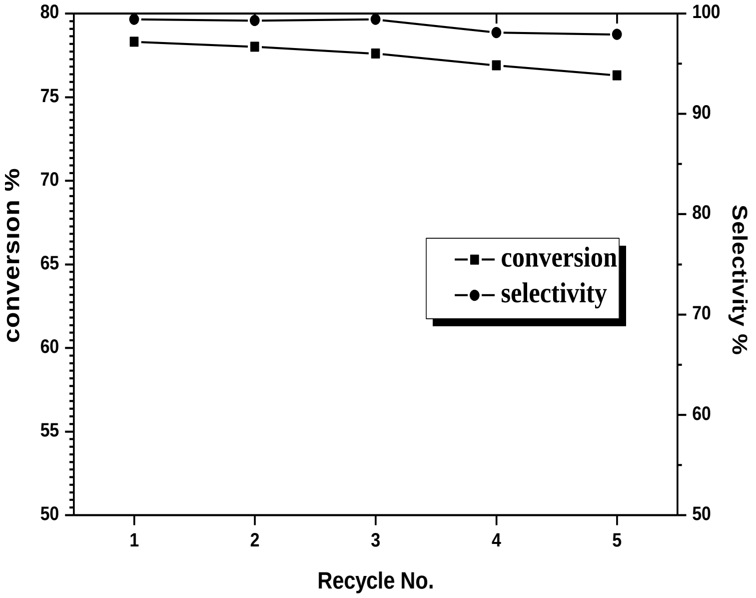


Fig. 4.8: Recycle study of Cucat-II

Reaction Conditions: Cucat-II (50mg), Aryl halide (1 mmol), Phenol (1 mmol), K_2CO_3 (1 mmol), DMSO (4 mL), 393 K, 24h.

For recyclability studies, catalyst was separated out after completion of reaction, washed with DCM and acetone, dried and added to the fresh reaction mixture with identical composition. The results show that catalyst was successfully recycled five times with minor loss of catalytic activity. This decrease in activity may be attributed to slight loss in catalyst quantity with each consecutive cycle.

4.5.2. C-S cross coupling reaction

The cross coupling reaction between aryl halide and thiophenol to aryl sulfide is a very important tool for organic chemists. The reaction product, aryl sulfide is useful as an organic intermediate for the synthesis.

4.5.2.1. Effect of base

Influence of different bases for the C-S coupling reaction was studied (Table 4.6) using Cu immobilized SBA-15 as catalyst. Among the bases used, inorganic carbonates gave better conversion and aryl sulfide yield compared to the organic bases. However, even the inorganic carbonate bases did not give very high selectivity or product yield unlike that was obtained for Ullmann reaction. As reported by Zheng *et al* [67], strong bases offer better conversion compared to relatively weak bases. Cesium carbonate gave the best conversion (83.8%) of substrate with a yield of aryl sulfide at

62.2% after 24h of reaction time. Marginally higher selectivity was observed when Rb_2CO_3 was used as a base, but the conversion of product was lower at 77.9%, leading to slightly lower yield of aryl sulfide compared to Cs_2CO_3. On the other hand, organic bases like NEt_3 (32.6%) and pyridine (21%) gave very low conversion of substrate with 15.7% and 9.4 % of product yield.

Table 4.6- Effect of base on conversion

S.No	Base	Conversion of 4-nitro iodobenzene (mol %)	Aryl sulfide (mol %)	
			Selectivity	Yield
1	Na_2CO_3	45.3	52.8	23.9
2	K_2CO_3	58.9	69.3	40.8
3	Rb_2CO_3	77.9	75.9	59.1
4	Cs_2CO_3	83.8	74.2	62.2
5	NEt_3	32.6	48.1	15.7
6	Pyridine	21.0	44.7	9.4

Reaction conditions: Cucat-II (50mg), 4-nitro iodobenzene (1 mmol), Thiophenol (1.2 mmol), Base (1.2 mmol), DMA (4 mL) as Solvent, 383 K, 24h.

4.5.2.2. Effect of solvent

Generally, the metal catalyzed organic transformations are performed in solution by bringing the reactants and catalyst in one phase and provide the thermal energy needed for the reaction [68]. Solvent is expected to play a critical role in this type of system. Hence, to study the effect of solvent on C-S coupling reaction, different polar aprotic and non polar solvents were used as shown in Table 4.7.

When 4-nitro iodobenzene was reacted with thiophenol in presence of DMA as solvent, the substrate conversion was 83.8% with 62.2 % yield of aryl sulphide. Slightly lower conversion (79.5%) was observed with corresponding drop in yield to 58.7%, when DMF was used as solvent instead of DMA (Table 4.7). Whereas, when DMSO was used as solvent, a very low substrate conversion (57.7%) along with 40.3% yield of product was observed. No product formation occurred, when reaction was carried out in non-polar solvents like toluene and dioxane.

Table 4.7- Effect of solvent on conversion of 4-nitro iodobenzene

S.No	Solvents	Conversion of 4-nitro iodobenzene (mol %)	Aryl sulfide (mol %) Selectivity	Yield
1	DMF	79.5	73.8	58.7
2	DMA	83.8	74.2	62.2
3	DMSO	57.7	69.8	40.3
4	Dioxane	--	--	--
5	Toluene	--	--	--

Reaction conditions: Cucat-II (50mg), 4-nitro iodobenzene (1 mmol), Thiophenol (1.2 mmol), Cs_2CO_3 (1.2 mmol), Solvent (4 mL), 383 K, 24h.

4.5.2.3. Activity of various catalysts

The three different Cu immobilized SBA-15 catalysts (Cucat) described in the experimental section were tested for C-S coupling reaction and results are shown in Table 4.8. Among the three catalysts, Cucat-II, prepared from pyridine-2-carboxaldehyde, gave maximum conversion of 4-nitroiodobenzene (83.8%) with 62.2% yield of product. The other two catalysts Cucat-I and Cucat-III gave lower yield of product as compared to Cucat-II yielding 29.4% and 55.9% of the product respectively

Table 4.8- Catalytic activity of different catalysts

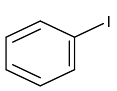
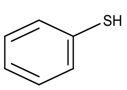
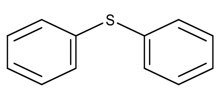
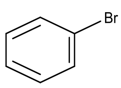
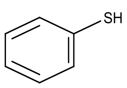
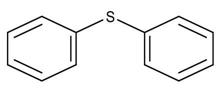
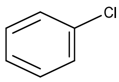
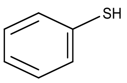
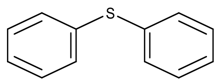
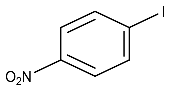
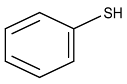
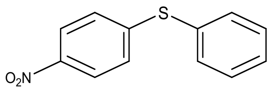
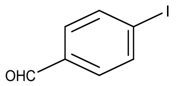
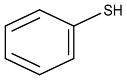
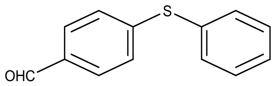
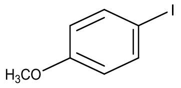
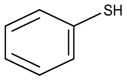
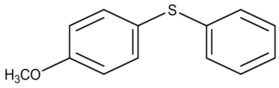
S.No	Catalysts	Conversion of 4-nitro iodobenzene (mol %)	Aryl sulfide (mol %) Selectivity	Yield
1	Cucat-I	39.6	74.3	29.4
2	Cucat-II	83.8	74.2	62.2
3	Cucat-III	73.6	75.9	55.9

Reaction conditions: 50mg of catalyst (50mg), 4-nitro iodobenzene (1 mmol), Thiophenol (1.2 mmol), Cs_2CO_3 (1.2 mmol), Solvent (4 mL), 383 K, 24h.

4.5.2.4. Comparison of substrate reactivity

In order to find the reactivity of various Cu catalysts, we choose iodobenzene and thiophenol as model substrates for C-S coupling reaction, results of which are shown in Table 4.9. Moderate yield of product was obtained in reaction. The reaction between iodobenzene and thiophenol in presence of Cs_2CO_3 as base and DMA as solvent at 383 K gave 46.5 % conversion of iodobenzene with 35.2% yield of aryl sulfide. The conversion (25.2%) as well as yield of product (19.7%) decreased when bromobenzene was used as substrate in place of iodobenzene. Whereas, no conversion was observed when chlorobenzene was the substrate, as C-Cl bond requires much more energy for its scission (Table 4.9, rows 1-3) compared to C-Br and C-I bonds.

Table 4.9- Activity of catalyst and substrate reactivity

S.No	Aryl halide	Phenol	Product	Conv %	Sele %	Yield %
1				46.5	75.7	35.2
2				25.2	78.3	19.7
3				--	--	--
4				83.8	74.2	62.2
5				74.0	76.9	56.9
6				44.0	69.8	30.7

Reaction conditions: Cucat-II (50mg), Aryl halide (1mmol), Thiophenol (1.2 mmol), $C_{S2}CO_3$ (1.2 mmol), DMA (4 mL), 383 K, 24h.

We have also studied the C-S coupling reaction of the derivatives of arylhalide and thiophenol in order to find out the effect of the activating or deactivating substituents on aryl halide at *p*- position on conversion and yield of product. As results show, the activated aryl halide gives better yield than the non activated aryl halide. When there is electron withdrawing group ($-NO_2$, -CHO etc.) on iodobenzene, it led to maximum (83.8%) conversion with 62.2% yield of the aryl sulfide product (Table 4.9). However, the conversion (44%) as well as yield decreased when electron donating groups are present at *p*-position. Only 30.7% yield of product was observed for *p*-methoxy iodobenzene (Table 4.9, row 6).

4.5.2.4. Recycle and leaching study

Investigations were carried out to find whether the reaction is truly heterogeneous or the leached Cu metal from the catalyst is active for the reaction. For this purpose, the catalyst was separated by filtration after reaction and the filtrate was analyzed for presence of Cu. The filtrate doesn't show any Cu species, confirming that the reaction is truly heterogeneous.

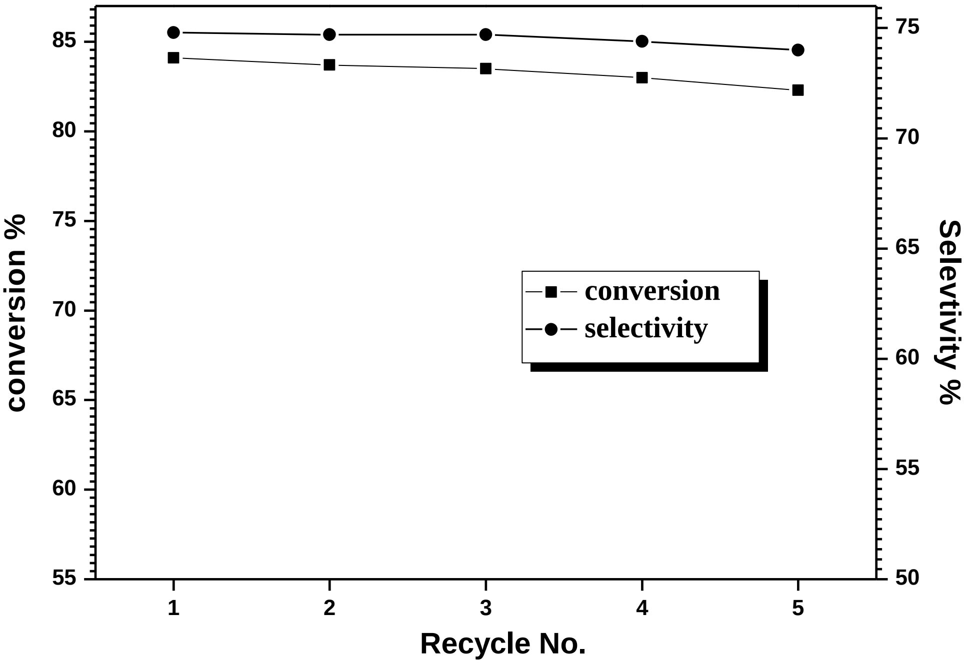


Fig. 4.9: Recycle study of Cucat-II

For checking recyclability, catalyst was separated out after completion of each run of the reaction, washed with DCM and acetone, dried and recharged into the fresh reaction mixture under identical conditions. Catalytic activity in C-S coupling reaction, after each cycle, is plotted as shown in Fig. 4.9. The results show that catalyst can be successfully applied repeatedly for five times with minor loss of catalytic activity. The conversion of substrate after 3rd recycle has dropped marginally alongwith the selectivity of product. This decrease in activity may be because of some loss of catalyst weight during recycling.

4.6. Conclusions

Copper immobilized SBA-15 (Cucat) catalysts were prepared successfully by heterogenizing copper on SBA-15 through complexing method. These were characterized by various physico-chemical techniques. X- ray diffraction patterns showed that, crystallinity of SBA-15 is retained to most extent as shown by the presence of sharp intense peaks even after immobilization of APTES and loading of the copper. However, there was a slight drop in intensity of the peaks after immobilization of the complex, which confirms the immobilization. The XRD of spent catalyst didn't show any change in XRD thus confirming the stability of the catalyst during the reaction. SEM images of the catalysts show the rope like morphology of typical SBA-15. This is further confirmed from TEM images which show hexagonal shape of the channel along with its mesoporous structure. The immobilization of linker group and copper on SBA-15 was confirmed by CP/MAS NMR and IR techniques.

The Cu catalysts, which were prepared through immobilization of copper complexes showed versatility and effectiveness for C-O (coupling of aryl halide with phenol) and C-S (coupling of aryl halide with thiol) reactions. These catalysts can be used with a varity of substrates leading to good yield of the products and all catalysts show activity for the non activated bromobenzene. These immobilized catalysts may have edge over other catalysts due to ease of separation and reuse. These catalysts are truly heterogeneous as they can be reused without much loss in activity.

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Chapter-V

Selective Oxidation of Hydrocarbons

Selective oxidation of substituted aromatics to corresponding carbonyl compounds over Co-KOMS-2

5.1. Introduction

Selective oxidation of substituted aromatics has many industrially important applications [1]. At present more than 62% of important industrial products are obtained through catalytic oxidation. Selective catalytic oxidation of aromatic hydrocarbons is widely applied for the manufacture of many chemical feed stocks, pharmaceutical intermediates, fragrances and polymers. Transition metal based catalysts are mostly active for these reactions [2].

The oxidation reactions are usually carried out in presence of an oxidant such as hydrogen peroxide (H_2O_2), tert-Butyl hydrogen peroxide (TBHP) or using oxygen in air [3]. In chemical industry, the liquid-phase oxidation of aromatic hydrocarbons by molecular oxygen is very attractive, both from an economic and environmental point of view. A range of valuable oxygenated compounds can be produced through this method. These oxygenated hydrocarbons are widely used as building blocks in the manufacture of plastics and synthetic fibres. Many oxygenated hydrocarbons are also important as intermediates in the syntheses of fine chemicals. For example, benzaldehyde and benzoic acid, which are important intermediates, are produced from toluene, while *p*-toluic acid and terephthalic acid are made from *p*-xylene [4].

Table 5.1 summarises several commercially important processes corresponding to oxidation of alkyl aromatic hydrocarbons [5]. The production volumes of the chemicals are impressive and serve to underline their importance in industry. In terms of tonnages, the conversion of *p*-xylene to PTA and dimethyl terephthalate (DMT) ranked as the highest among the oxidation processes.

5.1.1. Oxidation of *p*-cresol

Selective catalytic oxidation of side chain of an aromatic compound to corresponding products is very important in the manufacture of various industrial and pharmaceutical intermediates [6]. *p*-Hydroxybenzaldehyde, which is obtained on selective oxidation of *p*-cresol, is an important chemical intermediate for making dyes, pharmaceuticals such as semi-synthetic penicillin, amoxicillin, trimethobenzamide, flavoring agents such as vanillin, agrochemicals and various textile auxiliaries. It is also used as an additive for metal-plating brighteners while o-hydroxybenzaldehyde is quite useful for perfumery chemicals [7]. The synthesis of hydroxybenzaldehyde from cresol by selective oxidation with O_2 or air is difficult [8], as phenolic compounds easily undergo coupling, polymerization and ring opening along with oxidation [9].

Table 5.1- Major chemical processes practicing hydrocarbon oxidation

S. No.	Starting hydrocarbon	Final Product	Process Name	Application of product	Remarks
1	*p*-Xylene to terephthalic acid	Terephthalic acid (PTA)	Amoco Mid-Century	PET (fiber, film, resin)	Applicable to other alkyl-aromatics such as m-xylene, pseudocumene, 2,6-dimethyl naphthalene
2	*p*-Xylene and *p*-toluic acid	Dimethyl terephthalate (DMT)	Witten, BASF, DuPont	PET (fiber, film, resin)	Single or two-step process
3	Cumene	Cumyl hydro-peroxide (CHPO)	Hock (BP, Kellogg, etc.)	Phenol	Coproduct: acetone. Also applicable to cresols, resorcinol /hydroquinone from cymene, diiso-propylbenzenes
4	Cyclohexane Cyclohexanone or KA	Adipic acid	BASF, Bayer, Dupont,	Nylon-66 Nylon-6 (Perlon)	K:A ratio depends on use of boric acid

In the past, synthesis of o- or *p*-hydroxybenzaldehyde was carried out using different procedures. Some of them are: (i) Reimer Tiemann reaction using sodium hydroxide [10-11]; (ii) Gattermann reaction using phenol and HCN for *p*-hydroxybenzaldehyde production; (iii) Saligenin process in which base catalyzed reaction of formaldehyde with phenol to give *p*-hydroxybenzyl alcohol which in turn is oxidized over Pt or pd to yield *p*-hydroxybenzaldehyde [7d] and (iv) Side chain chlorination of *p*-cresol followed by saponification of the resulting dichloromethyl group [12]. These conventional methods of oxidation reactions use toxic reagents in stoichiometric amounts and involve tedious work up procedures. These procedures and work up lead to low yield of product and generation of poisonous chemicals including inorganic waste with disposal problems.

p-Hydroxybenzaldehyde can be synthesized by direct oxyfunctionalization of cresol at the benzylic position [13-18]. It was also reported to be prepared by electrochemical oxidation of *p*-cresol [19] and through phenolic/glyoxylic acid condensation [20], followed by oxidation of the resultant *p*-hydroxymandelic acid. This reaction is generally carried out in acetic acid or acetic anhydride [21] or in alcohol based medium [22] to protect –OH group as acetate or phenolate to avoid the formation of polymer and tars. Perrin-Janet *et al* reported supported platinum group metal (PGM) catalysts for the benzylic oxidation of a cresol without protection of the phenolic group [23]. However, most of these reactions result in very low yield of the desired product and also lead to consecutive oxidation or oligomerization. In addition, the recovery of these catalysts is difficult and thus process becomes very expensive [24].

Selective liquid phase oxidation of *p*-cresol is expected to help not only in reducing the disposal problems but also increase in product selectivity and thereby improving process efficiency. The partial oxidation of *p*-substituted toluene using oxygen to corresponding benzaldehyde in the liquid phase is carried out in the presence of a Co catalyst with acetic acid as solvent [25] or by anodic oxidation [26]. Cobalt catalysts were reported to be most favourable for selective oxidation of hydrocarbon because of their ability to switch between Co^{+2} to Co^{+3} [27-32]. The oxidation reaction requires reasonable activation energy to form an activated complex between C-H and oxygen via interaction with the active site of catalyst. It is also observed that [33], cobalt catalysts have better oxygen supply ability (Co_3O_4 > MnO_2 > CuO) as compared to manganese or copper catalysts, as the cobalt has low activation energy of exchange in molecular oxygen.

Nishizawa *et al* for the first time reported oxidation of *p*-cresol using homogenous cobalt catalyst and this methodology was followed by other groups [34-35]. Sharma *et al* reported about 60% selectivity to *p*-hydroxybenzaldehyde when oxidation of *p*-cresol was carried out using cobaltous chloride as homogeneous catalyst [36]. However, the problems of separation and reuse of catalysts were not resolved. To overcome these handicaps, heterogeneous catalysts have to be used as they have edge over homogeneous counterparts at least in this regard [37]. Recently, catalysts that have cobalt or bimetallic systems containing Co + Mn supported on molecular sieves [38], carbon [39] and resin [40] have been reported for oxidation reactions. But the problem is that the catalyst is either soluble in reaction media or the leaching of metal under reaction conditions. The dissolved species catalyze the reaction homogeneously [41]. Sarada and co-workers reported encapsulated cobalt Schiff base complexes as catalysts for the oxidation of *p*-cresol, but the leaching of cobalt was the main problem associated with that system [42]. Hence, there is need to develop catalysts which can overcome the above outlined problems while offering good catalytic activity and selectivity in selective oxidation reactions.

5.1.2. Oxidation of *p*-xylene

Selective oxyfunctionalization of alkyl aromatics has been a challenging task over the decades. It has been studied exhaustively because it is one of the important and useful organic transformations in industry [43]. It also paves the way to make wide range of functionalized molecules. Among various oxidations, the selective oxidation of *p*-xylene is an important process as the derived product; terephthalic acid (TPA) is the main raw material for polyesters, polymers such as polyoxadiazoles, polybenzimidazoles and various resins [44-46]. The global production and consumption of TPA in 2009 was approximately 39 million metric tons, while it is expected to grow at an average of 5.7% per annum for next five years and there after it is expected to be around 3.7% per year [47].

The first reported process for the oxidation of *p*-xylene was with nitric acid as an oxidant [48]. But, the main problem associated with this process was the generation of oxides of nitrogen in addition to high risk of an explosion and product purification issues. The major intermediate during *p*-xylene oxidation is *p*-toluic acid, which on oxidation gives terephthalic acid, but this step is very slow. By using only metal catalysts, *p*-toluic acid is formed as the main product but to achieve the oxidation of *p*-toluic acid, it needs a co-catalyst or a promoter. The use of promoters can increase the reaction rate as well as improve selectivity of the targeted product. In conventional homogeneous oxidation with cobalt, Mn and Br^- ions serve as promoters [49].

The second 'Mid-Century' oxidation process, which was developed by Amoco Chemicals, is known as the MC catalyst process [50]. The process is still carried out in HOAc using $Co(OAc)_2$/ $Mn(OAc)_2$/HBr as catalysts in industry throughout the world. Some other methods were reported for improving the oxidation of *p*-toluic acid, like using co-catalysts or promoters of metal catalysts, i.e., bromine compounds (Towle and

Baldwin 1964), methyl ethyl ketone (Brill 1960), acetaldehyde (Thompson and Neely 1966), paraldehyde (Nakaoka *et al*,1973) and zirconium salts (Ichikawa and Soma 1973) for *p*-xylene oxidation.

Generally, Oxidation of *p*-xylene is carried out in acidic medium at higher temperatures (473-523 K). Subsequently it is purified to obtain product TPA by hydrogenating the impurities in an aqueous solution in the presence of a reducing catalyst (e.g. Pd/C). Even though, this process is highly efficient and optimized, use of bromine initiator and higher temperature are serious concerns in terms of environment, economy and safety. The most important concern is the use of corrosive bromine and acetic acid, which corrodes expensive reactors. In addition, $CH_3Br(g)$ is reported to be formed as a side product [51]. The later compound can deplete the ozone layer [52]. In addition to these problems, a new process is needed that will have improvements in terms of (i) replacement of the homogeneous catalysts by heterogeneous catalysts ii) purification of crude TPA product containing 4- carboxybenzaldehyde (4-CBA), which is chain terminator in polymerization reactions. Due to large utilization of TPA in industry, even small improvements in the process become very vital from the economic point. Hence, researchers have been investing and developing better catalytic processes for *p*-xylene oxidation.

Ishii and Fierro reported use of bromine free initiator NHPI along with homogeneous catalyst system and showed [53] that the combination of NHPI with cobalt provides an effective solution for the oxidation of various organic substrates, e.g. alkanes [54] and alkyl aromatics [55]. N-Hydroxyphthalimide (NHPI) can catalyze the oxidation of a variety of hydrocarbons with molecular oxygen in the presence of transition metal salts or catalysts [56]. The phthalimide N-oxyl radical (PINO) is formed in situ from the NHPI and dioxygen. This radical abstracts the hydrogen from the hydrocarbon to form a corresponding alkyl radical, which is easily reacted with di-oxygen to form oxygenated-compounds [57]. The initiator NHPI is easily prepared by the reaction of phthalic anhydride and hydroxylamine. It is cheap, nontoxic and effective in abstracting species in the free radical processes mediated by this N-hydroxy derivative.

Most of the reported results are homogeneously catalyzed *p*-xylene oxidations (Co +Mn salt) and only few groups reported the oxidation reaction using heterogeneous catalysts. Chavan *et al* though used heterogeneous catalysts; NaBr was used as initiator at 423K [58]. Clark's group reported silica supported chromium catalysts for oxidation of alkyl aromatics [59] and there are also some reports on the use of heterogeneous catalysts such as heteropoly acid based catalysts [60-61]. Most of these reactions still use bromine as initiator with acetic acid as solvent at higher temperatures. Hence, there is a desperate need to develop a process that is purely heterogeneous and is free from bromine.

The literature shows that the transition metal Co in combination with Mn can be used as active catalyst system for the oxidation of *p*-xylene with NHPI as initiator. This process can replace the corrosive bromine based initiator process. We didn't find any reports that use OMS-2 materials with or without cobalt for *p*-xylene oxidation reaction. Hence, we chose Co substituted K-OMS-2 for *p*-xylene oxidation in the presence of initiator NHPI or its analogues such as NAPI (*N*-acetoxyphthalimide).

5.1.3. Octahedral molecular sieves as oxidation catalysts

Though homogeneous catalysts give excellent activity and selectivity for desired product, its industrial applications are restricted due to difficulty in product separation and the deactivation of active sites by self-aggregation. To avoid these problems, heterogeneous catalysts are in focus for these reactions. Use of various supports for metals or metal complexes including polymers, silica or inorganic oxides could be good option in oxidation reactions.

Microporous molecular sieves have pore dimensions near molecular size. They have been widely used in many chemical processes because of their porous structure, acidity and ion-exchange abilities. The most common molecular sieves are zeolites, which are tetrahedral network of aluminosilicates with well-defined three-dimensional framework structures. The pore opening of zeolites is less than 20 Å.

Similar to zeolites, manganese oxides prepared with tunnel structures exhibit molecular sieving properties [62] and are referred to as manganese oxide octahedral molecular sieves (OMS) [63], which include synthetic todorokite (OMS-1) and cryptomelane (OMS-2). Manganese oxide octahedra (MnO_6) are the basic structural units of OMS materials that combine to form tunnels in the order of 4.6 to 6.9 Å by linkages at their edges and vertexes.

OMS-2 is a microporous tunnel –structured manganese oxide material basic in nature. Inside the tunnel structure of manganese oxide materials, potassium (cryptomelane) or magnesium (todorokite) ions are present as exchangeable cations. Potassium containing cryptomelane type manganese oxide OMS-2 material has a composition of $KMn_8O_{16}.nH_2O$ [63]. The structure contains units of 4.6 X 4.6 Å tunnels because of the 2 X 2 arrangement of octahedral and K^+ ion with a small amount of water in the tunnel to provide charge balance and to stabilize the structure.

The average oxidation state of manganese in OMS-2 is 3.8 due to the presence of a mixture of Mn^{4+}, Mn^{3+} and Mn^{2+} ions [64]. The smaller pore opening is probably the cause of the higher stability of OMS-2. The metal oxides with mixed valency is important for electron transfer in chemistry e.g. for metal oxide act as a catalyst in redox reactions or electrode materials for electrochemical processes. It has the ability and tendency to cycle between different valence states of relevant cations and the mobility of oxygen ions [65]. From this standpoint, OMS materials have distinct advantages over aluminosilicate molecular sieve materials for applications in redox catalysis, batteries and chemical sensors because of mixed manganese valencies (mainly, 4^+, 3^+ or 2^+).

In recent years, KOMS has been used in catalytic oxidations [66]. OMS-2 produced by reflux method has advantages such as higher surface area, smaller particle size and multiple oxidation states of Mn that could be advantageous as redox active sites. Doping or incorporation of foreign metals particularly divalent or trivalent cations in OMS-2 changes its electronic, catalytic and structural properties [67].

5.2. Experimental procedures

5.2.1. Materials

Potassium permanganate, manganese (II) sulphate and cobalt nitrate were used (Loba Chemical Ltd.) for the preparation of K-OMS-2. *p*-cresol, acetic acid, methanol, NHPI (N-hydroxyphthalimide) and sodium hydroxide were purchased from Loba Chemie Pvt. Ltd. NAPI (N-acetoxyphthalimide) was prepared in laboratory. *p*-xylene was purchased from Sigma-Aldrich. All the chemicals were used without any further purification.

5.2.2. Preparation of catalysts

For the selective oxidation reactions, KOMS-2 as well as Co-K-OMS-2 catalysts was prepared as per the procedure given below. Co-K-OMS-2 was prepared with various Co contents and characterized using various physic-chemical techniques for obtaining information on chemical composition, texture and morphology.

I) Preparation of K-OMS-2

KOMS-2 was prepared by reflux method [68]. A solution of $KMnO_4$ (5.89g in 100 mL H_2O) was added drop-wise to a solution containing an aqueous mixture of manganese sulfate (8.8g in 30 mL water) and concentrated nitric acid (3 mL). This black precipitate formed was stirred and refluxed at 373 K for 24h. Subsequently, the precipitate was filtered and washed with distilled deionized water until the pH of the filtrate was neutral. Subsequently, the material was dried for 12h at 383 K before calcination in air at 623K for 3h.

II) Preparation of Co^{II}-K-OMS-2

The Co-K-OMS-2 catalysts were prepared on similar lines following KOMS-2 preparation. Cobalt nitrate was used as Co source. A solution of $KMnO_4$ (5.89 g in 100 mL H_2O) was added drop-wise to a solution containing mixture of manganese sulfate (8.8 g in 30 mL water), required amount of cobalt nitrate and concentrated nitric acid (3mL). Black precipitate obtained was stirred and refluxed at 373 K for 24h. Subsequently, the precipitate was filtered and washed with distilled deionized water until the pH of the filtrate was near neutral. The material was subsequently dried at 383 K for 12h and calcined in air at 623 K for 3h. A similar procedure was employed to prepare catalysts with different Co contents by varying the content of $Co(NO_3)_2$ solution. The samples were designated based on the Co loading as Cocat-I (2.40 % Co), Cocat-II (3.03 % Co), Cocat-III (3.46 % Co) and Cocat-IV (3.81 % Co).

5.2.3. Characterization of catalysts

Powder XRD measurements of the as synthesized materials and final catalysts were carried out using PANalytical powder XRD, Xpertpro-1712 diffractometer equipped with Ni filter using CuKα radiation ($\lambda = 1.5418$ Å). Data were collected at a scan speed of 2^o/min.

Specific surface area of the catalysts was measured by N_2 sorption at liquid N_2 temperature using a Quanta chrome Nova-1200 surface area analyzer employing multi point BET method. The catalyst samples were evacuated at 473 K for 3h at a residual pressure of $2x10^{-3}$ Torr prior to N_2 sorption. The isotherms were analyzed in a conventional manner in the relative pressure region of p/p^0 = 0.05 to 0.30.

Transmission electron micrographs (TEM) of the catalysts were recorded on high-resolution transmission electron microscope (HR-TEM) Tecnai-T30 model at an accelerated voltage of 300 kV. Samples were prepared by placing catalysts, dispersed in isopropyl alcohol suspensions, on carbon coated grids and dried through slow evaporation of the solvent at room temperature. Scanning electron micrographs of the samples were recorded using JEOL-JSM-5200 SEM to study the morphology and particle size characteristics. Thermal analysis of the samples was performed using a PerkinElmer Diamond thermal analysis instrument. The samples were analyzed at a heating rate of 283 K min^{-1}, in air flow (ca. 50 mL min^{-1}); in the temperature range 298-1273 K. Alpha-Al_2O_3 was used as reference. For each analysis, about 15-20 mg of the sample was used.

X-ray photoelectron spectra (XPS) of Co-K-OMS-2 samples were acquired on VG Microtech Multilab ESCA 3000 spectrometer using non monochromatized MgKα X-ray source (hν = 1253.6 eV), at a pass energy of 50 eV and electron take off angle of 60^0. Correction to the binding energy (B.E.) values was made by using the C_{1s} peak of carbon at 285 eV. The samples were dried at 373 K for 12h before their characterization by physicochemical methods. To analyze the chemical composition (Co content) using ICP-OES (Spectro Arcos), weighed amounts of the sample was dissolved in few mL of conc. HCl and diluted with distilled water to make upto 100 mL volume. The progress of the reactions was monitored by GC (Varian CP-3800, capillary BP5, 50m X 0.3 mm) using FID. The products were further confirmed by GC-MS.

5.2.4. General Procedure for oxidation reactions

5.2.4.1. Oxidation of *p*-cresol

The oxidation of *p*-cresol was carried out in a 50 mL stirred autoclave (Parr Instrument Series 4560, USA) equipped with a motor drive magnetically coupled to an internal turbine-type impeller, a speedometer, a thermocouple, a pressure gauge and a water-cooling coil. In a typical reaction, *p*-cresol (27.7 mmol), sodium hydroxide (*p*-cresol: NaOH=1:3), methanol (16 mL) and catalyst (0.2 g) were placed in the reactor. The reactor was heated to a set temperature under stirring. After reaching the desired temperature, oxygen was charged to the reactor through a dip tube and reaction was monitored for a finite time. After completion of the reaction, water was added to the reaction mixture and catalyst was recovered by filtration. The filtrate was neutralized with Conc. HCl. The organic phase was extracted with ethyl acetate and analyzed using GC with FID. The products were also confirmed using GC-MS.

5.2.4.2. Oxidation of *p-x*ylene

The oxidation of *p*-xylene was also performed using above described 50 mL titanium lined autoclave. In a typical run, reactor was charged with 8mmol of *p*-xylene, 20 mL of Acetic acid, 20 mol % of NAPI and 150 mg of catalyst. The mixture was stirred at 500 rpm speed, while heating to 373 K. After reaching the desired temperature, oxygen was fed into the reactor for a desired duration. After completion of the reaction, solid part containing catalyst, terephthalic acid and *p*-toluic acid was separated filtration and washed with DCM. The filtrate was analyzed using a GC equipped with a Flame ionization detector (Agilent 7890) and carbowax capillary column. Conversion of *p*-xylene and liquid product formation was observed through this analysis. Catalyst was separated from solid TPA and PTA by dissolving it in 30 mL of 0.7M NaOH+ Methanol (7:3) solution. The catalyst was subsequently recovered by filtration and filtrate was analyzed on UPLC quantitatively (waters UPLC, C18 coloumn).

5.3. Results and Discussion

5.3.1. Characterization

The cobalt content in the catalysts was analyzed by ICP and results are shown in Table 5.2.

5.3.1.1. X-ray diffraction

The XRD pattern of KOMS-2 and various Co-K-OMS-2 samples are shown in Fig. 5.1. XRD pattern of KOMS-2 (Fig. 5.1a) clearly shows that all peaks are well resolved and belong to parent K-OMS-2. The major peaks are (1 0 1), (0 0 2), (3 0 1), (2 1 1), (3 1 0), (1 1 4) and (6 0 0) corresponding to 2θ values at 12.7, 18.0, 28.7, 37.4, 41.8, 50.0 and 55.3.

Table 5.2- Cobalt content by ICP-OES analysis

S.No.	Catalyst	Co content (wt %) in the sample	
		Expected*	Actual
1	KOMS-2	0.0	0.0
2	Cocat-I	2.7	2.40
3	Cocat-II	3.2	3.03
4	Cocat-III	4.0	3.46
5	Cocat-IV	5.0	3.81

*Calculated based on the input Cobalt content

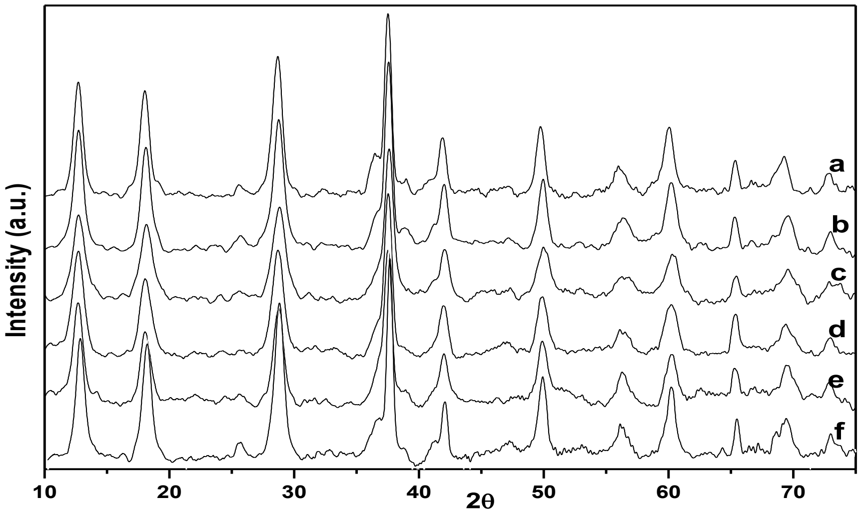

Fig.5.1: Powder XRD of (a) KOMS-2; (b) 2.40% Cocat-I; (c) 3.03% Cocat-II; (d) 3.46% Cocat-III; (e) 3.81% Cocat-IV and (f) Spent catalyst (Cocat-II)

XRD peaks of all catalysts match with the reported data of cryptomelane OMS-2 (JCPDS 05-0681). Peaks in Co-OMS catalysts are sharp and similar to the OMS-2, showing that the substituted Cobalt OMS-2 materials also have crystallized with cryptomelane structure. It also confirms that cryptomelane structure of OMS-2 material is retained even after substitution of cobalt. No additional peaks corresponding to cobalt oxides were observed, indicating the absence of any other cobalt containing oxides that confirms the substitution of Co into OMS-2. In case of XRD pattern of spent catalysts, no changes were observed which confirms that the catalyst is stable under reaction conditions.

The lattice parameters and unit cell volume of K-OMS-2 and Co-K-OMS-2 catalysts are given in Table 5.3. These values were obtained by full profile fitting method using highscore plus software. The lattice parameter and cell volume of the structure has reduced on substitution of Co, suggesting its substitution in the OMS-2 framework. The dopant influences the lattice parameters as well as unit cell volume of the K-OMS-2 only slightly without following any trend.

Table 5.3- Effect of Co substitution on lattice parameter value and unit cell volume

S. No.	Catalysts	Co content Wt %	Lattice parameter Å		Cell volume Å^3
			a	c	
1	KOMS-2	0.0	9.876	2.862	279.14
2	Cocat-I	2.40	9.813	2.856	275.05
3	Cocat-II	3.03	9.799	2.852	273.90
4	Cocat-III	3.46	9.822	2.856	275.59
5	Cocat-IV	3.81	9.811	2.858	275.14

5.3.1.2. Scanning electron microscopy

Scanning electron micrographs of the samples were recorded to investigate the morphology of the catalyst samples. Figure 5.2 shows the typical fibrous morphology of the prepared KOMS-2 and substituted Co-OMS-2 materials.

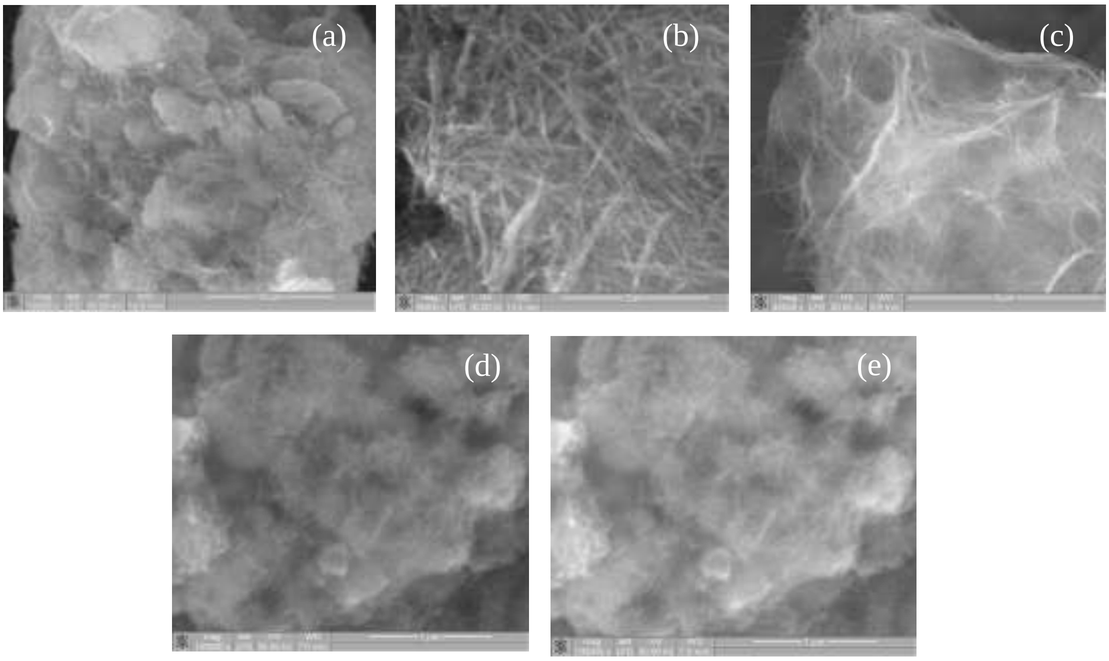

Fig. 5.2: SEM images of (a) KOMS-2; (b) 2.40% Cocat-I; (c) 3.03% Cocat-II; (d) 3.46% Cocat-III and (e) 3.81% Cocat-IV

The SEM photographs clearly show fibrous materials with needle shape, which are characteristic of cryptomelane structure of OMS-2 materials. In case of Co substituted OMS-2 materials, similar morphology was observed [69].

5.3.1.3. Transmission electron microscopy

The TEM photographs of KOMS-2 and Co-OMS-2 materials are shown in Fig. 5.3. The photographs of KOMS-2 show the fibrous nano rods with clear lattice fringes and the fiber length is mostly in the range of 20 to 200 nm [70] (Fig.5.3a and b). Similar images were obtained for Co substituted KOMS-2 material (Fig. 5.3c-f). This indicates that no changes occurred in cryptomelane structure on substitution of cobalt.

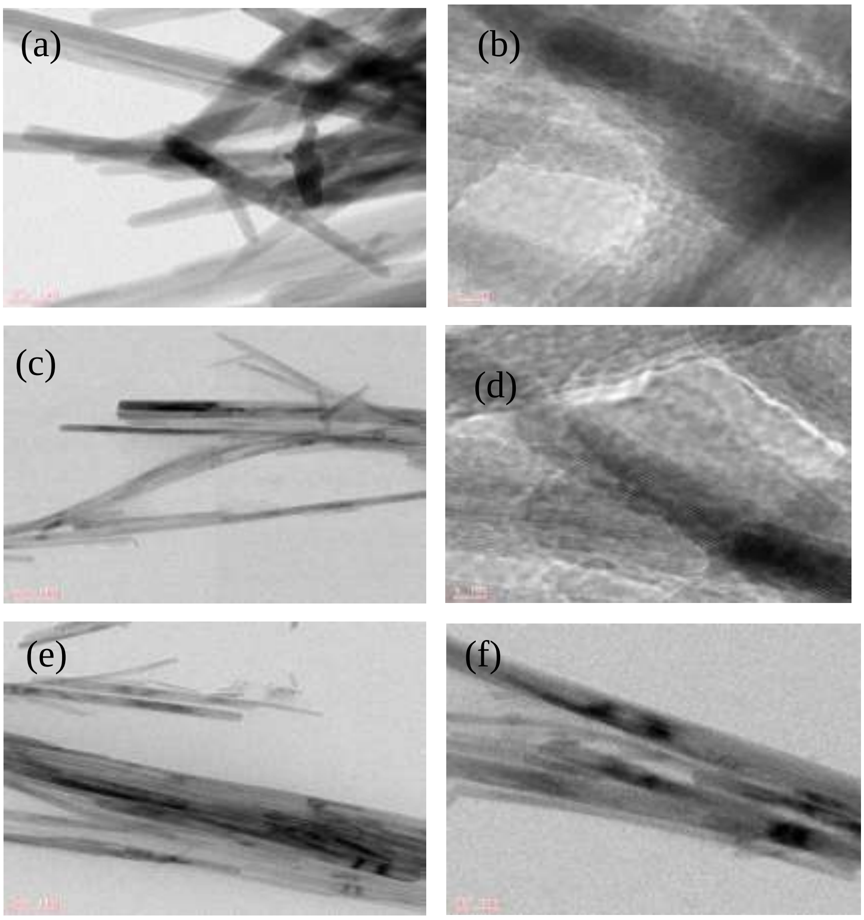

Fig. 5.3: TEM image of (a, b) K-OMS-2; (c) Cocat-I; (d) Cocat-II; (e) Cocat-III and (f) Cocat-IV

5.3.1.4. BET surface area by N_2 sorption

BET surface areas of parent K-OMS-2 material and cobalt substituted OMS-2 materials are given in Table 5.4. Surface areas of the synthesized OMS-2 materials are in the range of 90-160 m^2g^{-1}. To begin with, surface area of parent K-OMS-2 was $98m^2/g$; which has increased on substitution of cobalt. This increase in surface area at lower loading is probably due to smaller particle size of crystals [71]. A maximum in surface area (156 m^3/g) occurred for the Cocat-II with 3.03 wt. % Co (Table 5.4, row 3), which subsequently decreased with progressive increase in Co content. This decrease in surface area with Co content may be attributed to partial blockage of pores by extra lattice cobalt oxide which is not detected by XRD due to its very low content.

Table 5.4- Physiochemical properties of different catalysts

S. No.	Catalyst	S_{BET} m^2g^{-1}	Weight loss from TGA (wt %) 1st (303-550K)	2nd (653-963K)	3rd (963-1073K)
1	KOMS-2	98	7.0	5.0	3.1
2	(2.40%) Cocat-I	128	5.4	6.7	2.6
3	(3.03%) Cocat-II	156	13.6	4.9	3.2
4	(3.46%) Cocat-III	129	6.2	5.9	2.5
5	(3.81%) Cocat-IV	106	7.2	6.4	2.7

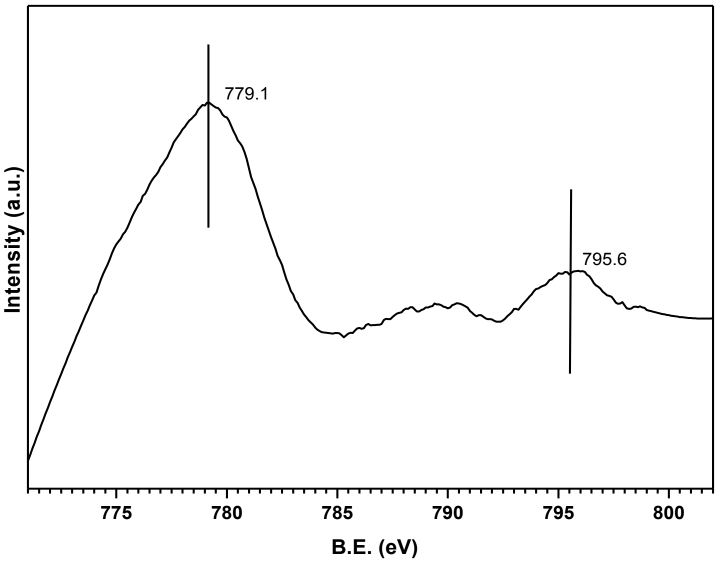

Fig. 5.4: XPS graph of Cocat-III

5.3.1.5. X-ray photoelectron spectroscopy

The Co-K-OMS-2 (Cocat) catalysts were also characterized by X-ray photoelectron spectroscopy (XPS). Fig. 5.4 shows the Co2p spectra of Cocat-II. The results show Co 2p3/2 and Co2p1/2 peaks at 779.1, 795.3eV respectively with an energy difference of 16.2 eV between $2p_{1/2}$ and $2p_{3/2}$ peaks, which is very close to that of Co^{2+} (16 eV) rather than Co^{3+} compounds (15.0 eV). This clearly indicates that the cobalt is in +2 oxidation state in the sample, in agreement with literature reports [72].

5.3.1.6. Thermal analysis

Thermal stability of Co-OMS-2 materials was studied with thermogravimetric analysis (TGA) in N_2 atmosphere in the temperature range of 303-1023 K while ramping at the rate of 283 K/min. Thermal stabilities of prepared KOMS-2 and Co-OMS-2 materials are summarized in Fig. 5.5 (Table 5.4). Parent K-OMS-2 material synthesized by reflux method shows weight loss in the temperature range between 300-1073 K. The initial weight loss (7%) in the temperature range 303-550 K is attributed to the loss of water in the sample. The second weight loss of about 5.0% in the 653-963 K temperature zone is due to loss of lattice oxygen, as the manganese cations reduce to lower oxidation state forming manganese oxide such as bixbyite (Mn_2O_3) [73].

The third weight loss of about 3.1%, observed in the temperature zone of 963-1073 K is attributed to a further loss of oxygen from bixbyite leading to the formation of more stable spinel hausmanite (Mn_3O_4) [74]. The general trend remained similar for each temperature zone but the weight loss differed based on cobalt content in the OMS-2 structures. The weight losses attributed to water loss in the samples was 5.4% for Cocat-I, 6.2% for Cocat-III, and 7.2% for Cocat-IV, whereas maximum weight loss was observed for Cocat-II (13.6%), suggesting that there was more water occluded in this sample compared to parent K-OMS-2.

The 2nd weight loss is due to change in phase of manganese from KMn_8O_{16} to Mn_2O_3 in the middle temperature zone of 653-963 K is more or less same for all catalysts as compared to KOMS-2. The weight losses were 6.7, 4.9, 5.9 and 6.4 wt % for Cocat-I, Cocat-II, Cocat-III and Cocat-IV respectively. The 3rd weight loss, for phase transition from Mn_2O_3 to Mn_3O_4, was almost similar as that of K-OMS-2 for all catalysts with slight shift in temperature range (600-900 K). The weight losses observed were 2.6, 3.2, 2.5 and 2.7 % for Cocat-I, Cocat-II, Cocat-III and Cocat-IV respectively. The C_O substituted OMS-2 materials show slightly lower thermal stability, which in turn may be attributed to the substitution of Co into OMS-2 lattice.

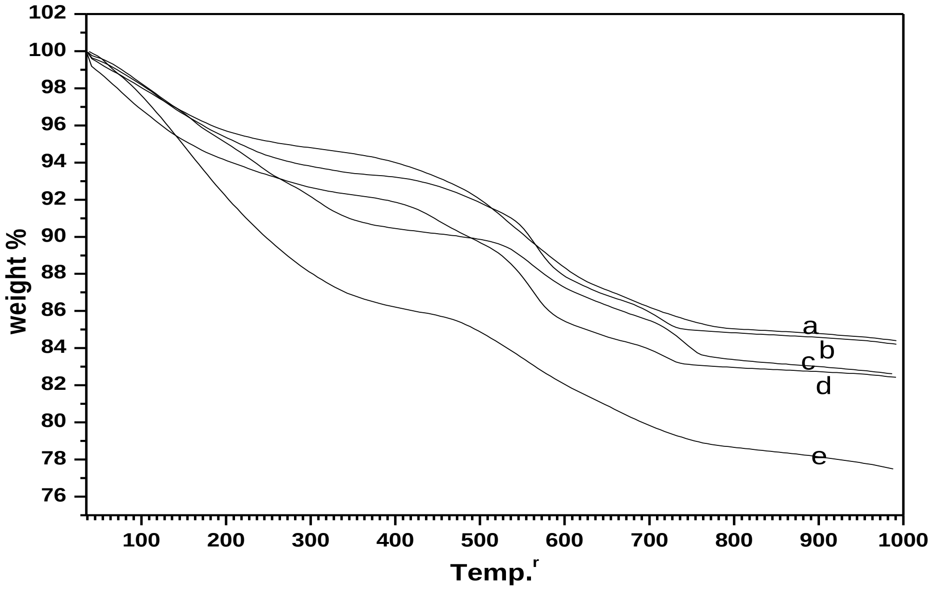

Fig. 5.5: TG of (c) KOMS-2; (a) Cocat-I; (e) Cocat-II; (b) Cocat-III and (d) Cocat-IV

5.4. Catalytic activity in oxidation reactions

5.4.1. Oxidation of *p*-cresol

Partial oxidation of *p*-cresol was carried out in a Parr reactor with *p*-cresol, sodium hydroxide in methanol as solvent using various cobalt containing octahedral molecular sieves catalysts under O_2 pressure as described in experimental section.

Table 5.5- Catalysts study in oxidation of *p*-cresol

S. No.	Catalyst	Conversion of *p*-cresol (mol %)	Yield (mol %)		
			PHBOH	PHB	PHBA
1	KOMS-2	--	--	--	--
2	Cocat-I	56.9	0.9	56.0	--
3	Cocat-II	64.9	0.5	64.4	--
4	Cocat-III	93.5	1.3	92.2	--
5	Cocat-IV	83.7	0.7	83.0	--

Reaction conditions: Catalyst (0.2 g), *p*-Cresol: NaOH: Methanol (1: 3: 16 molar ratio), 353 K, O_2 (20b), 3h.

5.4.1.1. Effect of catalyst concentration

All the catalysts with different Co contents gave good conversion of *p*-cresol and excellent selectivity for *p*-hydroxybenzaldehyde as shown in Table 5.5. Among the catalysts, Cocat-III catalyst (Co content 3.46 %) gave better results with 93.5% conversion of *p*-cresol along with 98.6% selectivity to *p*-hydroxybenzaldehyde. Small amount of *p*-hydroxybenzyl alcohol (1.3% yield) was observed in the product. However, further increasing Co content (Cocat-IV) in the catalyst did not help as there was decrease in *p*-hydroxybenzaldehyde yield (83.0 %) as well as conversion of *p*-cresol though the selectivity to PHB was similar.

The Cocat-I and Cocat-II catalysts with Co content 2.40 and 3.03% gave lower conversion (56.9% and 64.9%) of *p*-cresol and as a result lower yields of *p*-hydroxybenzaldehyde. No conversion of *p*-cresol was observed when parent KOMS-2 was used as catalyst, demonstrating the requirement of cobalt in the catalyst for partial oxidation of *p*-cresol.

Table 5.6- Effect of molar ratio of *p*-Cresol: NaOH

S. No.	Molar ratio *p*-cresol: NaOH	Conversion of *p*-cresol (mol %)	Yield (mol %)		
			PHBOH	PHB	PHBA
1	1:1	57.5	1.1	56.4	-
2	1:2	65.0	0.4	64.6	-
3	1:3	93.5	1.3	92.2	-
4	1:4	90.9	1.6	89.3	-

Reaction conditions: Cocat-III (0.2g), *p*-Cresol (3g), Methanol (16 mL), 353 K, O_2 (20b), 3h.

5.4.1.2. Variation of *p*-cresol : NaOH mole ratio

Since the phenolic hydroxyl group of *p*-cresol interferes in the oxidation process, it is necessary to convert *p*-cresol into its sodium phenolate salt in the presence NaOH. The effect of mole ratio of substrate (*p*-cresol) and NaOH on conversion of *p*-cresol is given in Table 5.6. On studying different mole ratios of *p*-cresol to sodium hydroxide, it was observed that among all ratios, 1: 3 mole ratio of *p*-cresol to NaOH gave higher conversion (93.5%) of *p*-cresol with 92.2% yield of *p*-hydroxybenzaldehyde. There was slight decrease in conversion and selectivity when molar ratio was increased further. When molar ratio was only 1:1, conversion of p–cresol was 57.5% and the yield of PHB was 56.4%. Both the conversion and yield of PHB increased along with NaOH.

5.4.1.3. Effect of catalyst content on performance

The results of variation in amount of catalyst are shown in Table 5.7. The weight of catalyst is varied from 50 to 250mg. The results show that 50mg of catalyst gave 57.7% conversion of *p*-cresol with 55.8% yield of PHB. At lower catalyst weight, yield of *p*-hydroxybenzyl alcohol is high due to suppression of further oxidation of *p*-hydroxybenzyl alcohol to PHB. With increasing weight of catalyst, substrate conversion as well as yield of product increased. The conversion was increased to 93.5% when 200mg of the catalyst was used, yielding 92.2% of PHB. However, no further increase in conversion or yield was observed on further increasing the catalyst weight. Similar trend was observed in regard to *p*-hydroxybenzaldehyde selectivity.

Table 5.7- Effect of catalyst weight on conversion of *p*-cresol

S. No.	Catalyst wt. (mg)	Conversion of *p*-cresol (mol %)	Yield (mol %)		
			PHBOH	PHB	PHBA
1	50	57.7	1.9	55.8	-
2	100	90.1	3.5	86.6	-
3	150	91.4	2.0	89.4	-
4	200	93.5	1.3	92.2	-
5	250	94.0	1.2	92.8	-

Reaction conditions: Cocat-III (0.2g), *p*-Cresol: NaOH: Methanol (1: 3: 16 molar ratio), 353 K, O_2 (20b), 3h.

5.4.1.4. Effect of temperature

Oxidation of *p*-cresol was carried out by varying reaction temperature in the range of 333-373 K and results are shown in Table 5.8. From results it was observed that as reaction temperature increased the conversion of *p*-cresol increased. At 333 K only 65.3% conversion was obtained accompanied by 62.5% yield of *p*-hydroxybenzaldehyde. The conversion of *p*-cresol was increased to 93.5% when reaction temperature increased to 353 K. Also, the yield of *p*-hydroxybenzyl alcohol decreased gradually from 2.8% to 1.3% to give 92.2% yield of *p*-hydroxybenzaldehyde.

When reaction temperature increased further to 373K, only slight increases in conversion of *p*-cresol and yield of PHB were observed, which were 94.2 and 93.1% respectively. The formation of *p*-hydroxybenzoic acid was not observed even at higher temperature.

Table 5.8- Effect of temperature on conversion of *p*-cresol

S. No.	Temperature K	Conversion of *p*-Cresol (mol %)	Yield (mol %)		
			PHBOH	PHB	PHBA
1	333	65.3	2.8	62.5	-
2	353	93.5	1.3	92.2	-
3	373	94.2	1.1	93.1	-

Reaction conditions: Cocat-III (0.2g), *p*-Cresol: NaOH: Methanol (1: 3: 16 molar ratio), O_2 (20b), 3h.

5.4.1.5. Recycle study

In order to check the stability and recyclability of catalyst, it was separated after completion of each reaction run, washed thoroughly with acetone till it's free of product. This catalyst was again recharged with fresh reactant and reaction was carried out under similar reaction conditions using same ratios of reactants to catalyst. Table 5.9 shows the results of recycle study on Cocat-III.

Table 5.9- Recycle study of Cocat-III catalyst

S. No.	Recycle No.	Conversion of *p*-cresol (mol %)	Yield (mol %)		
			PHBOH	PHB	PHBA
1	1	93.3	1.2	92.1	-
2	2	92.9	1.3	91.6	-
3	3	92.0	1.8	90.2	-
4	4	90.9	1.6	89.3	-

Reaction conditions: Cocat-III (0.2g), *p*-Cresol: NaOH: Methanol (1: 3: 16 molar ratio), 353 K O_2 (20b), 3h.

The catalyst was successfully recycled at least 4 times with only marginal loss in conversion of *p*-cresol and selectivity to the product. The loss in conversion of *p*-cresol may be attributed to loss in weight of catalyst during recycling. To check whether the reaction is purely heterogeneous or homogeneous reaction is also occurring due to leached Co, the catalyst was recovered after reaction, washed thoroughly with water followed by acetone. The filtrate as well as the spent catalyst was analyzed by ICP-OES analysis. The Co content in spent catalyst (3.40 %) was nearly same as in fresh catalyst (3.46 %), which confirms that no leaching of cobalt took place under reaction conditions and the reaction is entirely heterogeneous catalyzed.

5.4.2. Oxidation of *p*-xylene

Cobalt substituted K-OMS-2 catalysts were also evaluated for selective oxidation of *p*-xylene to terephthalic acid. The catalytic activity of Co-K-OMS catalysts for this reaction was excellent, as even 0.025 mmole of Co in the catalyst led to 85 % conversion of *p*-xylene and more than 70% yield of product within 90 min of time.

Table 5.10- Effect of temperature on selective oxidation of *p*-xylene over Co-OMS-2

S. No.	Temp K	Time minutes	Conversion of *p*-xylene (mol %)	Selectivity (mol %)			TPA Yield (mol %)
				TPA	PTA	PMB	
1	353	180	99.9	92.5	7.5	--	92.4
2	363	120	100	94.3	5.7	--	94.3
3	373	45	100	95.2	4.8	--	95.2
4	383	45	100	94.4	5.6	--	94.4

Reaction conditions: Cocat-II (150 mg), *p*-Xylene (8 mmole), NAPI (20 mole %), acetic acid (20 mL), O_2 (20b), TPA (terephthalic acid), PTA (*p*-toluic acid), PMB (*p*-methylbenzaldehyde).

5.4.2.1. Effect of temperature

The influence of temperature on the oxidation of *p*-xylene was studied in the temperature range 353-383K, results are shown in Table 5.10. The oxidation of *p*-xylene at 353K gave 99.9% conversion of *p*-xylene and 92.4 % yield of terephthalic acid along with 7.5 % of *p*-toluic acid in 3h. Both the selectivity and yield of TPA increased with increasing temperature, whereas yield of PTA decreased. Since, we were able to achieve 100% conversion in less time; we have reduced the reaction time to 45 from 180 minutes. The best yield (95.2 %) of TPA was obtained when reaction was carried out at 373 K for 45 minitues. A decrease in yield of TPA (94.4 %) and a slight increase yield of PTA (5.6 %) were observed when the reaction is carried out at 383 K.

5.4.2.2. Effect of type of initiator and its content

Results in regard to the effect of different initiator on yield of TPA are shown in Table 5.11. All the initiators gave almost 100% *p*-xylene conversion with 95% selectivity to terephthalic acid. The oxidation of *p*-xylene with NHPI (N-hydroxy-phthalimide) as an initiator at 373 K gave 90.1 % yield of TPA along with 9.8 % yield of PTA. When NAPI (N-acetoxyphthalimide) was used instead of NHPI under same reaction conditions, the yield of TPA has increased to 95.2% with only 4.8% of PTA. This probably can be attributed to the fact that acetylated derivative N-acetoxy-phthalimide slow in decomposition, which helps in better utilization of the initiator, particularly in the initial stages of the reaction. These results are in agreement with those reported earlier by Tashiro *et al* [75]. With NHSI (N-hydroxy succinimide) as the initiator, only 91.0 % TPA yield was obtained along with 9.0 % PTA.

Table 5.11- Effect of type of initator on TPA yield

S. No.	Initiator	Conversion of *p*-Xylene (mol %)	Selectivity (mol %)			TPA Yield (mol %)
			TPA	PTA	others	
1	NHPI	99.9	90.2	9.8	--	90.1
2	NAPI	100	95.2	4.8	--	95.2
3	NHSI	99.9	91.0	9.0	--	90.9

Reaction conditions: Cocat-II (150 mg), *p*-Xylene (8 mmole), Initator (20 mole %), acetic acid (20 mL), O_2 (20b), 373K, 45min.

The effect of NAPI mole % of was also tested for this reaction, the results (Table 5.12) show that when 5 mole % of NAPI was used in reaction, only 23.98% yield of TPA and 72.25% yield of *p*-toluic acid (PTA) were observed. Since, the reaction is a chain reaction, continuous availability of sufficient initiator is essential for the conversion of PTA to final product TPA by subsequent step. As mole % of initiator increased, the conversion of PTA to terephthalic acid also increased. When 20 mole % of NAPI was used, the yield of TPA remarkably rose to 95.2 % at 100% conversion of *p*-xylene. Under these conditions, only 4.8% PTA was remained unconverted to the final product. Surprisingly, increasing the initiator further did not help as the reaction yielded 91.2 % TPA.

Table 5.12- Effecet of intitator content on *p*-xylene conversion and TPA yield

S. No.	NAPI (mole %)	Conversion of *p*-xylene (mol %)	Selectivity (mol %)			TPA Yield (mol %)
			TPA	PTA	others	
1	5	96.3	24.9	75.03	--	23.98
2	10	99.5	51.9	48.1	--	51.6
3	15	100	91.6	8.4	--	91.6
4	20	100	95.2	4.8	--	95.2
5	25	100	91.2	8.8	--	91.2

Reaction conditions: Cocat-II (150 mg), *p*-Xylene (8 mmole), NAPI (mole %), Acetic acid ((20 mL), O_2 (20b), 373K, 45min.

5.4.2.3. Effect of cobalt content on *p*-xylene oxidation

The influence of Co content in the catalyst is shown in Table 5.13. All catalysts gave 100% conversion of *p*-cresol with more than 90% selectivity to terephthalic acid. There was not much influence of Co content on yield and selectivity of TPA. Probably, the Co content is in a high range in all catalysts, making it difficult to differentiate the performance in terms of Co content. Among the catalysts, Cocat-I gave lowest yield of TPA (92.2 %) in 90 min of reaction time. Whereas, Cocat-II with 3.03% Co showed relatively higher (95.2%) yield for TPA with 4.8% yield of PTA in 45 min. Cocat-III and Cocat-IV gave almost similar results with 94.5 and 93.3% yield of TPA.

Table 5.13- Effecet of cobalt content in the catalyst on TPA yield

S. No.	Catalyst	Conversion of *p*-xylene (mol %)	Selectivity (mol %)			TPA Yield %
			TPA	PTA	other	
1	Cocat-I	100*	92.2	7.8	--	92.2
2	Cocat-II	100	95.2	4.8	--	95.2
3	Cocat-III	100	94.5	5.5	--	94.5
4	Cocat-IV	100	93.3	6.7	--	93.3

Reaction conditions: Catalyst (150mg), *p*-Xylene (8mmole), NAPI (20 mole %), Acetic acid (20 mL), O_2 (20b), 373K, 45min, *90min.

5.4.2.4. Effect of catalyst content on performance

The results of variation in amount of catalyst (Cocat-II) are shown in Table 5.14. The results show that, as catalyst weight increases, the conversion and selectivity increases.

Table 5.14- Effect of catalyst weight on TPA yield

S.No	Cata wt. mg	Conversion of *p*-xylene (mol %)	Selectivity (mol %)			TPA Yield (mol %)
			TPA	PTA	others	
1	50	85.0	83.2	16.8	--	70.7
2	100	100	87.4	12.6	--	87.4
3	150	100	95.2	4.8	--	95.2
4	200	100	93.9	6.1	--	93.9

Reaction conditions: Cocat-II, *p*-Xylene (8 mmole), NAPI (20 mole %), Acetic acid (20 mL), O_2 (20b), 373K, 45min.

50mg of catalyst gave 85.0% of *p*-xylene conversion with 70.7% yield of TPA. With increasing weight of catalyst, substrate conversion as well as yield of product increased. The complete conversion of *p*-xylene was observed on further increase in weight of the catalyst. The best result, 100% conversion and 95.2% selectivity for TPA, was obtained when 150mg of catalyst was used. However, slight drop in TPA yield (93.9%) was observed on further increase of the catalyst weight.

5.4.2.5. Recycle study

In order to study the recyclability of Co-K-OMS-2 catalysts for *p*-xylene selective oxidation, catalyst was recovered after the completion of reaction, washed with dichloromethane till it is free from organic substrate and dried in air. This catalyst was re-used for the reaction with fresh reactants. The results are shown in Table 5.15. The results show that, catalyst was recycled at least three times with activity of catalyst mostly same for the 2nd cycle without much change in conversion of *p*-xylene or selectivity to TPA. However, for 3rd recycle, though conversion of *p*-xylene was close to 100%, TPA yield dropped substantially by 10%. At the same time, PTA content increased in the product. This shows that there is clear cut loss in activation at least for the consecutive oxidation of PTA to TPA.

Table 5.15- Recycle study of Cocat-II in *p*-xylene oxidation

S. No.	Recycle No	Conversion of *p*-xylene (mol %)	Selectivity (mol %) TPA	PTA	others	TPA yield (mol %)
1	1	100	94.6	5.4	--	94.6
2	2	100	93.9	6.1	--	93.9
3	3	99.8	83.7	16.2	--	83.5

Reaction conditions: Cocat-II (150 mg), *p*-Xylene (8 mmole), NAPI (20 mole %), Acetic acid (20 mL), O_2 (20b), 373K, 45min.

5.5. Conclusions

In this investigation Co substituted octahedral molecular sieves (Co-K-OMS-2) were prepared, to use them as selective oxidation catalysts for hydrocarbon conversion. Catalysts with different Co content were prepared by a simple reflux method. These were characterized by different physic-chemical techniques and to understand their structural and textural characteristics. No perceptible changes were observed in the cryptomelane phase of KOMS-2 on substitution of cobalt. Similarly, no additional phases belonging to cobalt or cobalt oxide were observed from powder XRD investigations. Co-OMS-2 material shows well resolved sharp XRD peaks. Only minor changes in lattice parameter and unit cell volume were observed, probably as a result of close resemblance in size of Mn and Co cations. This change in lattice parameters and unit cell volume on substitution of cobalt in OMS-2 suggests that cobalt is likely being present in the framework of OMS-2 (cryptomelane). Compared to the KOMS-2, cobalt substituted Co-OMS-2 catalysts have relatively higher surface area. TEM as well as SEM confirm pure phases of cryptomelane with fibrous morphology and no extraneous phases belonging to cobalt were seen in the samples. Thermo gravimetric analysis of Co-OMS-2 materials indicate similarity in weight losses in different temperature regimes when compared to K-OMS-2 materials, but slightly lower thermal stabilities as compared to the later.

The Co-OMS-2 catalysts were investigated for selective oxidation of p-cresol to p-hydroxybenzaldehyde and p-xylene to terephthalic acid. The catalysts showed their utility and versatility for both partial oxidation reactions. The catalysts were highly active for the above oxidations with good conversion, selectivity and short reaction time. Good conversion (93.5%) of p-cresol was obtained with 92.2% p-hydroxybenzaldehyde selectivity, while 100% conversion of p-xylene was attained to yield 95.2% of terephthalic acid in 45 min. Reaction conditions used for oxidation reactions were very moderate for both the selective oxidations. In case of p-xylene oxidation, toxic NaBr as initiator was replaced with environmental friendly NAPI. Further, the catalysts are stable under the reaction conditions and retain good activity and selectivity for at least upto five successive runs. The catalysts reported here are easy to prepare, the initiator and the process are a step forward in the direction for potential commercial exploitation of these materials for selective heterogeneously catalyzed oxidation reactions.

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Chapter-VI

Summery and Conclusions

6.1. Summary and Conclusions

The present thesis deals with the (i) preparation of different catalyst materials such as palladium containing octahedral molecular sieves (OMS-2), a microporous material which is basic in nature. (ii) Immobilized copper complexes on mesoporous silica and (iii) Cobalt substituted OMS-2 materials. It also contains in-depth characterization of these catalyst materials using various techniques, catalytic activity of these materials in various cross coupling and oxidation reactions.

Chapter 1

General introduction to heterogeneous catalysis, including a brief description of different methods used for the preparation of heterogeneous catalysts and their importance is given in chapter I. This chapter also presents an introduction to cross coupling reactions (carbon-carbon and carbon-heteroatom) and their significance in industrially important organic transformations. It also provides introduction to selective oxidation of side chain alkyl groups of aromatics to corresponding carbonyl compounds and the present status of these reactions. The chapter focuses on the role of transition metal oxides as catalysts and improvements that can be brought about in their catalytic properties through substitution of other transition metals. A review of the literature to date in these areas has been included.

Chapter 2

Chapter 2 describes preparation methods of various catalysts, tested in coupling and selective oxidation reactions, viz., Pd-OMS, immobilized copper imine catalysts on SBA-15 and Co containing OMS-2 catalysts. It also described various experimental techniques deployed for characterization of catalysts. Since, the characterization of these materials was carried out using powder XRD, BET surface area (by N_2 sorption), SEM, TEM, UV-Vis, IR and XPS for correlation with catalyst properties, a detailed description of these techniques, their theory and experimental procedures have been dealt with in this chapter.

Chapter 3

Chapter 3 provides detailed introduction to Heck, Suzuki and Sonogashira reactions and their mechanism. This chapter is divided into three parts. Part-A presents the preparation of support material K-OMS-2, loading of palladium by ion exchange method followed by its reduction and procedures used for coupling reactions. Three Pd-KOMS-2 catalysts were prepared with different Pd contents for their evaluation. Part-B presents the characterization results of Pd(0)-K-OMS-2 catalysts using XRD for structure elucidation, SEM and TEM to study their morphology before and after loading of Pd. In addition, the results from AAS, UV-VIS, XPS, N_2 sorption etc were discussed in detail. Part-C presents the activity of catalysts in Heck, Suzuki and Sonogashira cross coupling reactions, which are currently relevant and industrially important organic transformations. The best catalyst among the screened catalysts was used to study the effect of reaction parameters like temperature, catalyst weight, influence of base and solvent on product yields. Conclusions drawn from the catalytic studies and their correlation with the characterization results, for different C-C cross coupling reactions was also described at the end of this section.

Chapter 4

Chapter 4 provides an introduction to Ullmann (C-O) and carbon-sulphur coupling reactions. This chapter is divided into three parts. Part-A presents the preparation of mesoporous SBA-15 and immobilization Cu complexes on it. Different types of Cu immobilized catalysts were prepared by changing precursor before imine formation step. Part-B describes the characterization of Cu immobilized catalysts (CuSBA-I, CuSBA-II and CuSBA-III) with XRD, SEM, TEM, N_2 sorption etc. The characterization results show a fall in the intensity of XRD peaks, some drop in N_2 sorption values at higher loading of organic moiety on SBA-15. Part-C describes catalytic activity of these catalysts in some important carbon- heteroatom (C-O and C-S) cross coupling reactions.

The best among these catalysts was used for further study to understand the effect of reaction parameters like temperature, catalyst weight, base and solvent on the conversion of aryl halide to the desired product. The reaction was conducted with different starting substrates on immobilized copper catalysts to know the general applicability of these catalysts. From the results, it is clear that all the catalysts show good activity in both coupling reactions (C-O and C-S) and use of stronger base and polar solvent could provide excellent yield of desired product. At the end, correlation of catalytic data with their characterization results is given to arrive at conclusions.

Chapter 5

Chapter 5 gives detail introduction to oxidation of aromatic side chain alkyl groups with transition metal catalysts. It also discusses the role and mechanism of reaction. It is divided into three parts. Part-A presents the preparation of cobalt substituted KOMS-2 catalysts by direct reflux method. Using this method, three catalysts were prepared with different cobalt contents. Part-B describes the characterization results of Co-K-OMS-2 catalysts obtained from XRD, SEM, TEM, N_2 sorption and IR studies. Characterization shows that doped cobalt is present in K-OMS-2 lattice of cryptomelane with cobalt in +2 oxidation state. Part-C presents, the catalytic activity of the Co-KOMS-2 catalysts in selective oxidation reactions of methyl groups present on aromatics (p-cresol, p-xylene) to their corresponding intermediates. Since, there is cobalt along with manganese in these materials; it helps in achieving selective oxidations with very high yields of products.

Use of NAPI as an initiator for these reactions demonstrates advantage of this process Vis a Vis other reported processes. This initiator appears to be an excellent alternative to the traditionally used NaBr, which is toxic and harmful to the environment. One of the catalysts that were found to be relatively better among different cobalt containing compositions was used for further exploration to understand the effect of various reaction parameters. Influence of temperature, catalyst weight and the type of initiator on the selectivity and yield of the product was reported. The conclusions drawn from the above studies including interpretation of catalytic results and correlations with characterization results are presented at the end of the chapter.

Chapter 6

As it is mandatory at the end of any report to summarize the work for the benefit of the reader, this chapter summarizes the results and conclusions reached during these investigations. Initially it describes the content of each chapter in details with a glimpse of results at the end. This section also offers suggestions for further research work in these areas and scope of their applications.

6.2 General conclusions

- ✓ Pd-K-OMS-2 catalysts with different Pd content were prepared successfully using simple reflux method followed by exchange and reduction of palladium.

- ✓ The cryptomelane structure of KOMS-2 was retained after loading of palladium which was inferred through characterization of these materials using various physico-chemical techniques. No changes were observed in crystallinity of these materials through X- ray diffraction of catalysts before and after use in reaction. This confirms the stability of catalyst under reaction conditions. SEM studies show fibrous nature of K-OMS-2 and Pd-K-OMS-2, while TEM studies confirm the needle shape of the crystals in these microporous materials. The fine dispersion of nano sized palladium particles on OMS material was also confirmed through TEM.

- ✓ The Pd-K-OMS-2 catalysts show their versatility and effectiveness in different types of C-C bond formation reactions. Ligand free heterogeneous catalysts were demonstrated for their reactivity in Heck, Suzuki and Sonogashira cross coupling reactions with good conversion of substrate and excellent selectivity to the desired product under mild reaction conditions. The catalysts were effective even when different functional groups are present on the substrate and gave good conversion and selectivity.

- ✓ Immobilized copper on SBA-15 mesoporous material was prepared successfully by heterogenizing copper on SBA-15. These materials were found to be good catalysts for Ullmann reactions.

- ✓ Presence of sharp intense peaks in XRD, even after immobilization of APTES and loading of the Cu shows that SBA-15 crystallinity was retained. The XRD of spent catalysts didn’t show any observable change confirming the stability of catalyst under reaction conditions. SEM and TEM images of the SBA-15 and the derived catalysts show rope like morphology and hexagonal shape of the crystals. CP-MAS NMR and IR techniques unambiguously prove the immobilization of APTES and copper on SBA-15.

- ✓ The immobilized copper catalysts demonstrated promising activity for C-O and C-S cross couplings under mild reaction conditions, though the activities were slightly low when compared to their homogeneous analogues. These catalysts converted around 80% of the substrate with 99% selectivity to the desired product in Ullmann reaction. However, only 75% selectivity was for C-S coupling. These catalysts are relevant to variety of substrates including non activated bromobenzene compounds resulting in good yield of the product.

- ✓ Heterogeneous cobalt substituted octahedral molecular sieves (Co-OMS-2), were prepared through reflux method and used for selective oxidation of aromatic hydrocarbons (*p*-cresol, *p*-xylene).

- ✓ XRD pattern of as synthesized Co-K-OMS-2 show sharp peaks and no observable changes in cryptomelane phase (KOMS-2) were observed even after substitution of cobalt into OMS-2 material.

- ✓ The Co-OMS catalysts were evaluated for selective oxidation of *p*-cresol to p-hydroxybenzaldehyde. They offered very good conversion, selectivity and yield of the desired product. These catalysts were also used for oxidation of *p*-xylene to terephthalic acid. The product yields were more than 92% with close to 95-100% selectivity in both the reactions. Moreover, these yields could be achieved with very short reaction time (45 to 180 min). The oxidation of p-xylene is being reported for the first time using this environmental friendly and NAPI as the initiator.

- ✓ All the catalysts used for oxidation are stable under reaction conditions implying their utility and advantages when compared to other catalysts and processes reported so far. These catalysts are truly heterogeneous and can be reused without any loss in activity. They retain good activity and selectivity for at least upto five successive runs.

- ✓ The study shows the way forward in using simple catalyst systems for industrially important reactions with promising potential for commercial exploitation.

6.3 Suggestions for future research

The aim of the present investigation was to develop novel transition metal catalysts for carbon-carbon, carbon-heteroatom bond forming reactions and also for selective oxidation of hydrocarbons. Hence, this thesis deals with preparation and characterization of heterogeneous catalysts that were applied for coupling and oxidation reactions. An up to date survey of literature reveals that when a metal or a metal complex was heterogenized on an inorganic solid support (e.g. zeolites, mesoporous SBA-15 etc.) it led to high metal dispersion yielding to stable catalysts. These catalysts not only show good activity with high selectivity to the desired product, leaching of metal/metal complex is also prevented in solution, paving the way for development of alternate catalysts for the above cited reactions. Therefore, there is a good opportunity to develop these new heterogeneous catalysts further and scale them to accomplish new industrial processes. Further investigations are also needed, including testing of the catalysts for many more cycles to estimate the recyclability and deactivation pattern.

Selective oxidation of hydrocarbons is industrially important as currently more than 62% of industrial products are obtained through catalytic oxidation. Industry favours to practice green processes without having any toxicity problems. At the same time the process should be low cost and environmentally benign. Co substituted OMS-2 catalysts show a way forward in this direction as excellent activity and selectivity could be achieved during selective oxidation of p-cresol and p-xylene using CoKOMS-2 catalysts. The catalyst gave > 90 % conversion and ~99% product selectivity for both reactions. Use of NAPI in place of NaBr, a toxic initiator for the above oxidation reactions is an important finding. Moreover, using these catalysts, the reaction times are much lower. These results show high promise and the catalysts may have important applications in other hydrocarbon oxidations, including selective oxidation of renewable platform chemicals such as HMF (5-hydroxymetheyl furfural). Hence, these catalysts should be evaluated for a number of other substrates. These catalysts should also be scaled up and checked for reproducibility.