# STUDIES ON CATALYSIS BY MESOPOROUS CERIA MODIFIED WITH TRANSITION METALS

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*by*

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# Studies on Catalysis by Mesoporous Ceria Modified with Transition Metals

*Ph.D Thesis*

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# Certificate

Certified that the present work entitled **"Studies on catalysis by mesoporous ceria modified with transition metals"** submitted by Smt. Rose Philo K. J. is an authentic record of research work carried out by her under my supervision at the Department of Applied Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry of the Cochin University of Science and Technology and has not been included in any other thesis previously for the award of any degree.

*Dr. S. Sugunan*
*(Supervising Guide)*

Kochi-22
6-6-2012

# Declaration

I hereby declare that the research work entitled, **“Studies on catalysis by mesoporous ceria modified with transition metals”** is entirely original and was carried out by me independently under the supervision of Dr.S.Sugunan, Professor, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-22, India and has not been included in other thesis submitted previously for the award of any other degree.

*Rose Philo K.J*

Kochi-22
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*……To my dearest parents*
*and*
*My husband*
*for their love and constant support…*

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# Preface

Catalysis has wide ranging applications in chemical industry and has a major impact on the quality of human life as well as economic development. In recent years catalysis is looked up as a solution to eliminate or replace polluting processes. Solid acid catalysis is one of the most important areas of research and has assumed great relevance as an economic alternative to many homogenously catalysed, industrially important reactions. The solid acid catalysts can also be designed to give higher activity, selectivity, regenerability and longer catalyst life.

Among the different solid acid catalysts used, mesoporous materials are more widely studied nowadays. In the field of catalysis, much effort has been spent in the preparation, characterization and application of mesoporous metal oxides. Among different rare earth metal oxides studied, ceria has potential applications. Ceria and ceria based mixed oxide materials are used in automotive exhaust catalysis and oxidation of environmental pollutants. Cerium oxide is an excellent catalyst for redox reactions.

In this work mesoporous ceria is synthesized with cubic fluorite structure by templated route, using neutral surfactant hexadecylamine. The catalytic activity is enhanced by loading transition metals Cr, Fe, Cu, Co, Mn and Ni into this mesoporous network by wet impregnation method. The systems were characterized by low and wide angle XRD, FT-IR, BJH ($N_2$ adsorption/desorption studies), TG/DTA, EDX, ICP-AES, SEM, TEM, UV-Vis. DRS and TPR of $H_2$. Ammonia TPD and cumene cracking as the test reaction for acidity are adopted for the surface acidity determination. For the activity studies of the prepared systems, liquid phase reactions - oxidation of ethyl benzene using TBHP to get acetophenone as the main product, Friedel Crafts benzylation of toluene, o-xylene and anisole using benzyl chloride, acetalization and de-acetalization of cyclohexanone for the protection of ketone functional group and vapour phase reaction - methylation of phenol are also done.

The work is presented in 8 chapters. Chapter 1 is introduction and literature survey. Chapter 2 explains the method of preparation and characterization of the prepared catalysts. Chapter 3 contains results and discussions of physico-chemical characterization. Chapter 4, 5, 6 and 7 describe the various liquid phase reactions done for studying the catalytic activities of the prepared systems. Chapter 8 gives the summary of the work done and conclusions made on the basis of the different physico-chemical characterizations and catalytic activity studies. The most efficient catalysts for Friedel Crafts benzylation among the prepared samples are iron modified ones. The Cr loaded mesoporous ceria is found to be the most efficient among the prepared systems for oxidation of ethyl benzene using TBHP in liquid phase to get acetophenone selectively as the major product. From the study on acetalization and deacetalization of cyclohexanone it can be concluded that the prepared catalysts are successful in the protection of ketone group and afterwards the same catalysts can be used to regenerate the ketone group in the substrate by de-protection in a simple manner. We report herein the development of an environment friendly process for C-methylation of phenol with methanol using mesoporous ceria modified catalysts.

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Chapter 1

# INTRODUCTION AND LITERATURE SURVEY

Contents

Solid acids, micelle-templated metal oxides and other mesoporous high surface area support materials are beginning to play significant roles in the greening of fine and specialty chemicals manufacturing processes. A wide range of important organic reactions can be efficiently catalyzed by these materials, which can be designed to provide different types of acidity as well as high degrees of reaction selectivity. The solid acids generally have high turnover numbers and can be easily separated from the organic components. The combination of this chemistry with innovative reaction engineering offers exciting opportunities for innovative green chemical manufacturing in the future.

## 1.1 Introduction

Within the contest of sustainable technology, catalysis is a means to more efficient processes (lower energy demands, highly selective, waste-free), thereby providing a better use of raw materials. Industry relies heavily on heterogeneous catalysis to perform chemical transformations. Catalysis has wide ranging applications in chemical industry and has a major impact on the quality of human life as well as economic development. In recent years catalysis is also looked up as a solution to eliminate or replace polluting processes due to inherent characteristics of most catalytic processes as clean technologies. The catalytic reactions are generally classified as homogeneous or heterogeneous depending on the physical state of the catalyst. Both the categories have their advantages and disadvantages, though heterogeneous catalysis has been more widely used, as it is more environmentally benign. Catalyst has now become an indispensable component in majority of chemical reactions. In every field of human activity catalyst plays a vital role leading to the production of industrial chemicals, fuels, pharmaceuticals as well as environmental pollutant destruction. Catalysis is of particular importance in petroleum refining. Almost all petroleum feed stocks are being processed by catalytic reactions like catalytic cracking, alkylation, isomerization, hydrocracking, hydrodesulphurization, reforming, polymerizations, hydrogenation, and dehydrogenation.

Industrial catalysis was developed from an art to science and even today many industrial processes are based on enlightened empiricism rather than on scientific knowledge [1]. A typical industrial catalyst should be regenerable, reproducible, mechanically and thermally stable, and economical and should possess suitable morphological characteristics apart from its activity, selectivity, and stability [2].

The study of catalytic reactions begins with the dehydrogenation studies of alcohol using metals by Von Marum (1776). John Jacob Berzelius formulated the term ‘catalysis’ in the year 1835. The term catalysis as defined by Ostwald in 1894 “the phenomenon in which a small quantity of the substance that increases the rate of chemical reaction without being consumed” is a kinetic phenomenon. Catalysis has been the basis for most of the commercial processes in petroleum and petrochemical industry, where the solid catalysts are often used. The solid catalyzed reactions have major advantages of easy separation and of using on continuous manner and hence used in every large scale manufacture. Since the catalytic action occurs at specific sites on solid surfaces the rate can be significantly increased by using a high surface area catalyst. It is generally believed that higher the surface area of the catalyst higher will be the activity. Solid acid catalysts are appreciable since the nature of acid sites is known and their chemical behavior in acid catalyzed reactions can be explained by means of existing theories and models. It is possible to modify the acid properties of these materials by adopting various synthesis and post synthesis routes. It is possible to confirm these modifications by the available techniques. There exist a large variety of solid acids: natural clay minerals, mounted acids, cation exchange resins, metal oxides and mixtures of metal oxides and zeolites. The studies on catalysis by solid acids are extremely numerous.

Advancing catalytic technologies have played a vital role in the economic development of the chemical industries in the 20th century, with a total contribution of 20% of world GNP [3]. In the 21st century, we can expect the drive towards cleaner technologies brought about by public, legislative, and corporate pressure to provide new and exciting opportunities for catalysis and catalytic processes [4]. A rapidly growing area of heterogeneous catalysis is for environmental pollution control. Although heterogeneously catalyzed processes are widely used in large scale petrochemical processes, the majority of fine, speciality, and pharmaceutical chemicals manufacturing processes rely on homogeneous reagents and catalysts. Many of these processes were developed about 100 years ago and had been developed simply to maximize product yield, disregarding the environmental impact of inorganic waste and toxic byproducts formed during the reaction. Most of the waste is generated during the separation stage of the process when a typical water quench and neutralization (for acidic or alkaline systems) results in the waste disposal costs adding to the environmental costs and the societal costs of an increasingly hostile public toward chemical waste [5, 6]. Using solid acid catalysts, product isolation is easy and reactions often run under milder conditions and give higher selectivity. The atom efficiency of the reaction is improved, the process is simplified, precious raw materials used in the manufacture of the catalysts are given increased lifetime (through reuse), and the volume of waste is significantly reduced. Polymer-supported catalysts have been widely used in research and in process chemistry, but their use is restricted due to easy damage to the organic polymer (thermal or chemical) [7]. Zeolites have excellent thermal and chemical stability and have been incredibly successful in vapor phase chemistry, but they are less useful for many organic reactions in which molecular sizes can exceed the small zeolite pores and where liquid-phase reactions can lead to diffusion control. We have sought to exploit the recent emergence of mesoporous solids in organic synthesis by designing materials that can accommodate most organic molecules and have active surfaces that can catalyze important reactions [8]. By combining this with innovative engineering appropriate for smaller volume heterogeneous reactions, we hope to develop a range of novel greener processes for the manufacture of higher volume organic chemicals.

## 1.2 Solid Acids

Solid acid catalysis is one of the most important areas of research and has assumed great relevance as an economic alternative to many homogenously catalysed, industrially important reactions. Solid acid catalysts play a crucial role in the petrochemical industry, where they have largely replaced traditional acids active in the liquid phase for hydrocarbon transformations. The solid acid catalysts have many advantages over liquid Brönsted and Lewis acid catalysts [9]. They are non-corrosive, environmentally benign and easily separable from the reaction mixture and pose few problems of disposal. The solid acid catalysts can also be designed to give higher activity, selectivity, regenerability and longer catalyst life. In the last two decades substantial progress has been made and several industrial processes that use solid acid catalyst have been introduced successfully. As well as, being convenient to handle, solids can be used at high temperatures and give enhanced product selectivity. They are also finding increasing use in the production of feedstock organic chemicals and the synthesis of fine chemicals.

Many features of acid sites in solids are closely parallel to those in solution. Materials that are Brönsted acids (proton donors) and Lewis acids (electron acceptors) are known, with the action of Brönsted sites in zeolites being particularly well understood. Solid acids can be described in terms of their Brönsted / Lewis acidity, the strength and number of these sites, and the morphology of the support (typically in terms of surface area and porosity). Typically, Brönsted acid sites in mixed metal oxides occur where the oxygen atoms of a hydroxyl group attached to a metal atom of one kind are coordinating (acting as a Lewis base) to atoms of a different kind, resulting in more acidic centres. Lewis acid sites are usually associated with incompletely coordinated cations that accept electrons. In some cases, “super acid" sites (with stronger acidity than concentrated sulfuric acid) are also observed. High product selectivity can depend on the fine-tuning of these properties. For instance, some rearrangement reactions require pure Lewis acidity, Friedel-Crafts reactions require Lewis acidity (e.g., for alkylations using alkyl halides) or Brönsted acidity (e.g., for alkylation using alcohol), or indeed, a combination of both (e.g., for Friedel-Crafts acylations using acid chlorides). Pore constraints may influence product selectivity as a result of the sizes of substrates, intermediates & products. At a more fundamental level, the use of mesoporous supports have enabled supported reagents and catalysts to be used in reactions of much bulkier substrates than could be considered for micro porous (zeolite) materials [8]. The synthesis of pure Lewis or Brönsted solid acids is a particularly important challenge where some progress has been made. Chemically modified micelle-templated silica (MTS) materials as analogues for sulfonic acids have recently been reported and show great promise as solid Brönsted acids [10]. Pure Lewis acids are more difficult to achieve, because Brönsted acidity often arises from Lewis acid-base complexation. To obtain high selectivity toward the desired products in synthetic reaction all these properties must be considered. For example, acetal formation and hydrolysis reactions generally require medium acid strength sites, while electrophilic additions of alcohols or water to olefins, skeletal rearrangements, esterification, and alkylation reactions require strong acid sites. Likewise, the importance of the nature of the acid site is demonstrated in Friedel–Crafts alkylation reactions, where Lewis acid sites are required for alkylation of toluene using benzyl chloride, while Brönsted sites are preferred for reactions using benzyl alcohol [11]. In addition, steric constraints imposed by the pore structure of the solid acid can influence the reaction pathway resulting in "shape-selective catalysis". Recent development in the preparation of mesoporous materials has allowed liquid-phase reactions with bulky substrates.

Catalysis is a very complex process. The catalytic action consists in accelerating a useful reaction at the expense of other thermodynamically possible transformations. For saving energy and raw materials, catalysts must be extremely selective. This requires that surface composition be very precisely adjusted at the scale of the elementary catalytic process that is at the scale of molecules. This is necessary for the different surface atoms to work in co-operation with each other. Consequently, one of the major challenges in catalyst preparation is to synthesize highly dispersed solids (high surface area per unit mass of material) with a composition uniform at the atomic scale. This demand is far from being satisfied for catalysts and supports, neither in the laboratory nor in fabrication plants. Nanotechnology certainly goes in the direction of the goal. Catalysts demand not only nano-scale but also Angström-scale control [12].

## 1.3 Metal Oxides in Heterogeneous Catalysis

During the past decade, much attention has been paid to the replacement of homogeneous catalysts by solid acid catalysts. Most of the solid acid-base catalysts used in various chemical transformations is based on inorganic oxides. In most cases these oxides are to be modified chemically or physically so as to get desired catalytic activity for a particular reaction. Oxides because of their ability to take part in the exchange of electrons, protons or oxide ions are used as catalysts in both redox and acid-base catalysis [13]. In metal oxides, coordinative unsaturation is principally responsible for the ability towards adsorption and catalysis of various reactions. The exposed cations and anions of the metal oxide surfaces form acidic and basic sites as well as acid-base pairs. Beside this, the variable valency of the cation results in the ability of the oxides to undergo oxidations and reductions.

Generally these metal oxides are divided into four categories -simple, mixed, modified and supported. Simple oxides usually offer poor catalytic activity and selectivity when compared with multi component systems. The major advantage of multi component systems is that it is possible to tune oxygen sorption properties by meticulously choosing the required metal components so as to crystallise in a particular crystal pattern. Reactivity of oxygen in this case strongly depends on the kind of neighboring metal ions as well as M-O bond distance and bond strength. According to Fuller et al. [14] the correlation between the catalytic activity and acid-base properties of metal oxides can be explained by the strength of acid-base interactions between the reacting molecules and catalyst surface. The generation of the new acid sites on mixing two oxides was first proposed by Thomas [15] and further modified by Tanabe and co-workers [16]. This seems to be a common view in reports that the generation of new site is associated with the charge unbalance at locally formed $M_1$-O-$M_2$ bonding where $M_1$ is the host metal ion and $M_2$ is the doped or mixed metal ion. Supported metal oxides are extensively used as heterogeneous catalysts in numerous chemical processes ranging from hydrodesulphurization, cracking, polymerization and partial oxidation of hydrocarbons to the selective reduction of nitrogen oxides [17]. It is well established that the supported metal oxide species might have a variety of structures strongly depending on the experimental conditions such as loading, amount of the oxide and calcination temperature.

## 1.4 Rare Earth Oxides as Catalyst

Though the rare earth separation and purification is a difficult task, the use of its oxides as support or promoter in catalytic reactions has grown extensively due to its interesting properties. Several workers have suggested that there are a large number of basic sites on these oxides. This is due to the surface lattice oxide ions. The reactions relevant to basic sites of rare earth oxides include hydrogenation of olefins, double bond migration of olefins and dehydration of alcohols. According to Minachev et al. [18] the bonding energy of oxygen with the surface is responsible for the catalytic activity of rare earth oxides, in the oxidation of propylene. They also suggested that the catalytic activity of lanthanide oxide depends on the electronic configuration of inner 4f sub shells. Lattice oxygen present in the rare earth oxides is responsible for the decomposition of nitrogen oxides as evidenced by the activation energy of the reactions. The oxides of the lanthanide series of elements are proving increasingly important due to their use in many applications of significant technological importance. These include glasses, lasers, amplifiers, electroluminescent devices, ceramic capacitors, piezoelectrics, magnets and magnetic films. Rare earth oxides have been widely investigated as structural and electronic promoters to improve the activity, selectivity and thermal stability of the catalysts. The most significant of the oxides of rare earth elements in industrial catalysis has attracted in recent years, especially for those applications, such as oxidation and dehydrogenation reactions where ceria has shown great potential.

## 1.5 Mesoporous Solids

Heterogeneous catalysts are not just chemicals in the ordinary sense of the word: they are performance chemicals or surface-active materials. Naturally, the performance of the catalyst will depend not so much on the initial composition or surface of the starting material, as on the real surface, as it is formed and stabilized and then changes dynamically under the prevailing process conditions [1]. The increasing demand for new and selective catalysts with larger molecular dimensions led to the discovery of mesoporous catalytic materials. Unlike in the case of microporous and macroporous solids, catalysts with a mesoporous structure can achieve an optimum compromise of high site density and good transport characteristics [19]. Acidic and redox functionalities were generated in these materials by the incorporation of transition metals or by the encapsulation of well-defined homogeneous complexes inside the pores. Also, they opened up many new strategies for shape-selective, enantioselective, and regioselective, conversions. Since their first description in 1992 [20], the mesoporous materials have attracted much interest as catalysts for various organic transformations. Quite a few reviews are available in open literature [21] based on different aspects like synthesis and catalytic activity of mesoporous materials. In this critical approach, we have pointed out the potentialities of these materials both as catalysts and catalytic supports in reactions including alkylation. Meso, the Greek prefix, meaning “in between”, has been adopted by IUPAC to define porous materials with pore sizes between 2 and 50 nm [22]. Along with two other classes of porous solids (defined by pore size), microporous (< 2 nm) and macroporous (> 50 nm), [23] they have been used technically as adsorbents, catalysts and catalyst supports owing to their high surface area and large pore volume. Typical macroporous example includes porous hydrogels. Mesopores are present in aerogels, pillared layered clays which show disordered pore systems with broad pore-size distributions. Well known members of the microporous class are the zeolites, which provide excellent catalytic properties by virtue of their crystalline inorganic (e.g., aluminosilicate) network. However, their applications are limited by the relatively small pore openings [24]. Thus, a persistent demand has been developed for larger pores with well-defined pore structures.

The synthesis of mesoporous molecular sieves is believed to be one of the most exciting discoveries in the field of material science [26]. One of the major challenges in catalysis research is to develop methodologies for preparing stable, mesoporous materials for applications in catalytic transformation of bulkier organic molecules of fine chemicals. The formation of mesoporous structure relies on the template effect of the surfactant micelles [27]. Generally three kinds of interactions are involved in this process, i.e. electrostatic charge matching, hydrogen bonding and coordinative interaction [28]. After template-directed synthesis procedure, the after-treatment process is needed to remove the surfactant template. Two methods normally used to remove surfactant templates are calcination and solvent extraction. Mesoporous materials generated through the charge-matching pathway mainly depend on calcination method to remove the templates, while materials through the hydrogen bonding pathways can depend on both methods. Calcination is widely adopted for its simplicity and efficiency. But noncorrosive solvent extraction possesses the outstanding advantages of surfactant recovery and environmental friendliness [29]. Compared with solvent extraction, another obvious disadvantage of calcination is that high temperature may cause framework collapse in molecular sieves [30].

It has been shown that the type of support material used is a critical factor in the performance of the resulting supported catalyst or reagent in an organic reaction system [31]. The main factors that should be considered when employing a material as a support are

- Thermal and chemical stability during the reaction process and during the separation stage ,
- Accessibility and good dispersion of the active sites,
- The support must keep its structure and porosity for months or years at temperatures currently higher than 250°C,
- The composition of the support must be such that the desired reaction gets efficiently catalyzed.

There are a number of materials that partly or wholly satisfy these requirements, including pillared clays, some carbons, and mesoporous aluminosilicate pioneered by Mobil scientists [32] as well as mesoporous silica. Mesoporous activated carbon scan be modified either by (a) direct treatment with a silane, such as vinyl triethoxysilane, or (b) initial treatment with the vinylsilane leading to polymerization of the vinyl groups. It is the micelle-templated silica (MTS) that has attracted most attention in recent years. They offer high surface areas (often >1000$m^2$ $g^{-1}$, putting them at the top of the surface area league alongside some carbons) and controllable pore sizes (from 2-5 nm or larger) that can be important in controlling molecular diffusion and may affect product selectivity. Furthermore, since Pinnavaia's very important work in 1990s [33] we can now add ease of synthesis and "greenness" of the synthesis to the advantages, because the neutral templating method allows simple washing for separation as well as easy recovery and reuse of the template (e.g., a long-chain amine). Macquarie's landmark paper [34] along with others in the same period [35, 36] showed that the simple sol-gel preparation of the materials could be adapted to give inorganic-organic hybrids in situ. This method also gave rise to materials with a much higher degree of functionality (up to 5 mmol/ g) than was possible through post modification. Thus, it became apparent that a wide range of mesoporous materials could be prepared in a largely at room temperature in aqueous alcohol - a truly green preparation process for the next generation of green catalysts. A variation of the MCM family of materials was reported by Pinnavaia et al. [8] utilizing this neutral templating method using long-chain alkyl amines to form hexagonal mesoporous molecular sieves (HMS materials). This preparative route has the advantage that template removal is simpler and more environmentally benign, requiring only solvent extraction instead of calcination or ion exchange. Since the discovery of MCM-41 family periodic mesoporous materials in 1992, research has exploded in mesoporous silicate and other metal oxides with narrowly distributed pore diameters via the surfactant templated synthesis. In the early 1990s, another new material was made by [20] Kresge et al. by templating silica species with surfactant molecules leading to the formation of ordered mesoporous silica oxides. The design and synthesis of organic, inorganic and polymeric materials with controlled pore structure are important academic and industrial issues. In many applications, the precise control of pore dimensions, sometimes to a fraction of an angstrom, is the dividing line between success and failure. Zeolites and zeolite-like molecular sieves (zeotypes) often fulfil the requirements of ideal porous materials such as narrow pore size distribution and a readily tuneable pore size in a wide range.

The breakthrough came in 1992 with the discovery of MCM-41 (Mobil Composition of Matter) mesoporous materials [20]. These new (alumino) silicate materials, with well-defined pore sizes of about 2-10 nm, broke past the pore-size constraint (< 2 nm) of microporous zeolites. They also possess extremely high surface areas (> 1000 $m^2$ $g^{-1}$) and narrow pore size distributions. Instead of using small organic molecules as the templating compound as in the case of zeolites, Mobil scientists employed long chain surfactant molecules as the structure-directing agent during the synthesis of these highly ordered materials [20]. Rather than individual molecular directing agents participating in the ordering of the reagents forming the porous materials, assemblies of molecules, dictated by solution energetics, are responsible for the formation of these pore systems. This supra molecular directing concept has led to a family of materials whose structure, composition, and pore size can be tailored during synthesis by variation of the reactant stoichiometry, nature of the surfactant molecule, or by post-synthesis functionalization techniques.

Well-ordered mesoporous non siliceous metal oxides have attracted significant attention in recent years because of their excellent textural characteristics such as high surface area, large pore volume, and uniform pore size distribution, high thermal and hydrothermal stability. The chemistry of non-siliceous materials is much more diverse than that of the siliceous ordered mesoporous oxides, and thus, the synthesis strategies for their production need to be more diverse. However, the basic requirement for many applications of these materials is the preparation, which is not only reproducible on the nano–scale but also with a high surface area, tailored structure and morphology. Ordered mesoporous materials [37] show a large BET surface area, high porosity, controllable and narrowly distributed pore sizes, and an ordered pore arrangement. Pore sizes of mesoporous materials allow not only an easy accessibility for molecules with sizes up to a certain range but also a possible controllability in functions depending on the pore geometries. Mesoporous materials have been often employed as a catalyst support and showed significant catalytic activity, probably because the active metals can be highly dispersed in the characteristic pore structure with high surface area.

## 1.6 Synthesis Pathways to Mesoporous Metal Oxides

A variety of methodologies for synthesizing mesoporous metal oxides have been investigated such as nanocasting (replica) method, evaporation-induced self-assembly (EISA) method, sol–gel method, and hydrothermal method.

The high thermal stability of mesoporous phases is perhaps the most critical requirement for their use in several functional applications [38]. In general, the thermal stability of meso structured metal oxide phases will depend on:

- Degree of charge-matching at the organic–inorganic interface,
- Extend of interaction between inorganic species and surfactant head-groups,
- Tamman temperature of the metal oxide,
- Flexibility of the M–O–M bond angles in the constituent metal oxides, and
- Occurrence of redox reactions in the metal oxide wall.

The charge matching at the organic–inorganic interface generally allows control over the wall composition, and facilitates cross-linking of the inorganic species into a robust meso structured framework. The presence of strong covalent bonds between metal oxide species and surfactant head-groups, for example M-N bonds, means that harsh conditions such as combustion, are required for surface removal, leading typically to collapse of the meso structure. On the contrary, metal oxide species should possess low lattice mobility at elevated temperatures in order to prevent transformation of the meso structured metal oxides into more thermodynamically stable dense phases.

A large number of studies have been carried out to investigate the formation and assembly of meso structures on the basis of surfactant self-assembly. The initial liquid-crystal template mechanism first proposed by Mobil's scientists is essentially always "true", because the pathways basically include almost all possibilities. Two main pathways, that are, cooperative self-assembly and "true" liquid-crystal templating processes, seem to be effective in the synthesis of ordered meso structures.

### 1.6.1 Soft Template Method

This employs surfactants to form micelles in aqueous solutions, and allows for a lot of mesoporous metal oxides and mixed oxides to be synthesized. The formation of molecular sieve materials concerns the concepts of structural directing agent or template. Templating has been defined, as a process in which an organic species functions as a central structure about which oxide moieties organize into a crystalline lattice. A template is a structure (usually organic) around which a material (often inorganic) nucleates and grows in a "skin- tight" fashion, so that upon the removal of the templating structure, its geometric and electronic characteristics are replicated in the (inorganic) materials. They are

- The space- filling species,
- Structural directing agents, and
- Templates.

Soft-templating can be defined as a process in which organic molecules serve as a ‘mould’ around which a framework is built up. The removal of these organic molecules results in a cavity which retains the same morphology and structure of the organic molecule [39].

Mechanism of formation

A large number of studies have been carried out to investigate the formation and assembly mechanism of periodical meso structures and to understand the roles of surfactants. The initial liquid-crystal template mechanism was first proposed by Mobil’s scientists, which covers almost all of the possibilities. On the basis of recent developments, two main pathways, i.e. cooperative self-assembly and the ‘true’ liquid-crystal templating process, are seemingly efficient to synthesize ordered meso structures from the soft-templating method, as shown in Figure 1.1

The cooperative self-assembly pathway is based on the interactions occurring between surfactants and inorganic species such as silicates to form inorganic–organic meso structured composites. Silicate poly anions such as oligomers interact with positively charged groups of surfactants driven by coulomb forces. The silicate species at the interface cooperatively polymerize and cross-link, and further change the charge density of inorganic layers. With the reaction, the cooperative arrangements of surfactants and the charge density between inorganic and organic species influence each other. Hence the compositions of inorganic–organic hybrids differ to some degree. The matching of charge density at the surfactant /inorganic interfaces governs the assembly process. The final meso phase is the ordered 3-D arrangement with the lowest energy

In liquid crystal templating pathway, true or semi-liquid-crystal meso phases are involved in the soft- templating assembly to synthesize ordered mesoporous solids using high concentration surfactants as templates. The condensation of inorganic precursors is improved by reaction of the confined growth around the surfactants, forming ceramic-like frameworks. After condensation, the organic templates can be removed by either calcination or extraction, or by other methods. The inorganic materials ‘nanocast’ the mesostructures, pore sizes and symmetries from the liquid-crystal.

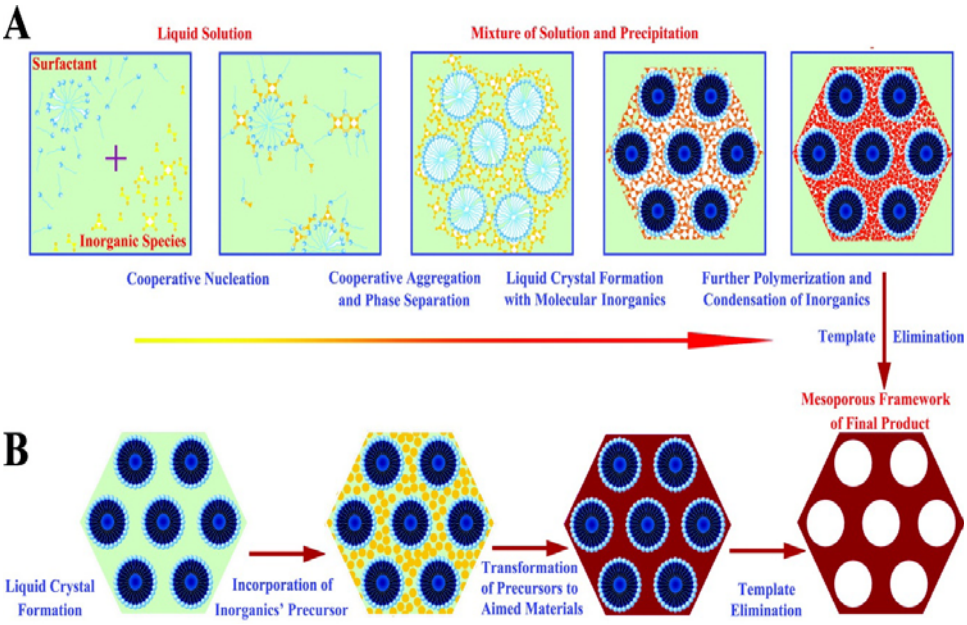

**Fig.1.1 Two synthetic strategies of mesoporous materials: (A) co-operative self-assembly; (B) “true” liquid-crystal templating process [39].**

### 1.6.1.1 Evaporation Induced Self Assembly (EISA) Method

EISA is a well-suited approach to prepare ordered mesoporous metal oxides. The high concentration of surfactant can be achieved by inducing solvent evaporation, therefore this process is called an EISA. The EISA method is believed to be a powerful and versatile strategy for the synthesis of ordered mesoporous materials with diverse components and various morphologies, especially for the efficacious synthesis of ordered mesoporous metal oxides. Self-assembly is defined as spontaneous reversible organization of materials by means of non-covalent interaction mainly through hydrogen bonding, Van der Waals forces, and electrostatic forces without any external influence. The evaporation-induced self-assembly (EISA) denomination was coined by Brinker et al. (40) to encompass the synthesis methods leading to ordered hybrid meso phases from dilute solutions, upon solvent evaporation. When preparing meso structured metal oxides, via EISA, several parameters that influence the self-assembly process may be considered. Sanchez's group divided these parameters in two categories: (a) the chemical parameters, related to sol–gel hydrolysis–condensation reactions and relative quantities of surfactant and inorganic precursor; and (b) the processing parameters related to the diffusion of alcohol or tetra hydro Furan (THF). The formation of the meso structure is favoured when neutral templates such as block copolymers are combined with inorganic precursor solutions in the vicinity of the isoelectric point [41].

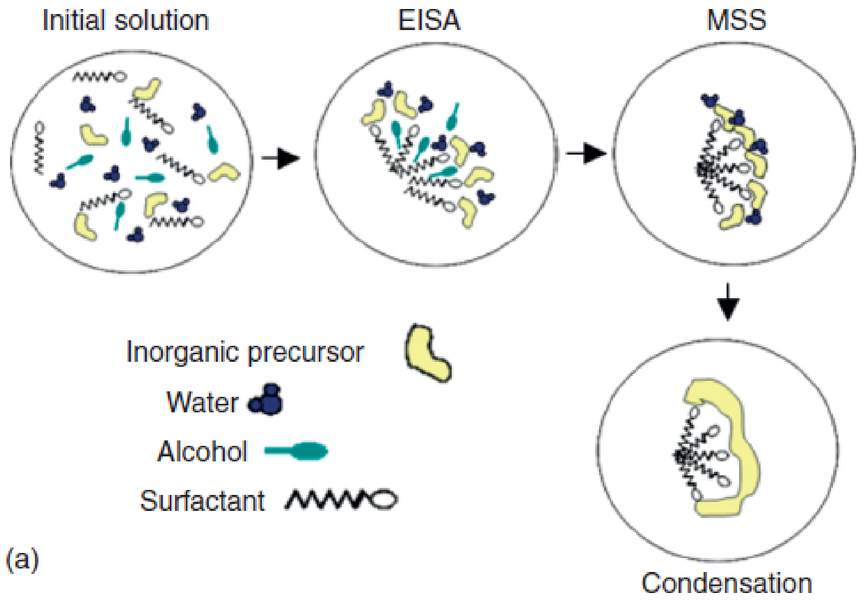

**Fig.1.2** **Schematic representation of evaporation-induced-self-assembly for the preparation of long-range ordered meso structures [40]**

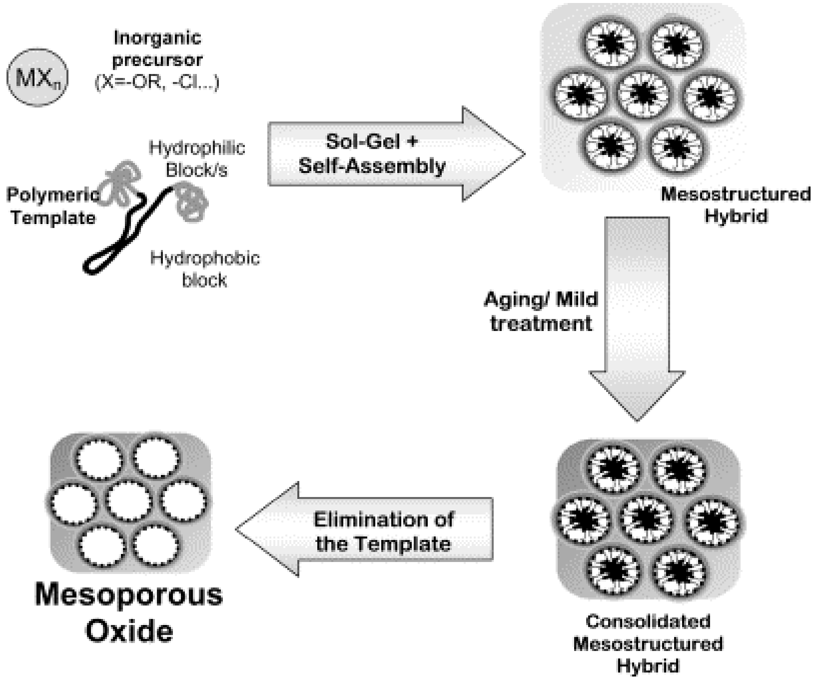

**Fig.1.3** **Schematic views of the steps leading from composite solution to mesoporous oxide [42]**

### 1.6.1.2 Nanocasting Method

Another method is the nanocasting strategy where the pores and channels of mesoporous silica are infiltrated with suitable precursors and then the mixture was subjected to heat treatment at a certain temperature to convert the precursors to oxides. After the final selective removal of the organic templates, the shape-reversed moulded structures may be obtained. For control over the synthesis of mesoporous solids, the key is to understand the interactions of micellar surfactants with condensable inorganic framework building units.

Soft-templating is versatile, but it is also complicated and unpredictable. The selection of soft templates is often very flexible. The obtained meso structures from the self-assembly process are very dependent on temperature, solvent, concentration, hydrophobic/hydrophilic properties, interface interaction, ionic strength and many other parameters. This makes the prediction of the resulting meso structure more difficult.

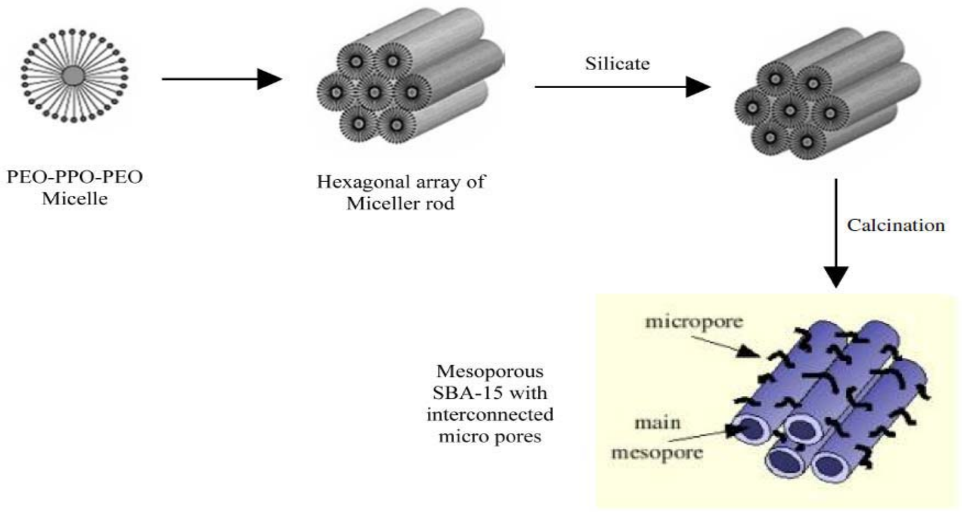

**Fig.1.4 Mechanistic pathway for the formation of SBA-15**

### 1.6.2 Hard Template Method

The synthesis procedure for mesoporous oxides employing hard templates is quite different from that used with soft templates. The use of activated carbon as structure directing agent (SDA) for the synthesis of mesoporous materials was reported by researchers at the Toyota central R & D lab in Japan. The activated carbon powder is loaded with the precursor solution by the incipient wetness method which after drying and calcination will give the mesoporous materials. The use of polymeric resins as templates for the synthesis of mixed oxides has also been reported in the literature. Polymeric resin template confers a negative replica of its structure. SBA-15 is generally used as hard template because of the presence of interconnecting porosity which is required for successful replication [43].

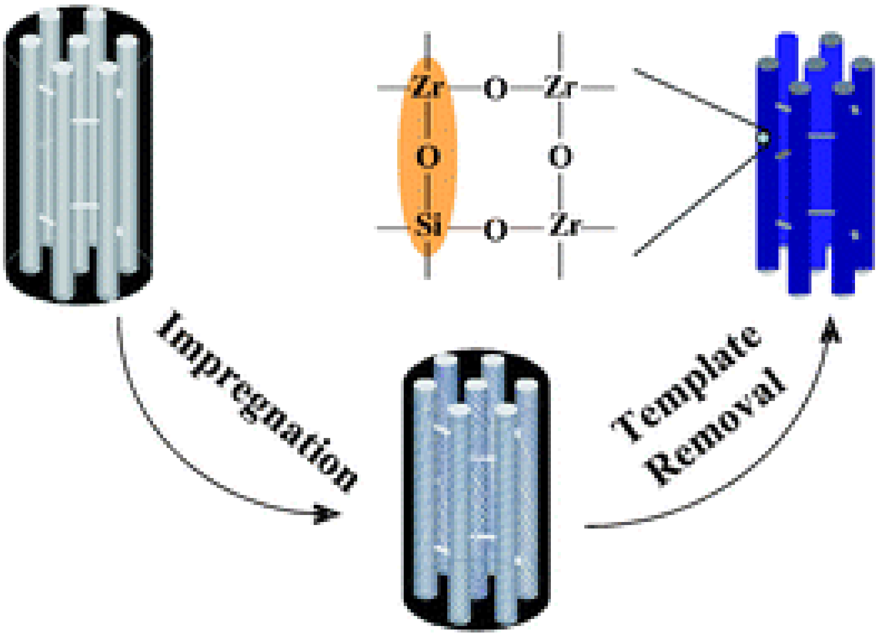

Fig.1.5 Schematic representation of the replica process (64)

## 1.7 Types of surfactants

The incorporation of surfactant reduces surface tension of water. It can be added to reduce the interfacial energy and thereby decrease the surface tension of water contained in the pores. This will reduce the shrinkage and collapse of the network during drying and calcinations, and help to maintain high surface area. There are wide varieties of surfactants, with different properties,

- Anionic, zwitter ionic, cationic, even two-tailed species can be used as the ionic surfactant. In this surfactants can be covalently bonded to the inorganic precursor as a ligand. The mesoporous material that is formed using ionic surfactant has long ordering lengths, thick walls and large pores.
- Amphiphilic block copolymers: when surfactant of this type is used materials formed are hydrothermally stable. Larger pores, up to 140Å, can be synthesised by using this type of surfactants.
- Neutral templating: This involves non-charged species (often primary amines (with carbon tail lengths between C-8 and C-18) in which interactions are based on hydrogen bonding. The resultant framework structures are shown to have thicker walls (i.e., 1.7-3.0 nm). They form hexagonal mesoporous molecular sieves (HMS materials). This preparative route has the advantage that template removal is simpler and more environmentally benign, requiring only solvent extraction instead of calcination or ion exchange. Noncorrosive solvent extraction possesses the outstanding advantages of surfactant recovery and environmental friendliness [29]. Compared with

solvent extraction, another obvious disadvantage of calcination is that high temperature may cause framework collapse in molecule sieves [30].

A neutral templating route for preparing mesoporous molecular sieves is demonstrated based on hydrogen-bonding interactions and self-assembly between neutral primary amine micelles (S degrees- $S^0$) and neutral inorganic precursors (I degrees- $I^0$). The $S^0I^0$ templating pathways produces ordered mesoporous materials with thicker framework walls, smaller X-ray scattering domain sizes, and substantially improved textural mesoporosities in comparison with M41S materials templated by quaternary ammonium cations of equivalent chain length. This synthetic strategy also allows for the facile, environmentally benign recovery of the cost-intensive template by simple solvent extraction methods. The $S^0I^0$ templating route provides the synthesis of other oxide meso structures (such as alumina) that may be less readily accessible by electrostatic templating pathways. The much thicker framework walls of the HMS materials prepared by the $S^0I^0$ pathway may be expected to afford superior thermal and hydrothermal stability.

The mechanism of precipitation of cerium oxide in the presence of the surfactant is significantly different to that in its absence. It suggests that there is interaction between the micelles and the cerium ions in solution, and as polymerization of the Ce- O- Ce bonds takes place, of the ceria framework is formed. Furthermore, where the reaction was carried out at a basic pH lower than 11.5 (but still above the isoelectric point of cerium oxide), the extent to which this interaction takes place is decreased giving the lesser number of surface OH groups through which this is achieved, leading to a lowering of the BET surface area [44]. Terribile et al. suggest that hydrated ceria and CTABr interact through electrostatic interactions between the cationic surfactant and the anionic deprotonated hydrated ceria in basic condition above the isoelectric point of ceria (pH = 6.75–8). While this is a plausible explanation in the case of CTABr, it would not explain any interaction in the case of the non-ionic Pluronics. The plausible explanation in this case is given by Yuan et al. [45] a 'cooperative assembly' of P123 was represented where the template assembles side by side in an orderly manner, through which the oxide would also be set up. The catalytic activity is much higher for the small particle samples, which have a higher content of acidic centres: the size of the particle has, however, no effect on the acid strength. On the other hand, large particles retain the structural and textural properties of the original silicate. The long-range ordering, surface area and pore values are diminished in small particle sample.

## 1.8 Mesoporous ceria

In the field of catalysis, much effort has been spent in the preparation, characterisation and application of ceria and ceria based mixed oxide materials for automotive exhaust catalysis and oxidation of environmental pollutants. Cerium oxide is an excellent catalyst for redox reactions. The influence of the redox properties of ceria on several reactions has also been investigated systematically. The number of effective redox sites and their ability to exchange oxygen can be manipulated by incorporating transition metal ions into the ceria lattice and promoted by noble metals dispersed on ceria particles. In general, the high activity of ceria in redox reactions has been attributed to the ceria reducibility and its high oxygen storage capacity (OSC) [46], and formation of defects, such as oxygen vacancies [47]. Also, an advantage in the TWC context is the ability of ceria to disperse transition metals. The interest in cerium oxide ($CeO_2$) has increased in the past decade because it plays a vital role in emerging technologies for environmental and energy-related applications [48]. Among a variety of oxides, cerium oxide ($CeO_2$) is particularly interesting to several catalytic processes. For instance, ceria has been used as catalyst or support in selective oxidation, synthesis of fine chemicals, methane steam reforming, phenol hydrogenation at atmospheric pressure, and solid oxide fuel cell applications [49]. One of the important applications of ceria is its use in environmental catalysis, particularly in the design of the new generation of three-way catalysts for simultaneously controlling NO, CO and hydrocarbon emissions in oxygen-rich conditions. This happens because ceria has a large capacity to store oxygen and an ability to transfer bulk oxygen to its surface quickly [50]. Cerium oxide is a critical and multifunctional component of automotive emission catalysts. One function of ceria is to act as an "oxygen storage" component. Ceria is capable of oxygen uptake during excursions of the oxidizing regime and oxygen release during excursions into the reducing regime, thus facilitating the maintenance of the proper stoichiometric ratio for sustained CO and HC oxidation and simultaneous $NO_x$ reduction, that is, three-way catalysis (TWC). With all of its tetrahedral holes filled with oxygen (oxygen rich state), it can oxidize CO and hydrocarbons with the creation of oxygen vacancies and the formation of non-stoichiometric cerium oxide. These non-stoichiometric oxides still retain the fluorite structure and can be easily re-oxidized to cerium (IV) oxide. In such a state, the $NO_x$ is thus reduced to $N_2$. Therefore, ceria acts as oxygen container with a high oxygen storage capacity (OSC) [47]. Cerium oxide is also known to extend the lifetime of the noble metal component of the catalyst and to lower the effective activation barrier to CO oxidation, thus improving the catalyst performance at engine start up. Many of the key properties of ceria that contribute to its success in automotive catalysis are thought to arise from the fact that cerium has two stable oxidation states, $Ce^{3+}$ and $Ce^{4+}$. As a consequence, cerium oxide may exist over a range of possible stoichiometry $CeO_{(2-x)}$ $[0 \leq x \leq 0.5]$. Ceria has the ability to store excess oxygen under fuel lean period and release it under fuel rich conditions for the oxidation of CO and hydrocarbons. This happens due to its ability to switch between $Ce^{4+}$ and $Ce^{3+}$ oxidation states depending on the oxygen partial pressure in the exhaust gas composition. Ceria can undergo a number of reactions by exchanging oxygen with gas molecules in the exhaust environment.

Under lean conditions,

$$Ce_2O_3 + 0.5\ O_2 \rightarrow 2CeO_2$$
$$Ce_2O_3 + NO \rightarrow 2CeO_2 + 0.5\ N_2$$
$$Ce_2O_3 + H_2O \rightarrow 2CeO_2 + H_2$$

Under rich conditions,

$$2CeO_2 + H_2 \rightarrow Ce_2O_3 + H_2O$$
$$2CeO_2 + CO \rightarrow Ce_2O_3 + CO_2$$

The structural properties of $CeO_2$ have been investigated by several authors providing valuable information on redox properties and oxygen mobility in the ceria lattice. Ceria is a pale yellow coloured solid due to $O^{2-} \rightarrow Ce^{4+}$ charge transfer and is known to crystallize in fluorite structure ($CaF_2$) with a space group of Fm3m. Mesoporous ceria is quite an unusual material consisting of a hexagonal arrangement of pores with ordered crystalline walls [51]. The unit cell of ceria is shown in figure 1.6. In the face centred cubic (FCC) structure of ceria, $Ce^{4+}$ ions form a cubic close packing arrangement and all the tetrahedral sites are occupied by the oxide ions whereas the octahedral sites remain vacant. The unit cell of ceria can be considered as a simple cube, in which the face centre positions and corners are occupied by $Ce^{4+}$ ions. The tetrahedral sites can be visualized by dividing the cube into eight smaller cubes. The body centre positions of all the small cubes are occupied by oxide ions and the alternate corners are occupied by $Ce^{4+}$ ions.

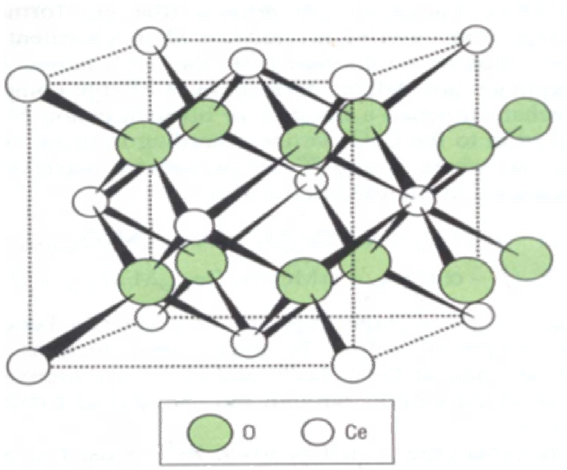

**Fig.1.6 Fluorite crystal structure of $CeO_2$.[68]**

Under reducing atmosphere, ceria is known to form nonstoichiometric oxides of general composition $CeO_{2-x}$ where $0<x<0.5$. The fluorite structure of ceria is retained up to 900 K under reducing atmosphere. However, the lattice parameter is found to increase with reduction temperature indicating an expansion in the FCC lattice. The increase in the lattice parameter is attributed to the reduction of $Ce^{4+}$ ions to $Ce^{3+}$. The radius of $Ce^{3+}$ is larger than the radius of $Ce^{4+}$ resulting in the lattice expansion. The non-stoichiometric phases formed during the reduction process can be easily oxidized to the pure $CeO_2$ phase upon exposure to air or under mild oxidizing conditions. However, the reversibility of this process is decreased when ceria is reduced at higher temperatures. When ceria is reduced at 1070-1170 K, a cubic $Ce_2O_3$ phase has been detected. The cubic $Ce_2O_3$

phase reoxidizes slowly in air compared to the expanded ceria phases. Reduction of ceria at temperatures greater than 1273 K leads to the formation of hexagonal $Ce_2O_3$ phase. This phase is stable at room temperature and possesses identical structure as that of $La_2O_3$. The ability of the cerium ion to switch between the $Ce^{4+}$ and $Ce^{3+}$ oxidation states depending on the ambient oxygen partial pressure is represented as:

$$CeO_2 \rightarrow CeO_{2-x} + x/2\ O_2$$

The amount of oxygen released in the forward reaction and the oxygen consumed in the reverse reaction is generally referred as the oxygen storage capacity (OSC) of ceria material [48]. The most crucial role of ceria is its ability to exchange oxygen with environment. Ceria is a non-stoichiometric compound with low redox potential. The oxygen storage on catalyst is simply described as cyclic reduction and oxidation of $CeO_2$. The process of oxygen storage and transport in ceria can be described by the defect mechanism and there are two types of defects: intrinsic and extrinsic. The former is due to the oxygen anion vacancies created upon the reduction of $Ce^{4+}$ to $Ce^{3+}$. The extrinsic defects are due to the oxygen anion vacancies created by charge compensation effect of foreign cations, which have a valence, lower than that of the host Ce ions they substitute. Trivalent cations generally produce a higher ionic conductivity, i.e. oxygen mobility than divalent ones. Both of these vacancies are believed to provide a practical way to increase the OSC of $CeO_2$. The performance of $CeO_2$ in catalysis could be optimized by increasing the surface area and decreasing particle size distribution simultaneously.

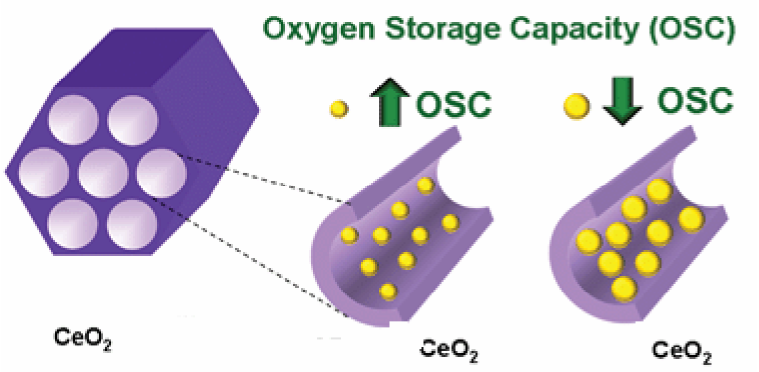

**Fig. 1.7 OSC of Ceria**

### 1.8.1 Redox properties of ceria.

As an important component in catalysts, ceria promotes high oxygen storage capacity (OSC), oxygen ion conductivity, and oxygen vacancy. The radius of the $Ce^{3+}$ ion (1.14Å) is larger than that of $Ce^{4+}$ (0.97Å), and hence the lattice expansion is a consequence of the reduction of $Ce^{4+}$ ions to $Ce^{3+}$. There is a gradual decrease in the concentration of oxygen vacancies extended from the surface to the bulk. Such gradient enables the outward diffusion of lattice oxygen to the surface. Therefore, the reduction of $Ce^{4+}$ to $Ce^{3+}$ by oxygen ion leads to the generation of surface oxygen vacancy. These oxygen vacancies can be acted as promoting sites for NO and CO conversion [52].

The mobility of surface oxygen species in ceria is found to be higher compared the conventional oxides such as $SiO_2$, $Al_2O_3$, MgO and $ZrO_2$ [53]. These mobile surface oxygen species can be removed easily under reduction atmosphere leading to the formation of non-stoichiometric ceria, $CeO_{2-x}$ ($0 \leq x \leq 0.5$). The $Ce^{3+}$ ions form the main defect centres and the charge imbalance is neutralized by the formation of oxygen ion ($O^{2-}$) vacancies [54]. Ceria retains its fluorite structure when reduced at temperatures below 900 K. The reduced form of ceria can be completely oxidized when exposed to air at room temperature. This easy availability of lattice oxygen and retention of the structural feature has been exploited in several cases for catalytic reactions involving oxidative process. Temperature programmed reduction (TPR) is unique to study the temperature dependence reduction behaviour of ceria based materials [54]. The reduction of high surface area ceria takes place essentially in two temperature regions. The first region is 573-873K with $T_{max}$ around 790 K and the second region is 973-1273 K with $T_{max}$ around 1100 K. These two reduction regions are characteristics of ceria and are attributed to the surface oxygen ions and bulk oxygen ions respectively, while the sintered ceria shows only one reduction feature at higher temperature due to bulk reduction. The higher mobility of the surface oxygen ions helps in the removal of lattice oxygen during reduction process. The co-ordinately unsaturated surface capping oxygen ions can be easily removed in the low temperature region. However, bulk oxygen requires to be transported to the surface before their reduction. Consequently, the bulk reduction takes place at higher temperature compared to the surface reduction. The extent of reduction in the low temperature region depends on the surface area of the sample. Oxygen storage measurements consist in the determination of the amount of a reducing gas ($H_2$, CO) which is oxidized after passing through an oxygen pre saturated catalyst. It deals with the study of a reducer oxidation under transient conditions and in the absence of gaseous oxygen (anaerobic oxidation). Two different measurements of the oxygen storage capacity may be distinguished:

a) The OSC (Oxygen Storage Capacity) is related to the most reactive oxygen species and the most readily available oxygen atoms. OSC may characterize the dynamic nature of the system.

b) The OSCC (Oxygen Storage Capacity Complete) is the total or maximum oxygen storage capacity. OSCC contains information about the overall reducibility of the solid.

Besides its role in TWCs, ceria has also been used in diesel emission control. Trovarelli [47] reported that the presence of ceria in the size range of 5–25 nm greatly reduces the auto ignition temperature of soot particles deposited on the filters of diesel engines. Seshadri [55] suggested that for such application, ceria particles of size smaller than 10 nm are advised, otherwise a homogeneous dispersion in the diesel fuel will not be possible. Nano-sized ceria has been synthesized in various particle shapes by different methods. Hydrolysis and subsequent precipitation is a conventional method to synthesize inorganic oxides [55]. These reactions are usually directed by increasing the pH of the system and/or increasing the temperature [55]. In order to result in nanoparticles, a high control of the process is needed to avoid growth and aggregation of the particles [56].

The bulk and surface properties of $CeO_2$ can be modified by doping. Doping can improve the sintering properties of ceria, by stabilizing the ceria surface area and crystal size. Doping with divalent and trivalent dopants leads to formation of oxygen vacancies, and modification of oxygen mobility and ionic conductivity [57]. The reduction properties and oxygen storage capacity of ceria are also reported. Ceria reduction depends on two factors: (i) surface area of ceria and (ii) metal-ceria interactions. When the surface area of $CeO_2$ is increased, the amount of surface oxygen also increases. Further; the metal particle associated with $CeO_2$ crystallite decreases the reduction temperature of surface oxygen species from 790 K to 400 K by promoting the reduction process efficiently. The underlying mechanism of this process is the spill over of hydrogen from metal to ceria crystallite [58]. Both M-$CeO_2$ interaction and oxygen migration to metal (or hydrogen spill over to oxide) are responsible for the observed low temperature reduction under TPR conditions [54]. Otherwise it is difficult to reduce low surface area pure ceria sample. Therefore, $ZrO_2$ substituted ceria materials can be easily reduced/oxidized at low temperatures in the presence of metals, irrespective of their surface areas. These materials must be suitable as supports for low temperature as well as high temperature applications such as in exhaust catalysts and expected to show good oxygen storage capacities due to the bulk reduction [59]. Metallized ceria is seen to undergo reduction at slightly lower temperature. The presence of metal makes a lot of difference in the reduction process in the oxide solid solution. Pure $CeO_2$ exists in fluorite structure and is difficult to reduce below 600 K or under mild reducing conditions. However, the reducibility of ceria is enhanced significantly with dopants such as $ZrO_2$, $HfO_2$ and in the presence of transition metals as well [60]. The reduction mechanism of ceria-based materials is essentially related to the kinetic model proposed for pure ceria reduction. The reduction of $CeO_2$ and $CexZr_{1-x}O_2$ occurs due to the direct dissociative chemisorption of $H_2$ on surface site leading to the formation of water via hydroxyl groups followed by the creation of surface oxygen vacancies and reduction of $Ce^{4+}$ ions to $Ce^{3+}$ ions. This can be written as,

$$2H_{ad} + 2\,Ce^{4+} + O^{2-} \rightarrow 2Ce^{3+} + H_20 + \Delta,$$

where $\Delta$ is a surface oxygen vacancy. Surface reduction is more pronounced in the first stage of reduction process and is evidently influenced by the surface area of the samples. The diffusion of surface anion vacancies into the bulk ceria occurs at relatively high temperature contributing to slow bulk reduction. The presence of metal strongly modifies the reduction kinetics causing the oxide reduction around 350-400K. Metal participation helps in hydrogen dissociation and rapid supply of H atoms to support oxide by the spill-over process. This mechanism favours the high rate of formation of water and oxygen vacancy sites on $CeO_2$ surfaces even at very low temperatures. Ceria reduction occurs in two steps: (i) first one is the extraction of surface capping $O^{2-}$ ions by chemisorbed H atoms creating anion vacancies; (ii) the second step is the diffusion of surface anion vacancies into the bulk.

Support reduction takes place at faster rate in the presence of metal particles due to hydrogen spill over.

At high temperatures, the oxygen storage capacity of ceria strongly decreases upon thermal aging due to the growth of ceria crystallite size losing the active surface area. The growth of ceria crystallite and the thermal sintering process can be considered as due to the mass transport at an atomic scale caused by a concentration gradient set at higher temperature. The sintering process of ceria has been explained through six elementary steps: oxygen adsorption, oxygen vacancy creation and diffusion, oxygen desorption, cerium vacancy diffusion or vacancy annihilation, improvement of the thermal properties of ceria and retention of active surface area at high temperature. Thus it is necessary to exploit the redox property of ceria for various applications especially in TWC. Incorporation of aliovalent cations into the lattice of ceria improves its thermal stability besides affecting the physical properties of ceria such as density, ionic conductivity and lattice parameters. The oxygen diffusion in the defective fluorite structure of ceria has been explained by a vacancy mechanism. In general, it is well known that the activity of ceria-supported catalysts can be largely affected by the surface area of the support, since this leads to (i) an increased oxygen storage capacity (OSC) [10, 61] (ii) a higher amount of ceria defect sites and, as a result of that (iii) a stabilization of the dispersed metal particles. An influence of the ceria surface area has been observed for a broad range of reactions, including decomposition of methane, methanol, ethanol, propane/ butane CO oxidation the oxidation of aromatic hydrocarbons dehydration of hydrocarbons [53] and the WGS reaction.

## 1.9 Supported Metal Catalysts

Supported metals are used in large scale in heterogeneous catalysis. The role of the support is to disperse the metal particles and maintain them from sintering. The supports widely used are $SiO_2$, $Al_2O_3$, $TiO_2$, $Nb_2O_5$, $CeO_2$ and $ZrO_2$. In addition to the dispersion of the metallic components the support can influence the electronic and catalytic properties of the supported metal. When a metallic function is added to an acid function, a bifunctional catalyst is obtained. This catalyst presents in general a more beneficial behaviour than the catalyst having only the acid function. The bifunctional metal acid catalysts are generally porous oxides with acid properties that have a small amount of a metal supported on them. The acid function of the support and the metal function may be tuned to promote the desired reaction selectivity by the addition of promoters [62]. Sanchez and Gasquez have proposed a general model on the basis of structural considerations to account for the metal support interaction $M/CeO_2$. They propose the anchoring of the metal crystallite on the surface oxygen vacancies of ceria created by high temperature reduction. This model explains the absence of any drastic change in adsorption and catalytic properties of M/$CeO_2$ materials along with the resistance of the metal particles from thermal sintering. The M/$CeO_2$ systems have been extensively used as catalysts for several industrially and environmentally important chemical reactions [47]. Particular attention has been given to the noble metals such as Pt, Pd and Rh because of their use in three way catalysts. Numerous studies on metal supported ceria, however, clearly point to the active role of ceria in catalytic processes. Ceria influences the catalytic property of the supported metal by metal-support interaction. The oxygen storage capacity, $Ce^{4+}/Ce^{3+}$ redox couple and the defect sites such as anionic vacancies at the metal-ceria interface can directly contribute to the catalytic activity of the ceria-supported materials. Catalytic properties of cerium oxides are actually related to the presence of lattice defects associated with the reduction of a certain proportion of $Ce^{4+}$ cations to $Ce^{3+}$ and/or to the introduction of dopants into the lattice [47]. In certain cases mutual promoting effect between ceria and metal component has been found to be the cause for higher catalytic activity [54]. For example, in Pd/$CeO_{2-x}$/$Al_2O_3$ system the synergistic effect between the supported Pd metal and $CeO_2$ has been observed during methane oxidation reaction [63]. In addition to the metal support interaction, the supported metal can also influence the physico-chemical properties of ceria support such as the oxygen storage capacity and reducibility. The presence of a small amount of Rh has been found to modify the low temperature reducibility of ceria [54]. Structural defects and the facile reduction of the surface oxygen are the major factors responsible for the increase in the oxygen storage capacity .Ceria exhibits unique redox properties which can be attributed to the retention of the fluorite structure. Surface oxygen ions are easily removed during reduction compared to the bulk oxygen ions. Doping with $Zr^{4+}$ ions enhances the oxygen mobility in ceria and the materials can be reduced

/oxidised at lower temperatures. Oxygen storage capacity increases considerably in the Zr-doped ceria samples. In addition to the redox nature, metal-ceria interactions are crucial for oxygen exchange and catalytic properties. The method of preparation matters in the dispersion/ incorporation of transition metal oxides in ceria. CuO dispersion on ceria by combustion synthesis shows the presence of variety of copper oxide species. It is reported that the doping of transition metal ions (Zr, Mn) into $CeO_2$ can promote the redox behaviour, oxygen storage capacity, thermal stability and catalytic property [64].

Supported metals are used in large scale in heterogeneous catalysis. The role of the support is to disperse the metal particles and maintain them from sintering. The supports widely used are $SiO_2$, $Al_2O_3$, $TiO_2$, $Nb_2O_5$, $CeO_2$ and $ZrO_2$. In addition to the dispersion of the metallic components the support can influence the electronic and catalyst particles by electron transfer or chemical bond formation. Metal support interactions have been extensively studied by using chemisorption techniques after the discovery of the strong metal support interaction (SMSI) effect by Tauster et al. The occurrence of SMSI has been well established for reducible support such as $TiO_2$ and $Nb_2O_5$ using chemisorption of hydrogen and carbon monoxide as probe molecules. At high reduction temperature, the partially reduced support covers the surface of the metal particles, thereby blocking the sites for $H_2$ and CO chemisorption and catalysis [43]. The SMSI effect has been observed on (i) reducible supports, (ii) induced by high temperature reduction treatment (> 800 K), (iii) accompanied by significant changes in chemisorptive and catalytic properties of the supported metal and (iv) is reversible. The reducible nature of ceria and ceria-based composite oxides prompted some investigations to examine the SMSI phenomenon in these materials. Ceria supported Pt, Pd, Rh, Ni and Ru metals have been investigated for metal-support interactions and catalytic applications. Despite large number of investigations, no clear picture seems to have emerged on metal-ceria interactions. In some cases the metal ceria interaction has been ascribed to classical SMSI where as in other cases alternative explanations have been proposed. For example for Pt supported on $TiO_2$ and $CeO_2$, though a decrease in hydrogenolysis activity has been observed for both the catalysts after high temperature reduction at 773K, the surface morphology of the $Pt/CeO_2$ catalyst is little affected unlike the $Pt/TiO_2$ catalyst. Defect sites on ceria are important for the WGS reaction, because water dissociates to OH group on these sites. The OH groups are involved in the formate build-up, which itself is an intermediate in the WGS reaction [65]. It is clear that the activity must be related to the presence of metal particles or ionic species, since the activity of pure ceria is orders of magnitude lower under these conditions.

While the role of ceria as a redox promoter has been well established, there is much scope to investigate the acid base properties of ceria-based materials. Promoting effect of ceria is attributed to both redox and mild acid–base properties of the ceria component [66]. The mobility of the surface oxygen in ceria has also been correlated with the catalytic activity for alcohol transformation. Among the predominant oxide materials, ceria seems to show the highest surface oxygen mobility which can be correlated well with the basicity of ceria [67]. The extent of dispersion, surface area and the substitution of suitable metal ions are some of the major factors affecting the reducibility and catalytic activity of ceria related materials. Catalytic chemistry of ceria continues to be an important and promising area of research in oxide catalysis and a voluminous knowledge on various aspects of this material has recently been published [68].

Among other properties, special attention has been paid to their surface area and particle size, since both features affect significantly their catalytic behaviour [69]. The surface areas reported for cerium oxides range from near 0 for high temperature sintered materials to 185 $m^2/g$ for ceria prepared by the reverse microemulsion method [70], 200 $m^2/g$ for ceria prepared using surfactants [71] or 240 $m^2/g$ for flame-made ceria [72]. On the other hand, particle size of ceria has been reported to range between only few nanometres and more than 100 nm. As a general behaviour, the analysis of data available in the literature leads to the conclusions that high surface areas are related with small ceria particles and vice versa. Mesoporous ceria was quite an unusual material consisting of a hexagonal arrangement of pores with ordered crystalline walls [51]. The coordination of cerium ions in mesoporous materials can affect the catalytic properties because the incorporation of cerium atoms into the walls of mesoporous material allows creation of Lewis and Brönsted acid sites and preparation of materials with various acidities.

### 1.9.1 Transition Metal Modified Mesoporous Ceria

The outcome of many catalytic reactions can be influenced by the introduction of small amounts of promoter elements. A catalyst promoter is defined as an element or compound without catalytic activity by itself, but when it is added to an active catalyst, it enhances the catalyst’s activity, selectivity, and/or stability. Two types of promoter elements are normally considered: structural promoters, which increase the number of exposed metal sites and therefore improve the metal-time yield, and textural promoters, which increase the reaction rate per exposed metal site, that is, the turnover frequency.

The redox properties of ceria play an important role in catalysis by ceria. The bulk and surface properties of $CeO_2$ can be modified by doping. Doping can improve the sintering properties of ceria, by stabilizing the ceria surface area and crystal size. Doping with divalent and trivalent dopants leads to formation of oxygen vacancies, and modification of oxygen mobility and ionic conductivity [57]. Acidic and redox functionalities were generated in mesoporous materials by the incorporation of transition metals or by the encapsulation of well-defined homogeneous complexes inside the pores [73].

Supported chromium oxide catalysts have been of significant industrial importance for many decades. Chromium compounds, in general, oxidize all organic functional groups in homogeneous medium [74]. In recent years, attempts have been made to develop chromium-based heterogeneous catalysts e.g., molecular sieves, pillared clays and supported catalysts. Cr-doped Hβ zeolite is found to have better catalytic performance than Hβ zeolite in the Friedel–Crafts acylation of anisole, with acetic anhydride [75]. Recently ceria supported chromia catalysts have been used for the oxidative dehydrogenation of isobutene. Harrison et al. studied chromium promoted cerium oxide catalysts for oxidation of CO and propane [76].

A substantial amount of research has focussed on the homogeneous catalytic oxidation of alkyl aromatic substrates with cobalt salts and dioxygen under corrosive conditions [77]. But a more environmentally benign and selective catalytic process is clearly desirable. Metal supported heterogeneous catalysts that can operate in conjunction with an oxidant in the liquid phase have the advantages that they are recoverable and have minimal environmental impact [78]. A pseudo-tetrahedral Co (II) complex has been grafted onto the surface of SBA-15 and successfully utilized for the catalytic oxidization of alkyl aromatic substrates with tert-butyl hydroperoxide (TBHP) via a H-atom transfer mechanism [79]. Ernst et al. reported the effect of highly dispersed ceria addition on reducibility, activity and hydrocarbon chain growth of a Co/$SiO_2$ Fischer –Tropsch catalyst [80].

Iron loaded MCM-41 materials have received much attention because of their redox properties and unusual activity in alkylation and oxidation reactions [81] which is higher compared to conventional mineral acids [82] Lewis acids [83], ion exchange resins [84], mixed oxides [85] and iron supported zeolites, clay catalysts [86, 86b]. The use of iron loaded mesoporous materials as catalyst can also eliminate the pore size constraint, recyclability, thermal and hydrothermal stability etc. posed by other support materials. In the past, benzylation of benzene has been carried over different iron containing mesoporous materials like silicate catalysts [87] and FeSBA-15 [88] but so far no such work has been carried out over Fe loaded mesoporous ceria. Introduction of iron into the mesoporous material by wet impregnation technique showed high redox property.

Non–stoichiometric NiO has high catalytic activity for deep oxidation. NiO mixed with solid acids such as $SiO_2$ [89], $SiO_2$-$Al_2O_3$ [90], $NiSO_4$ [91] are active for dimerization of olefins. Nickel has been known to be a possible substitute for precious metals. Nickel based catalysts are inexpensive and possess high activity for synthesis gas forming reaction [92].

Copper oxides CuO and $Cu_2O$ are semiconductors and effective for redox-type reactions such as oxidation or dehydrogenation. Many copper based catalysts such as CuO-ZnO [93], Cu-ZnO-$Al_2O_3$ [94] have been reported to be effective for dehydrogenation of cyclohexanol to cyclohexanone. Rao et al. [95] investigated the surface and catalytic properties of Cu-Ce-O composite materials prepared by solution combustion method. Maya G. studied the surface and catalytic properties of Cu modified $CeO_2$ prepared by sol-gel method [96]. The results showed that $CeO_2$ could enhance the surface dispersion of copper and prevent it from sintering. It is suggested that the high activity, selectivity and stability of $CeO_2$ promoted catalysts have been resulted from higher copper dispersion and smaller copper crystallites [97].

Complete catalytic oxidation of toluene was investigated on Cu−Mn doped mesoporous and Microporous catalysts, i.e., Cu−Mn/MCM-41, Cu−Mn/β-zeolite, Cu−Mn/ZSM-5 and Cu−Mn/porous silica, in the presence of excess oxygen [98]. $MnO_x$-$CeO_2$ mixed oxides have been developed as environmental friendly catalysts for the abatement of contaminants in both liquid phase and vapour phase, such as oxidation of ammonia, pyridine, phenol and acrylic acid [97]. It was further reported that $MnO_x$-$CeO_2$ mixed oxides have much higher catalytic activity than those of pure $MnO_x$ and $CeO_2$. Incorporation of Mn into ceria lattice greatly improved the oxygen storage capacity of ceria as well as oxygen mobility on the surface of mixed oxides. Qi et al. [99] reported that $MnO_x$-$CeO_2$ is a superior catalyst for NO reduction by ammonia.

## 1.10 Surface acidity of metal oxides and its measurements

The term catalytic activity is used to describe the effectiveness of a catalyst in bringing out a reaction with desired product. Surface acidity and basicity investigation has received great attention now a day due to its application in determining catalytic behaviour. A systematic investigation of activity, selectivity, and acid base properties enable us to identify the optimum catalyst with desired acid base properties for a specific reaction.

In reactions occurring by acid catalysis, the activity, stability and selectivity of solid acids are determined to a large extent by their surface acidity (the number, nature, strength, and density of their acid sites). The acidity required for transformation of reactants into valuable products or into by products can be quite different. Certain reactions demand strong acid sites, while very weak acid sites catalyse others [100]. The acidity of the solids plays a significant role when these are used as supports. The characterization of the acidity of catalysts is an important step in the prediction of their catalytic utility [9]. The dependence of the catalytic properties on the acid properties of solid catalysts demands accurate methods for the acidity measurements.

Solid acids can be described in terms of their Brönsted/ Lewis acidity, the strength and number of these sites. The fine-tuning of these properties can give high product selectivity, activity and stability of the catalyst. The dependence of the catalytic properties on the acid properties of the solid catalysts demands accurate methods for the acidity measurements. Dealing with catalytic systems that involve at least one acid/base catalytic step it is important to evaluate nature and amount of surface acidic centres. This need becomes important in the case of systems in which both protonic Brönsted acidity (B acid sites) and aprotic Lewis acidity (L acid sites) are present.

The chemisorption of bases such as pyridine, ammonia and aliphatic amines is frequently used to characterize solid acid catalysts and to correlate their catalytic activity with the concentration of a particular type of acid site because it is an easy and reproducible method. Pyridine and ammonia, because of their capability of interacting with both Brönsted and Lewis sites are widely used to get total acid amount of the systems. Brönsted and Lewis acid sites play different roles in various types of reactions, and strength of various acid sites strongly affects the catalytic performance [101]. It has been reported that 2, 6-dimethyl pyridine is a useful probe molecule for the selective determination of Brönsted acid sites. Temperature programmed desorption of ammonia, thermo desorption of 2, 6-dimethyl pyridine are the thermal analytical methods to correlate between catalytic activity and acid strength of the solid acids [102]. Test reactions like cumene cracking, and decomposition of cyclohexanol are the most direct methods for the measurement of surface acidity. The nature of the products formed during the reaction, can be used to obtain nature of the acidity present in the samples [103].

### 1.10.1 Test Reactions for Acidity

The vapour phase conversion of cumene is a model reaction for identifying the Lewis to Brönsted acid ratio of a catalyst. Cumene is cracked to benzene, ethyl benzene, styrene and propene over Brönsted acid sites, whereas dehydrogenation to α-methyl styrene occurs over Lewis acid sites. The relative amounts of benzene and α-methyl styrene in the product mixture can therefore be a good indication of the types of acidities possessed by catalyst [104].

Kooli et al. [105] used cumene cracking to compare titania pillared clays using montmorillonite, saponite and rectorite hosts. Various rare earth phosphates were characterised by catalytic activities on cracking/ hydrogenation reaction of cumene [106].

## 1.11 Reactions selected for present study

### 1.11.1 Ethyl benzene Oxidation

Side chain oxidation of alkyl aromatics using cleaner peroxide oxidants catalysed by heterogeneous catalysts still attracts interest. Classical laboratory procedures preferably use stoichiometric oxidants such as permanganates and dichromate, which are hazardous [107]. Hence there has been an interest to develop eco-friendly catalysts for the oxidation of alkyl aromatics. The presence of molecular oxygen or single oxygen donors such as tert-butyl hydroperoxide (TBHP) for the oxidation of alkanes to ketones are shown to be important [108]. Chromium substituted aluminophosphates are found to favour the formation of ketones from alkyl arenes with TBHP as the oxidant [109]. Based on this report in the present study, we utilized ceria containing transition metals as catalysts for the oxidation of ethyl benzene using TBHP as oxidant in liquid phase. Effective utilization of ethyl benzene available in the xylene stream of the petrochemical industry for more value added products is an interesting proposition. Oxidation of ethyl benzene has not drawn much attention due to the complexity of the products that could be formed. Recently there has been an interest in the development of clean and economical processes for the selective oxidation of ethyl benzene to higher value added product acetophenone [110].

Autoxidation reactions are very important milestones in the development of new petrochemical processes. These kinds of reactions use the most abundant and cheapest oxidant that minimizes the production and use of pollutants [111]. Oxygenated products are the required intermediates for many chemical feed stocks, agrochemicals, fragrances, pharmaceuticals, and polymers [112]. A substantial amount of research has been focussed on the homogeneous catalytic oxidation of alkyl aromatic substrates with cobalt salts and dioxygen under corrosive conditions, but a more environmentally benign and selective catalytic process is clearly desirable. Selective oxidation reactions of relatively inert C–H bond of hydrocarbons using air or oxygen is one of the most desirable and challenging reactions, since the obtained products are themselves important or act as valuable intermediates for industrial organic chemicals [113]. Effective utilization of ethyl benzene, available in the xylene stream of the petrochemical industry to more value added products is an interesting proposition. Well known are the isomerization of ethyl benzene to xylenes and dehydrogenation to styrene monomer. Oxidation of ethyl benzene has not drawn much attention due to the complexity of the products that could be formed, particularly in the vapour phase catalytic oxidation using molecular oxygen [114].

Aromatic ketone, acetophenone is an important intermediate for perfumes, drugs and pharmaceuticals [115]. Production of this aromatic ketone by Friedel Craft's acylation of aromatic compound by acid halide or acid anhydride using stoichiometric amount of anhydrous aluminium chloride or a homogeneous acid catalyst leads to a the formation of a large volume of highly toxic and corrosive wastes [116, 117]. In the past, efforts have been made to produce aromatic ketones by oxidizing the methylene group attached to an aromatic ring using stoichiometric quantities of oxidizing agent e.g., the oxidation of ethyl benzene to acetophenone by $KMnO_4$ [118]. In this waste produced is very large and the separation of reactants and the products from the reaction mixture is difficult. Acetophenone can also be produced by the liquid phase oxidation of ethyl benzene by oxygen of the air using heterogeneous transition metals (viz. Co, Mn, Cu or Fe) compounds as catalysts [119, 120, 121, 122]. In this reaction, the reaction conditions are harsh, the product selectivity is poor, separation of the catalysts from the reaction mixture is difficult and catalyst cannot be reused. A lot of tarry waste products are formed. It is therefore great practical interest to develop a more efficient easily separable, reusable and environmental friendly catalyst for the production of aromatic ketone.

### 1.11.2 Friedel-Crafts benzylation reaction

Friedel-Crafts alkylation enables the introduction of alkyl chains to aromatic rings. Alkyl chlorides, alcohols and alkenes are the commonly employed alkylating agents [123]. A wide range of homogeneous catalysts like $FeCl_3$, $AlCl_3$ and $BF_3$ and protonic acids like HF and $H_2SO_4$ have been found to be well suited for the reaction [124, 125]. The environmental concern and the drive towards a “clean technology” urge the replacement of the liquid acids by eco-friendly solid acid catalysts. Benzylation of o-xylene with benzyl chloride, which is a typical example of Friedel-Crafts alkylation, is generally known to proceed over a homogeneous Lewis acid catalyst, $AlCl_3$ [126]. Catalytic behaviour of rare earth oxides has been explored for many reactions and a wide variety of catalytic properties have been known [127]. These oxides can be used in Friedel-Crafts reactions, too [128]. Bhaskaran et al. reported that rare-earth oxides like $CeO_2$ and $Pr_2O_3$ are effective for benzylation o-xylene. They stated that the presence of strong as well as weak acid sites on the catalyst surface appears to be very important for the feasibility of the reaction [129].

### 1.11.3 Acetalization and deacetalization reactions

Acetalization is one of the most widely used synthetic method for protecting aldehydes and ketones in the course of preparation of a variety of multifunctional complex organic molecules since dimethyl acetals display higher stability towards strong bases, Grignard reagent, lithium aluminium hydride, strong oxidants, and esterification reagents than their parent carbonyl compounds [130].

The acetalization reaction is a process that is widely used in organic synthesis to protect the carbonyl group of aldehydes and ketones [131]. Besides, acetals became important reactants for synthesis of enantiomerically pure compounds which were widely used as steroids, pharmaceuticals, and fragrances [132]. Previously, the catalysts used in the acetalization reactions were generally proton acids, Lewis acids and a number of transition metal complexes including Rh, Pd and Pt [133]. Although good results were obtained, the separation of the products from the catalyst system after the reaction was still difficult to overcome and the noble metal catalysts used were quite expensive and usually unstable [134]. Therefore, to design and synthesize a catalytic system that may be stable, easily separable, and reusable has long been pursued [135]. The nature of the pores of the solid acid catalysts determines acetalization efficiency of a particular catalyst. Dimethyl acetals of ketones, cyclohexanone, acetophenone and benzophenone have been prepared by reacting ketones with methanol under mild reaction conditions.

Acetalization is a reversible reaction catalyzed by an acid environment and is usually performed in the liquid phase, which leads to the elimination of water as a by-product thereby requiring azeotropic distillation to remove the water formed during the reaction, or else leading to the deactivation of the catalyst.

### 1.11.4 Vapour phase reaction: methylation of phenol

Alkylation of aromatic substrates catalyzed by solid acids such as zeolites and metal oxides constitutes a class of reactions important both academically and industrially. Among alkylation reactions, methylation of phenol has attracted considerable attention due to industrial importance of methyl phenols as chemical intermediates in the manufacture of pharmaceuticals, agrochemicals, resins, various additives, polymerization inhibitors, antioxidants and various other chemicals [136]. Selective C-methylation of phenol to o-cresol and 2, 6-xylenol in high yields has been carried out with methanol over various solid acid catalysts. In particular, ortho-alkylated phenols such as o-cresol, 2, 6-xylenol and trialkyl substituted phenols are more important alkyl phenols. After suitable processing o-cresol is used in the synthesis of herbicides as well as in sealing material for integrated circuits, whereas 2,6-xylenol is used in manufacture of disinfectant and in high impact resistant resins [137]. The alkylation of phenol with methanol being an acid–base catalysed reaction, the product selectivity depends upon the acidity as well as basicity of the catalyst. Phenol alkylation using various acid and base catalysts has been reported. Phenol conversion as well as product selectivity is found to depend on the acid–base properties of the catalyst, temperature [138] and residence time [139].

## 1.12 Major Objectives of the Present Work

From the literature, it is obvious that surface properties and catalytic activities of mesoporous ceria can be modified by controlling the pore size, pore distribution and surface area there by improving the acidic/ basic nature and redox properties. The distribution and pore nature depends on method of preparation. High surface area mesoporous ceria can be prepared successfully by surfactant method and the surface area can be maintained high by lowering the calcination temperature by using neutral surfactant. The thesis is based on the templated method of preparation of mesoporous ceria using neutral surfactant hexadecyl amine (HDA) from the inorganic precursor cerium nitrate hexahydrate. Mesoporous ceria is modified by different percentages of transition metals by wet impregnation method.

Major objectives of the present work includes:-

- To prepare mesoporous Cerium Oxide by "Soft template " method using neutral surfactant hexadecyl amine (HDA) and modify the prepared system with different percentages of transition metals (Fe, Co, Ni, Cu, Mn & Cr).
- To investigate the surface properties of the systems by techniques such as BET surface area, pore volume measurements, pore diameter, and pore distribution by sorption studies of nitrogen, low and wide angle XRD, UV-Vis DRS, SEM, TEM, FT-IR, EDAX, ICP-AES, TPR-$H_2$ etc.
- To examine the surface acidic properties of the catalytic systems using temperature programmed desorption of ammonia and the test reaction of vapour phase cumene cracking.
- To explore the catalytic activity of the systems towards the liquid phase oxidation of ethyl benzene.
- To test the catalytic activity of the systems towards the liquid phase benzylation of toluene, o-xylene & anisole.
- To examine the catalytic activity of the systems towards the liquid phase acetalization and deacetalization of cyclohexanone.
- To investigate the catalytic activity of the systems towards the vapour phase methylation of phenol.

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# Chapter 2

# MATERIALS AND METHODS

Contents

The performance of a catalyst depends on the method of preparation and catalyst pretreatment condition along with the reaction parameters. The materials and the experimental procedures used for catalyst preparation, surface acidity and catalytic activity measurements are described in this chapter. The structural and morphological characteristics of the prepared samples were investigated by the techniques like wide and low angle XRD, BET surface area and pore volume measurements, BJH sorption studies, TEM, FT- IR, TG-DTA, SEM, EDX, ICP–AES, TPR in $H_2$ and UV-Vis DRS. These techniques are expected to be powerful tools to study the changes of the local environment and nature of ceria species. Ammonia TPD and vapour phase cumene cracking as the test reaction for acidity are adopted for the surface acidity determination. For the activity study of the prepared systems, liquid phase reactions like oxidation of ethyl benzene using TBHP to get acetophenone as the main product, Friedel Crafts benzylation of toluene, o-xylene and anisole using benzyl chloride, acetalization and deacetalization of cyclohexanone for the protection of ketone functional group and vapour phase reaction of methylation of phenol are done.

## 2.1 Introduction

Catalysis is a complex surface phenomenon occurring on the surface of a catalyst. The adsorption of the reactant molecules and their interaction to give product on the active phase of the catalyst depend not only on the reaction variables, but also on the nature of sites on the catalyst surface, which in turn determines the quality of the catalyst [1]. In the preparation of the commercial catalysts even a minute change in the conditions of preparation, changes the quality of the catalyst. Hence utmost care should be taken during the preparation of systems. When designing and making reliable catalysts, it is necessary to take into account process parameters such as temperature, pressure, reactant concentration and space velocity, as well as variable factors such as feed composition and unpredictable or unsuspected factors such as impurities and poisons in the feed [2].

We have prepared six series of ceria catalysts modified with chromium, manganese, iron, cobalt, nickel and copper. The experimental procedures used to prepare the pure and supported catalysts are given in this chapter. All the prepared catalyst systems were characterized and tested for catalytic activity with various techniques. The materials used and the methodologies adopted are described in the following sections.

## 2.2 Catalyst Preparation

The metal oxide was prepared via templated method (surfactant assisted route) [3] using cerium nitrate [Ce $(NO_3)_3$. $6H_2O$] as the precursor.

### 2.2.1 Materials

The materials used for the catalyst preparations are given below

Table 2.1 Chemicals used for catalysts preparations

| Materials | Suppliers |
|---|---|
| Cerium nitrate hexahydrate | Indian Rare Earth Ltd. |
| Nitric acid | Merck |
| Ammonia | Qualigens |
| Chromium nitrate | S. D. Fine Chemicals Ltd |
| Manganese Acetate | Merck |
| Ferric Nitrate | Qualigens fine Chemicals |
| Cobalt Nitrate | S. D. Fine Chemicals Ltd |
| Nickel Nitrate | S. D. Fine Chemicals Ltd |
| Copper Nitrate | S. D. Fine Chemicals Ltd |
| Hexadecyl amine | Sigma Aldrich |
| Methanol | Merck |

## 2.2.2 Methods

A detailed discussion of the experimental procedures used to develop the catalyst systems is given below.

### 2.2.2.1 Preparation of Cerium oxide [4]

Mesoporous ceria was prepared by surfactant assisted method using the neutral surfactant hexadecyl amine as the template. 0.05M cerium nitrate solution was added to a solution of hexadecyl amine in 1:1 water-ethanol mixture with stirring. A molar ratio of 2 was kept for precursor to the surfactant. The pH of the mixture was maintained above 10. The mixture was stirred for 6 hours and then aged for 3 days at 60$^{o}$C. The precipitate obtained was washed with ethanol- water mixture several times and then with deionized water and filtered. The dried precipitate is precalcined at 250°C for 6 hours. The powdered sample is then calcined at 350°C for 4 hrs.

### 2.2.2.2. Preparation of metal incorporated Cerium oxide

0.5M solution of the corresponding metals [Cr $(NO_3)_3.9H_2O$, Mn $(NO_3)_3$, Fe $(NO_3)_3$, Co (AC) $_2.4H_2O$, Ni $(NO_3)_2.6H_2O$ and Cu $(NO_3)_2.3H_2O$,] containing required amount of metal (2, 4 and 10wt% of metal) was added to the previously prepared mesoporous ceria and was mechanically stirred for 6h, kept overnight and dried at 80°C which was further dried at 110°C. It is powdered and calcined at 350°C to obtain metal incorporated cerium oxide.

## 2.3 Catalyst Notation

The catalyst systems developed for the present investigation and its designation are given below.

**Table 2.2 Notations for catalysts prepared**

| Notation | System |
|---|---|
| Ce | Pure cerium oxide |
| CeCr (X %) | Chromium incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight % of Cr respectively |
| CeMn(X %) | Manganese incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight% of Mn respectively |
| CeFe (X %) | Iron incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight % of Cr respectively |
| CeCo (X %) | Cobalt incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight % of Co respectively |
| CeNi (X %) | Nickel incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight % of Ni respectively |
| CeCu (X %) | Copper incorporated ceria with x= 2 ,4, 10 for 2, 4 & 10 weight % of Cu respectively |

## 2.4 Characterization Techniques

Catalyst characterization is a highly relevant area in catalysis. Catalytic properties of a surface are determined by its composition and structure on atomic scale. The performance of a catalyst depends on two parameters, physical properties, which influence the lifetime, mass and mass transfer phenomena and active site parameters, which judge the reaction behavior, which is correlated with the number and nature of active sites. The prepared catalyst samples were characterized by adopting a variety of Physico-chemical methods.

### 2.4.1 Materials

The materials used for catalyst characterization is given in Table 2.3.

**Table 2.3 Chemicals used for characterisation**

| Materials | Suppliers |
|---|---|
| Liquid Nitrogen | Sterling gases, Ambalamugal |
| Magnesium oxide | Merck |
| Con.$H_2SO_4$ | S. D. Fine Chemicals |
| Sodium Hydroxide | Merck |
| Oxalic acid | Merck |
| Cumene | Sigma Aldrich chemicals |

### 2.4.2 Methods

A brief discussion of each method of characterization adopted along with its experimental aspects is presented in the following sections. Before each characterization, the samples were activated at 350 $^{o}$C for 1 hour.

### 2.4.2.1 X- ray diffraction studies (XRD)

X-ray diffraction is one of the most important tools in solid state chemistry since it is a powerful and readily available method for the identification and characterization of crystalline solid phases in heterogeneous catalysis. It can provide information about specific component in a system, purity of substance, transition to different phases etc.

The principle of XRD is based on the interaction of X-rays with the periodic structure of a polycrystalline material, which acts as a diffraction grating. A fixed wavelength is chosen for the incident radiation and the diffraction patterns obtained by observing the intensity of the scattered radiation as a function of scattering angle 2θ.

The relationship among the wavelength of X-ray beam, the angle of diffraction and the inter planar distance or d-spacing d, is given by Bragg's equation [5],

$$n \lambda = 2d \sin\theta$$

Where,

$n$ - Order of diffraction

$\theta$ - Bragg angle

$d$ - Inter planar spacing

$\lambda$ - Wavelength of x-rays

This relation demonstrates that interference effects are observable only when radiation interacts with physical dimensions that are approximately the same size as the wavelength of the radiation. Since the distances between atoms or ions are of the order of 1Å, diffraction methods require radiation in the X-ray region of the electromagnetic spectrum, or beams of electrons or neutrons with similar wavelength. So, through X-ray spectra one can identify and analyse any crystalline matter. The degree of crystallinity or order will decide the quality of the obtained result. In order to do this, a diffractometer is needed. Basically, an X-ray diffractometer consists of X-ray generator, sample holder and an X-ray detector, such as photographic film or a movable proportional counter. The most usually employed instrument to generate X-rays is X-ray tubes, which generate X-rays by bombarding a metal target with high energy (10-100 keV) electrons which knock out core electrons. Thus, an electron in an outer shell fills the hole in the inner shell and emits an X-ray photon. Two common targets are Mo and Cu, which have strong Kα X-ray emissions at 0.71073 and 1.5418 Å, respectively. Apart from the main line, other accompanying lines appear which have to be eliminated in order to facilitate the interpretation of the spectra. These are partially suppressed by using crystal monochromator. Perhaps the most routine use of diffraction data is for phase identification [6, 7]. Each crystalline powder gives a unique diffraction diagram, which is the basis for a qualitative analysis by X-ray diffraction.

The X-ray diffraction pattern of a crystalline phase is a characteristic fingerprint, which enables the determination of phase purity and of the degree of crystallinity. Identification is practically always accompanied by the systematic comparison of the obtained spectrum with a standard one (a pattern), taken from any X-ray powder data file catalogues, published by the American Society for Testing Materials (JCPDS). Structural details of porous materials on a scale covering from approximately 1 to 100 nm may be determined from measurements of the small angle scattering (SAS) of both X-rays (SAXS) and neutrons (SANS). For mesoporous materials reflexes are observed in X-ray powder patterns at low 2θ angles ($0.5 < 2\theta < 10^{o}$). These reflexes are due to the long-range order induced by the very regular arrangement of the pores. Because *d*-spacings are rather big for the mesopores, the reflexes appear at low angles. Unit cell parameter ($a_o$) of cubic lattice can be calculated from,

$$a_0 = d\,(h^2 + k^2 + l^2)^{1/2}.$$

The unit cell dimension determined by XRD is also used to calculate the frame wall thickness (FWT) of the channels of the mesoporous materials.

A rough estimate of crystallite size can be obtained from the line broadening using the Scherrer's equation [8]

$$d = 0.9\lambda / \beta \cos\theta$$

Where

β : Full Width half maximum (FWHM) of the strongest peak

d : Inter planar spacing

2θ : Scattering angle

Powder XRD of the prepared samples were taken on a Rigaku *Xpert PRO MPD* model with Ni filtered Cu Kα radiation (λ-1.5406 Å) within the 2θ range 0-10° at a speed of 1°/min. The crystalline phases were identified by comparison with standard JCPDS (Joint Committee on Powder Diffraction Standards) data file [9].

### 2.4.2.2 Adsorption Isotherm

Gas adsorption is a prominent method to obtain a comprehensive characterization of porous materials with respect to the specific surface area, pore size distribution and porosity. This requires, however, a detailed understanding of the fundamental processes associated with the sorption and phase behaviour of fluids in porous materials and their influence on the shape of sorption isotherms, which serves as a basis for surface and pore size analysis. Pore width, pore shape and the effective adsorption potential are the factors that determine the pore filling. In case of so-called micropores (pore width < 2 nm, according to IUPAC classification) the pore filling occurs in a continuous way, whereas in case of mesopores (pore widths in the range from 2-50 nm) pore filling occurs by pore condensation, which reflects a first order gas-liquid phase transition. Nitrogen physisorption is a commonly applied technique to characterize porous and nonporous materials [10, 11, 12]. Properties like surface area pore size pore volume, and pore size distribution can be obtained by careful analysis of the measured data. The amount of adsorbed/desorbed nitrogen is measured as a function of the applied pressure, giving rise to the adsorption/ desorption isotherm. The shape of the isotherm depends on the porous texture of the measured solid. According to the IUPAC classification six types of isotherms can be distinguished as shown in Fig. 2.1

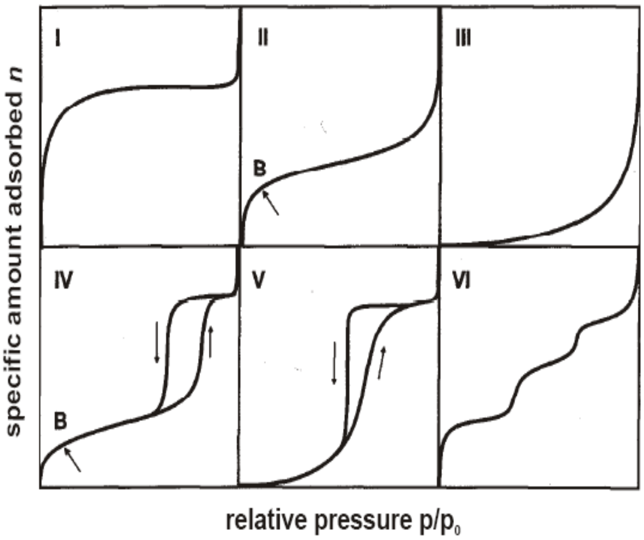

**Fig. 2.1 Isotherm types according to IUPAC definition.**

*Type I – microporous material,*
*Type II – macro- or non-porous material,*
*Type III – macro- or non-porous material with weak adsorbate-solid interactions,*
*Type IV – mesoporous material,*
*Type V – mesoporous material with weak adsorbate – solid interactions,*
*Type VI – stepwise adsorption at very weak adsorbate- solid interactions.*

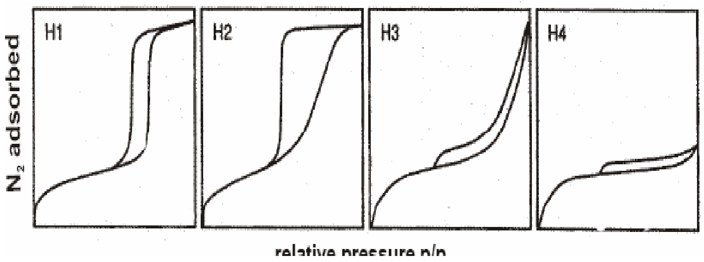

**Fig. 2.2 Hysteresis types according to IUPAC definition.**

*H1 – typical for type IV isotherms,*
*H2 – characteristic for "ink-bottle" pores,*
*H3 and H4 – slit pores*

### 2.4.2.3 BET Surface area and pore volume measurements

Surface area determination is an important factor in predicting the catalyst performance. Of the several techniques to estimate the surface area and pore volume of the porous materials, BET method [13] is the widely adopted procedure and this method is based on the extension of the Langmuir theory to multilayer adsorption. This method was established by Brunauer, Emmet and Teller [9]. The model, on which it is based, assumes that the heat of adsorption on the bare surface is different from the heats of adsorption of all successive layers. The BET equation extends the Langmuir isotherm to multilayer adsorption,

The general form of BET equation can be written as

$$P/ V (P_0-P) = 1/CV_{mono} + C-1/CV_{mono} (P/P_0) \text{---------------------} (2.1)$$

Where

P : Adsorption equilibrium pressure

$P_0$ : Saturated vapor pressure of the adsorbate

V : Volume occupied by the molecules adsorbed at equilibrium pressure

$V_m$ : Volume of the adsorbate required for monolayer coverage

C : Constant related to the heat of adsorption

The BET plot is linear as long as only multilayer adsorption occurs. Plot of $P/V (P_0-P)$ against $P/P_0$ is a straight line with slope $C-1/CV_m$ and intercept 1/CVm. From the slope and intercept $V_m$ can be calculated and the specific surface area of the sample can be calculated using the relation,

$$A = V_m N_o A_m / W \times 22.414 \quad \text{------------------------------------------(2.2)}$$

Where

$N_o$ : Avogadro number

$A_m$ : Molecular cross sectional area of the adsorbate ($0.162 nm^2$ for $N_2$)

W : Weight of the catalyst sample

In BET method, adsorption of nitrogen is carried out at liquid nitrogen temperature. Previously activated samples were degassed at 200°C under $N_2$ for 2hrs and then brought to –196°C using liquid $N_2$ for adsorbing $N_2$ gas at various pressures. The pore volume is measured by the uptake of nitrogen at a relative pressure of 0.9. When data points in the pressure range of capillary condensation are included in the BET analysis, the plot is not linear. The obtained specific surface areas are too large. To avoid that, data points in the relative pressure range of $0.02 < p/p_0 < 0.2$ were used in this work.

In the t-plot method the measured adsorbed volumes are plotted against the statistical layer thickness‘t’ [14]. The t-plot allows the examination of three properties of an adsorbent (a) to detect the onset of capillary condensation, denoted by deviation from linearity in the higher regions of the plot; (b) to detect the micro porosity from an estimate of the amount of micro pores, from the intercept of the extrapolated plot on the ordinate, (c) to compute the $V_m$ from the multi-layer region of the isotherm. This method of isotherm data analysis was introduced by de Boer. The statistical thickness is specific for the combination of an adsorptive capacity, the temperature, and the surface of a solid material. The specific pore volume is calculated from the intercept of the straight line that is drawn through the second linear region in the t plot. From the slope of this line a value for the external surface area could be calculated.

Pore diameter distributions were calculated by the BJH method developed by Barret, Joyner and Halenda [14]. In this approach the filled pores are taken as a starting point. The emptying of the filled pores with decreasing relative pressure is incrementally evaluated to obtain a pore diameter distribution. For each increment the pore diameter of pores emptied is calculated according to the Kelvin equation (equation 2.3).

$$P/P_0 = \exp(-2\gamma v^1/r_k RT) \text{ ----------------------------------------------- } (2.3)$$

The Kelvin equation ( $P/P_0$) is the relative vapour pressure over a curved surface, $\gamma$ is the surface tension, $V^l$ is the molar volume of the liquid, and $r_k$ is the radius of curvature expresses mathematically that adsorption on a curved surface is more favourable than on a flat surface. According to equation (2.3), the vapour pressure over a concave surface is lower than over a flat surface. This causes the filling of the mesopores at relative pressures, which are characteristic for the pore diameter. This process is often called capillary condensation because the environment of the adsorbate in filled mesopores is comparable to a liquid state environment. Since the assumptions of Kelvin equation (2.3) are not completely fulfilled in small mesopores, the real pore diameter may vary a little from the calculated value. But in a relative sense the BJH distributions are correct.

Nitrogen adsorption measurements were performed at liquid nitrogen temperature with a *Micromeritics Tristar 3000* surface area and porosity analyzer. Prior to the measurements the samples were degassed for 1hour at 90ºC followed by 200ºC overnight.

### 2.4.2.4 Energy dispersive X-ray analysis (EDX)

The EDX analysis is a relatively new technique for qualitative and quantitative elemental analysis of solid samples. In this method, the characteristic X-rays are separated on the basis of photon energies rather than on their wavelength. The Si (Li) detector cooled by liquid nitrogen receives the undispersed characteristic X-rays from the specimen. The amplified detector output is then digested and the pulses are accumulated in the channels, which represents a small range of energy. For qualitative analysis the data are transferred into a computer for calculation of elemental concentrations. For quantitative analysis, the data may be displayed in a number of ways such as a series of peaks (intensity Vs energy) on a cathode ray oscillograph. The simultaneous measurement and display of the energy spectrum result in rapid qualitative and quantitative elemental analysis. EDX analysis of the samples was recorded in a JSM-840 EDX analyzer.

The fundamental principle is that, when incident beam bounces through the sample creating secondary electrons, it leaves thousands of sample atoms with vacancies in the electron shells. If these vacancies are in inner shells, the atoms are not in a stable state. To stabilize the atoms, electrons from outer shell will drop into the inner shells, however, because the outer shells are at a higher energy state, to do so the atom will lose some energy. Energy will be lost in the form of X-rays. The X-rays emitted from the sample atoms are characteristic of the element.

### 2.4.2.5 FT-IR Spectroscopy

Infrared spectroscopy is a very useful technique for characterization of materials, providing information about the structure of molecules [15].

IR spectrum of a compound is the superposition of absorption bands of specific functional groups. The advantages of infrared spectroscopy include wide applicability, nondestructiveness, measurement under ambient atmosphere and the capability of providing detailed structural information. Besides these intrinsic advantages the more recent infrared spectroscopy by Fourier transform (FT-IR) has additional merits such as higher sensitivity, higher precision (improved frequency resolution and reproducibility), quickness of measurement and extensive data processing capability. IR spectra originate in transitions between two vibrational levels of a molecule in the electronic ground state and are usually observed as absorption spectra in the infrared region. For a molecule to present infrared absorption bands it is needed that it has a permanent dipole moment. When a molecule with at least one permanent dipole vibrates, this permanent dipole also vibrates and can interact with the oscillating electric field of incident infrared. Thus, if the vibrational frequency of the molecule, as determined by the force constant and reduced mass, equals the frequency of the electromagnetic radiation, then adsorption can take place. As the frequency of the electric field of the infrared radiation approaches the frequency of the oscillating bond dipole and the two oscillate at the same frequency and phase, the chemical bond can absorb the infrared photon and increase its vibrational quantum number or increase its vibrational state to a higher level. As an approximation, larger the strength of the bond higher will be the frequency of the fundamental vibration. In the same way, the higher the masses of the atoms attached to the bond, the lower will be the wavenumber of the fundamental vibration. As a general guide, the greater the number of groups of a particular type, more polar the bond, the more intense the band. The infrared spectrum can be divided into two regions, one called the functional group region and the other the fingerprint region. The functional group region is generally considered to range from 4000 to 1500 $cm^{-1}$ and all frequencies below 1500 $cm^{-1}$ are considered characteristic of the fingerprint region. The fingerprint region involves molecular vibrations, usually bending motions that are characteristic of the entire molecule or large fragments of the molecule and these are used for identification. The functional group region tends to include motions, generally stretching vibrations, which are more localized and characteristic of the typical functional groups, found in organic molecules. While these bands are not very useful in confirming identity, they do provide some very useful information about the nature of the components that make up the molecule. FT-IR spectroscopy is one of the most widely used analytical techniques used for material analysis. This characterization technique has a decisive role in identifying the surface species of supported ceria catalysts. Dispersion of metal species and their structure, support-metal interaction, metal-metal interaction, surface acidity of catalysts, bulk catalyst structure etc. are some of the valuable informations that can be attained from FT-IR spectroscopy. The intensities of FT-IR absorption bands depend on the effects induced by the acid-base interactions in the spectral features of the absorbed probe molecules. FT-IR spectra of the prepared samples were measured by the KBr pellet procedure over the range of 4000-500 $cm^{-1}$ region using *JASCO FTIR* spectrometer. The entire frequency range of the electromagnetic waves transmitted through the sample was recorded simultaneously and the output was fed to a computer, which reinforces the spectrum using Fourier transform.

### 2.4.2.6 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface by analyzing electrons emitted from a specimen. Scanning Electron

Microscopy allows the imaging of the topography of a solid surface by using back scattered or secondary electrons with good resolution of about 5nm. In this technique, a fine probe of electrons is scanned over the sample surface using deflection coils. The interaction between the primary beam and specimen produces various signals, which are detected, amplified and displayed on a cathode ray tube screened synchronously with the beam. They can also be conveniently deflected and focused by electronic or magnetic field so that magnified real-space images can be formed. This makes the technique suitable for producing very impressive, in focus images from a highly irregular structure, typical of catalyst specimens. This technique is of great interest in catalysis particularly because of its high spatial resolution [16]. In SEM analysis finely powdered sample was applied on to a double sided carbon tape placed on a metal stub. The stub was then inverted in such a manner that the free side of the carbon tapes gently picked up a small amount of the sample, thereby creating a thin coating. It was then sputtered with a thin layer of gold to obtain better contrast and provide improved cohesion [17]. During SEM inspection, a beam of electrons is focused on a spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons, are attracted and collected by a positively biased grid or detector, and then translated into a signal. To produce the SEM image, the electron beam is swept across the area being inspected, producing many such signals. These signals are then amplified, analysed, and translated into images of the topography being inspected. Finally, the image is shown on a cathode ray tube. SEM analysis of the samples was done using *JEOL* JSM-840 A (Oxford make) model 16211 scanning electron microscope analyzer with a resolution of 13eV. The sample was dusted on alumina and coated with a thin film of gold to prevent surface charging and to protect the material from thermal damage by electron beam. A uniform film thickness of about 0.1 mm was maintained for all samples.

### 2.4.2.7 Transmission electron microscopy

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is transmitted through a specimen, then an image is formed, magnified and directed to appear either on a fluorescent screen or layer of photographic film or to be detected by a sensor such as a CCD camera (charge couple device) [18]. The transmission electron microscope is based on the fact that electrons can be ascribed a wavelength but at the same time interact with magnetic fields as a point charge. A beam of electrons is applied instead of light, and the glass lenses are replaced by magnetic lenses. The lateral resolution of the best microscopes is down to atomic resolution. Like SEM, TEM uses an electron gun to produce the primary beam of electrons that will be focused by lenses and apertures into a very thin, coherent beam. This beam is then controlled to strike the specimen. A portion of this beam gets transmitted to the other side of the specimen, is collected, and processed to form the image. The HR-TEM of the samples was carried out in ultrahigh resolution analytical electron microscope JEOL 3010. This gives a lattice resolution of 0.14 nm and a point to point resolution of 0.12 nm. Bulk materials have to be thinned to make them electron transparent. The typical column vacuum in the machine is $< 1x10^{-5}$ pa.

### 2.4.2.8 Thermo gravimetric analysis (TGA)

Thermo gravimetry (TG) in which the catalyst sample is subjected to a controlled heating to higher temperatures at a specified heating rate is a well-established technique in heterogeneous catalysis. It finds widest applications in the determination of drying range, calcinations temperature, phase composition, percentage weight loss and stability limits of the catalyst. Thermo gravimetric analysis (TGA) is an analytical technique used to determine thermal stability of a solid and its fraction of volatile components by monitoring the weight change that occurs as the specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve (DTG) can be used to tell the point at which weight loss is most apparent. A sample of material (ranging from 1 to 100 mg) is placed on an arm of a recording microbalance, also called thermo balance where that arm and the sample are placed in a furnace. The furnace temperature is controlled in a pre-programmed temperature/time profile (most commonly), or in the rate controlled mode, where the pre-programmed value of the weight changes imposes the temperature change in the way necessary to achieve and maintain the desired weight-change rate. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans: (Differential thermal analysis or DTA) or the heat flow into the specimen pan compared to that of the reference pan (differential scanning calorimetry or DSC). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process. Any transition that the sample undergoes results in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. A plot of the differential temperature ($\Delta T$) versus the programmed temperature T indicates the transition temperatures and whether the transition is exothermic or endothermic. When an endothermic change occurs, the sample temperature lags behind the reference temperature because of the heat in the sample.

Exothermic behaviour is associated with the decrease in enthalpy of a phase or a chemical system. DTA and thermo gravimetric analyses are often run simultaneously on a single sample [19].

In TG, the weight loss of a sample is being continuously recorded over a period of time under controlled heating rate. Changes in weight are due to the rupture and /or formation of various physical and chemical bonds at elevated temperatures, which lead to the evolution of volatile products or the formation of heavier reaction products. From the thermo gram, where we plot weight against temperature, information about dehydration, decomposition and various forms or products at various temperatures can be obtained. The first derivative of the thermogram (DTG) gives a better understanding of the weight loss and can also be used to determine the thermal stability of the samples.

Perkin Elmer TG analyzer instrument was used for carrying out thermo gravimetric studies. About 20mg of the sample was used at a heating rate of 20 ºC per min in nitrogen atmosphere. The TG data were computer processed to get thermogram. Any decomposition of the sample is indicated by a dip in the curve. These dips correspond to the weight loss due to decomposition and hence provide an idea about the species lost during the heating step.

### 2.4.2.9 Diffuse Reflectance UV-VIS Spectroscopy (UV-Vis DRS)

UV-Vis spectrophotometer measures the intensity (I), of light passing through a sample and compares it to the intensity of light ($I_o$) before it passes through the sample. The ratio $I / I_o$ is called the transmittance, and is usually expressed as a percentage (%T). The absorbance A is based on the transmittance:

$$A = -\log (\%T)$$

A spectrophotometer can be either single beam or double beam. In a single beam instrument, all of the light passes through the sample cell. $I_o$ must be measured by removing the sample. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference, the other beam passes through the sample. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam.

Diffuse reflectance UV-Visible spectroscopy allows the study of electronic transitions between orbital or bands in the case of atoms, ions and molecules in gaseous, liquid or solid state. In catalysis, the information given by DRS mainly includes the active phase–supports interaction, the chemical changes during a modification procedure leading to the active phase and the nature of the co-ordination sphere of the active surface species.

Electronic transitions of transition elements are two types, metal centred transitions (d-d) or [(n-1)d-ns] and charge-transfer (CT) transitions. (d-d) transitions give information about the oxidation state and co-ordination environment of transition metal ion. [(n-1)d - ns] transitions are often too high in energy to be observed in the spectrum. The CT transitions are intense since they are sensitive to the nature of donor and acceptor atoms [20]. In DR measurements, the light emitted by the sample and the integration sphere collects the reference material and detector of the double beam spectrometer gives the apparent absorbance. Diffuse reflectance UV-Vis. spectroscopy is widely used in the surface characterization of supported ceria catalysts.

Diffuse reflectance UV-Vis. spectra of the samples were recorded using a conventional spectrophotometer (Ocean Optics 2000) with CCD detector. Magnesium oxide (MgO) was used as the reference material.

### 2.4.2.10 Elemental Analysis-Inductively Coupled Plasma-Atomic Emission Spectroscopy

Inductively Coupled Plasma-Atomic Emission Spectroscopy is used for the elemental analysis of prepared samples. Most of the elements in the periodic table can be analyzed by this technique. The main advantages of the technique are that some elements can be analyzed with greater sensitivity or can be analyzed simultaneously. The elemental composition is carried out by analyzing the atomic spectrum emitted by a sample. The wave length at which emission occurs identifies the element, and the intensity of radiation emitted can be used to find out the amount of the element present.

High temperature non-flame atomic emission spectroscopy has more advantages because of the greater concentration of emitting atoms. Main high temperature non-flame sources are usually plasmas and can operate at temperature in the range of 7000-15000K. Thus the plasma source produces a greater number of excited emitted atoms, especially in the UV region. Plasma is a cloud of highly ionized gases, composed of ions, electrons and neutral particles. In plasma emission spectroscopy the gas, usually Argon is ionized by the influence of a strong electrical field either by direct current or by radio frequency. Both types of discharge produce plasma, the direct current plasma (DCP) or the inductively coupled plasma (ICP).

The Plasma source produces a greater number of excited atoms, especially in the UV region. The plasma source is able to produce atomization. ICP source comprises three concentric silica quartz tubes;

each is open at the top. The Ar stream that carries the sample in the form of an aerosol passes through the central tube. The excitation is provided by two or three turns of a metal induction tube through which flows a radio frequency current(frequency ≈ 27MHZ) . The second gas flow of Ar at a rate between 10 and 15 $\text{min}^{-1}$ maintains the plasma. It is this gas stream that is excited by the radio frequency power. The plasma gas flows in a helical pattern which provides stability and helps to isolate thermally the outside quartz tube. The plasma is initiated a spark from a Tesla coil probe and thereafter self-sustaining. ICP-AES were done on Thermo electron IRIS INTERPID II XSP DUO model. The application of this instrument is in elemental level analysis of environmental samples, pharmaceuticals, research samples, soil etc. The sample is used to introduce by solution nebulization which converts the sample into a form more amenable to rapid atomization.

#### 2.4.2.11 Temperature Programmed Reduction - Hydrogen (TPR-$H_2$)

Temperature programmed reduction (TPR) is unique to study the temperature dependence reduction behaviour of ceria based materials [19a]. The reduction of high surface area ceria takes place essentially in two temperature regions. The first region is 573-873 with $T_{max}$ around 790K and the second region is 973-1273K with $T_{max}$ around 1100K. These two reduction regions are characteristics of ceria and are attributed to the surface oxygen ions and bulk oxygen ions respectively, while the sintered ceria shows only one reduction feature at higher temperature due to bulk reduction. The higher mobility of the surface oxygen ions helps in the removal of lattice oxygen during reduction process. The co-coordinately unsaturated surface capping oxygen ions can be easily removed in the low temperature region. However, bulk oxygen requires to be transported to the surface before their reduction. Consequently, the bulk reduction takes place at higher temperature compared to the surface reduction. The extent of reduction in the low temperature region depends on the surface area of the sample. Oxygen storage measurements consist in the determination of the amount of a reducing gas ($H_2$, CO) which is oxidized after passing through an oxygen pre saturated catalyst.

Temperature-programmed reduction (TPR) was carried out in a Micromeritics Instrument: Chemi Soft TPx V1 TPR system and 0.1725 mg sample was used for each measurement. Prior to the reduction, the sample was pretreated in an air stream at room temperature for 30 min. After that, $H_2$-$N_2$ mixture (5% $H_2$ by volume) was switched on and the temperature was increased linearly at a rate of $10^{o}C\ min^{-1}$. A thermal conductivity cell detected the consumption of $H_2$ in the reactant stream.

## 2.5 Surface Acidity Measurements

Quantification and characterization of surface acid sites forms an important aspect of characterization of catalysts [21]. The concentration and strength of acid sites in solids cannot readily be measured using the types of basic molecular indicators used in the study of acid solutions because the sites in solids may be inaccessible to these molecules. Consequently, alternative techniques have been developed that are more applicable to solids and that enable their acidity to be compared with that of liquid acids. These include the thermal desorption of basic probe molecules (such as pyridine) coupled with IR spectroscopy. An estimate of the number of acid sites, their types, and their strength can be made in this way. Catalytic test reactions, such as alkane cracking, are also widely used to estimate acidity, because the rate and product distribution is indicative of the type and strength of active sites. Several quantitative and quantitative methods have been employed to study surface sites. Here we used adsorption technique Temperature Programmed Desorption (TPD) of ammonia for the measurement of acid amount. Cumene cracking was used as the test reaction for determining the ratio of the amount of Lewis to Brönsted acid sites.

### 2.5.1 Materials

The materials used for surface acidity measurements are given below.

**Table 2.4 Materials used for acidity measurements**

| Materials | Suppliers |
|---|---|
| Ammonia | Qualigens |
| Sulfuric acid | Merck |
| NaOH | CDH |
| Liquid Nitrogen | Sterling gases, Ambalamugal |
| cumene | Aldrich |

### 2.5.2 Adsorption Techniques

The chemisorption of bases such as pyridine, ammonia, and aliphatic amines is frequently used to characterize solid acid catalysts and to correlate their catalytic activity with the concentration of a particular type of acid site. Pyridine and ammonia, because of their capability of interacting with both Brönsted and Lewis sites are widely used to get total acid amount of the systems. Temperature programmed desorption of ammonia, thermo desorption of 2, 6-dimethyl pyridine and test reactions like cumene cracking and decomposition of cyclohexanol can be used to obtain acidity of the samples.

### 2.5.3 Temperature Programmed Desorption (TPD) of Ammonia

Temperature programmed desorption (TPD) is one of the basic experimental tool in surface science for identifying the desorbing species and hence can obtain their adsorption kinetics. TPD analysis helps us to identify the strength, the number and active sites that are available on the catalyst surface. Determining the quantity and strength of the acid sites on catalyst is crucial to understand and predict performance. The technique consists of adsorption of a reactive gas previously chemisorbed on the surface by a linear temperature rate increases. Three types of probe molecules are used for TPD studies: $NH_3$, non- reactive vapour and reactive vapours.

The probe molecules generally used are ammonia, pyridine and methylamine to identify acid sites and $CO_2$ or NO to identify the basic sites. As a probe molecule ammonia has its advantages:

- Its molecular size facilitates access into all pores in a solid.
- It is highly basic, hence titrates even weak acid sites. Strongly polar adsorbed $NH_3$ also capable of adsorbing additional $NH_3$ from gas phase. The rate of adsorption is achieved either by detecting the desorbing species or by monitoring the remaining coverage on the surface.
- When chemisorbed on a surface possessing acid properties, ammonia can interact with the acidic protons, electron acceptor sites and hydrogen from neutral or weakly acidic hydroxyls and thus can detect most of the different type of acid sites [22].
- An ammonia molecule can be retained on the surface of oxides in different modes [23].

- Hydrogen bonding via one of its hydrogen atoms to surface oxygen or to the oxygen of surface hydroxyl group.
- Transfer of proton from surface hydroxyl to the adsorbate.
- Co-ordination to an electron deficient metal atom. It is the strongest mode of interaction.

Thus a fairly reliable interpretation of the TPD pattern of Ammonia from solid acids can be attributed to ammonia chemisorbed on weak, medium and strong acid sites respectively, being not possible to discriminate between Brönsted and Lewis acid sites.

In this technique a definite weight of pelletalised activated sample is placed in a specially designed reactor that is heated at linear rate. The sample is preheated at 300°C for 30 minutes under nitrogen flow. After that, the sample is cooled to room temperature. A definite amount of (20ml) ammonia was injected into the system and was allowed to attain equilibrium. Then excess physisorbed ammonia is flushed out of the reactor by a current of nitrogen. The temperature is gradually increased and ammonia desorbed at an interval of 100°C is scrubbed into dilute sulphuric acid. The ammonia desorbed at each stage is determined by titrating the unreacted sulphuric acid against standard sodium hydroxide using phenolphthalein indicator. The amount of desorbed ammonia was calculated using the equation,

Ammonia desorbed in mmol /g = $(N_{NaOH} \times V \times 5)/W$

Where

V : The difference in titre value between the blank and the scrubbed acid with desorbed $NH_3$ at different temperatures

W : Weight of the sample in gram

N : Normality.

Finally by knowing the correct stoichiometry of the gas/solid reaction, it is possible to quantify the total number of active acid sites that is available on the catalyst surface. The adsorption temperatures indicate the strength of the active sites of the catalyst. The ammonia desorbed in temperature ranges 100-200, 201-400, 401-600°C is considered to represent the surface sites of physisorbed or weakly chemisorbed, medium and strong acid sites respectively.

### 2.5.4 Test reaction for acidity

Catalytic cumene cracking reaction was performed as test reaction for acidity.

#### 2.5.4.1 Vapour phase cumene cracking reaction.

Vapour phase cumene cracking reaction is a model reaction for identifying the Lewis/Brönsted acid ratio of a catalyst. The major reactions taking place during the cracking of cumene are dealkylation to give benzene and propene over BAS and dehydrogenation to give α-methyl styrene over LAS. A comparison of the amount of benzene and α-methyl styrene gives an idea about the BAS and LAS possessed by the catalyst.

The vapour phase cumene cracking reaction was carried out in a fixed bed, down flow vertical glass reactor inside a double zone furnace. 0.25g of the catalyst activated at 350°C for 1hr was immobilized inside the reactor using glass wool. The catalyst was loaded in the middle of the reactor and packed with glass beads. The temperature was measured by a thermocouple placed in the middle of the catalyst bed. Cumene was fed into the reactor at a flow rate of 4mL/h. The temperature of the reaction bed was kept at 400°C. The product analysis was achieved by gas chromatography (Chemito GC1000) by comparison with authentic samples. The analytical conditions are given in the Table 2.6.

## 2.6 Catalytic Activity Measurements

In recent years, organic reactions on solid support such as zeolites or mesoporous molecular sieves have attracted much attention because of advantages such as mild acidic properties, shape-selectivity, environment-friendly nature of catalysts, the easy work-up, the high purity of the products and the recycling of catalysts [24, 25, 26]. In 1995, the preparation of a new type of hexagonal mesoporous molecular sieves (HMS) by neutral assembly pathways was reported by Tanev and Pinnavaia [4]. This HMS was reported to possess physical and catalytic properties different from those of MCM-41 prepared by electrostatic assembly pathways [27]. Even though HMS can be prepared much more easily than MCM-41 or other zeolites and has certain advantages such as thicker framework walls, superior thermal stability and a smaller crystalline size, HMS itself has not yet been fully exploited as a new catalyst [28, 29].

Therefore we undertook a study aimed at discovering reactions that can be catalyzed by mesoporous ceria prepared using a neutral assembly pathway as proposed by Tanev and Pinnavaia et al. [4] modified by transition metals. The catalytic activities of the prepared catalysts are studied for the industrially important liquid phase reactions: oxidation of ethyl benzene, Friedel-Crafts benzylation, acetalization and deacetalization of cyclohexanone and Friedel-Crafts methylation of phenol using methanol in vapour phase.

### 2.6.1 Materials

The materials used for the catalytic activity measurements are given below, Table.2.5 Materials used for activity studies

| Materials | Suppliers |
|---|---|
| Ethyl benzene | CDH |
| Acetonitrile | Qualigens |
| Tert-butyl hydro peroxide (70%) | Aldrich |
| o-Xylene | Merck |
| Toluene | S.D. Fine |
| Anisole | Merck |
| Benzene | Qualigens |
| Cyclohexanone | Rankem |
| Benzyl chloride | Spectrochem |
| Methanol | Spectrochem |

### 2.6.2 Liquid phase Reactions

All the liquid phase reactions were carried out batch wise in a 50mL double necked glass round bottom flask fitted with a condenser. In a typical run, a known optimized weight of catalyst was dispersed in the substrate with/without solvent. The mixture was refluxed at an optimized temperature with thorough stirring in an oil bath. At the end of the reaction the products were filtered off and identified by GC-MS. Conversion and product selectivity were analysed using GC with FID detector. The analytical conditions are given in the Table 2.6.

#### 2.6.2.1 Oxidation of ethyl benzene

The catalytic selective oxidation is the main route to obtain monomers and intermediates for organic synthesis. The catalysts used are solids, most often mixed oxides with elements with different oxidation states which present redox properties. Selective oxidation reactions of relatively inert C–H bond of hydrocarbons using air or oxygen is one of the most desirable and challenging reactions since the obtained products are themselves important or act as valuable intermediates for industrial organic chemicals [30, 31]. Metal containing molecular sieves have attracted great interest and applications in heterogeneous catalysis due to their size, shape selective and recyclable properties [32, 26].

The experimental procedure adopted for the catalytic activity measurement is described below. The liquid phase oxidation of ethyl benzene [33] was carried out in a 50 ml R.B. flask fitted with a condenser. The temperature was maintained using an oil bath. In a typical run, 0.05 g of the catalyst was added to ethyl benzene in acetonitrile solvent. The reaction mixture was magnetically stirred. After attaining reaction temperature tert-butyl hydroperoxide was added drop wise. The aromatic compound being taken less, the yields were calculated based on the amount of the ethyl benzene. The selectivity for a product was expressed as the amount of the particular product divided by the total amount of the products multiplied by 100. The products were analyzed by gas chromatography (Chemito 1000 Gas Chromatograph equipped with a flame ionization detector and SE-30 Column-(2m length). Column temperature was adjusted between 60-200$^{o}$C at a heating rate of 10°C/ min. (injector temp. 250°C, detector temp. 250°C). The major product obtained was acetophenone. The reaction conditions were optimized for the molar ratio of the substrate, oxidizing agent, catalyst weight, temperature, duration of the run, volume of the solvent and type of solvent. The present work also attempted to study the metal leaching to understand the molecular aspects of the reaction and reusability of the system thereby confirming the true heterogeneity of the process.

### 2.6.2.2 Friedel-Crafts benzylation reaction

Friedel-Crafts alkylation enables the introduction of alkyl chains to aromatic rings. Alkyl chlorides, alcohols and alkenes are the commonly employed alkylating agents [34]. A wide range of homogeneous catalysts like $FeCl_3$, $AlCl_3$ , $BF_3$ and protonic acids like HF and $H_2SO_4$ have been found to be well suited for this reaction [35, 36]. The environmental concern and the drive towards a ‘clean technology’ urge the replacement of the liquid acids by eco-friendly solid acid catalysts. Benzylation of o-xylene with benzyl chloride, which is a typical example of Friedel-Crafts alkylation, is generally known to proceed over a homogeneous Lewis acid catalyst $AlCl_3$ [37]. Catalytic behaviour of rare earth oxides has been explored for many reactions and a wide variety of catalytic properties have been known [38]. These oxides can be used in Friedel-Crafts reactions too [39].

The liquid phase catalytic runs were carried out batch wise in a mechanically stirred, closed 50 mL glass reactor fitted with a reflux condenser, a thermometer and a septum for withdrawing the product samples. The temperature of the reaction vessel (353 K) was maintained using an oil bath. In a typical run, appropriate amounts of substrate and benzyl chloride (5:1 molar ratio) were charged in the reactor along with 0.05 g catalyst. Samples were withdrawn periodically and analyzed with a gas chromatograph (Chemito GC 1000) fitted with a flame ionization detector and a capillary column (SE-30). Some selected runs were analyzed by GS-MS for product identification. The composition of the reaction mixture was also determined by comparing their gas chromatograms with those of authentic samples. The reactions were done for the benzylation of toluene, o-xylene and anisole.

### 2.6.2.3 Acetalization and deacetalization reactions

Acetalization is one of the most widely used synthetic method for protecting aldehydes and ketones in the course of preparation of a variety of multifunctional complex organic molecules since dimethyl acetals display higher stability towards strong bases, Grignard reagent, lithium aluminium hydride, strong oxidants and esterification reagents than their parent carbonyl compounds [40]. The acetalization reaction is a process that is widely used in organic synthesis to protect the carbonyl group of aldehydes and ketones [41]. Besides, acetals became important reactants for the synthesis of enantiomerically pure compounds which were widely used as steroids, pharmaceuticals, and fragrances [42]. Previously, the catalysts used in the acetalization reactions were generally proton acids, Lewis acids, and a number of transition metal complexes including Rh, Pd and Pt [43]. Although good results were obtained, the separation of the products from the catalyst system after the reaction was still difficult to overcome and the noble metal catalysts used were quite expensive and usually unstable [44]. Therefore, to design and synthesize a catalytic system that may be stable, easily separable and reusable has long been pursued [45].

The nature of the pores of the solid acid catalysts determines acetalization efficiency of a particular catalyst. Dimethyl acetals of ketones: cyclohexanone, acetophenone, and benzophenone have been prepared by reacting ketones with methanol under mild reaction conditions.

Acetalization is a reversible reaction catalyzed by an acid environment and is usually performed in the liquid phase, which leads to the elimination of water as a byproduct thereby requiring azeotropic distillation to remove the water formed during the reaction, or else leading to the deactivation of the catalyst.

Acetalization reactions of cyclohexanone with methanol were carried out under batch reaction conditions. Cyclohexanone purchased from Aldrich Chemical Company, USA and commercial-grade methanol (available from S.D. Fine Chemicals, India) were used as received. One-pot acetalization reactions of carbonyl compounds were carried out in a 50 mL glass batch reactor equipped with a magnetic stirrer, thermometer, water condenser and temperature controller. In a typical run, cyclohexanone and methanol in a specific ratio was added to 0.05gm of catalyst in to the R.B. flask and magnetically stirred. The products were withdrawn at the end of the reaction and were analyzed with a Chemito GC1000 gas chromatograph equipped with a SE-30 capillary column under the analysis conditions specified in the Table 2.6. The products were further analyzed by GC-MS.

Hydrolysis of dimethyl acetal was done using 1:20 mixture of water and acetone as solvent. Here also the analysis was done by Chemito 1000 gas chromatograph with a capillary SE-30 column.

To have an optimum conversion of cyclohexanone, reaction conditions such as temperature of the reaction, cyclohexanone to methanol molar ratio, duration of reaction and the amount of the catalyst were studied to optimize the reaction parameters. To study heterogeneous nature of the reaction metal leaching studies also carried out.

### 2.6.3 Vapour phase reaction-methylation of phenol

Alkylation of aromatic substrates catalyzed by solid acids such as zeolites and metal oxides constitutes a class of reactions important both academically and industrially. Among alkylation reactions, methylation of phenol has attracted considerable attention due to industrial importance of methyl phenols as chemical intermediates in the manufacture of pharmaceuticals, agrochemicals, resins, various additives, polymerization inhibitors, antioxidants and various other chemicals [46]. Selective C-methylation of phenol to o-cresol and 2, 6-xylenol in high yields has been carried out with methanol over various solid acid catalysts. In particular, ortho-alkylated phenols such as o-cresol, 2, 6-xylenol and trialkyl substituted phenols are more important alkyl phenols. After suitable processing o-cresol is used in the synthesis of herbicides as well as in sealing material for integrated circuits, whereas 2, 6-xylenol is used in manufacture of disinfectant and in high impact resistant resins [47]. The alkylation of phenol with methanol being an acid–base catalyzed reaction, the product selectivity depends upon the acidity as well as basicity of the catalyst. Phenol alkylations using various acid and base catalysts have been reported. Phenol conversion as well as product selectivity is found to depend on the acid–base properties of the catalyst, temperature [48] and residence time [49]. Methylation was carried out in a vertical down flow glass reactor. All the reactions are carried out using 0.25gm of the catalyst. Prior to the reaction the catalysts were activated for 1hr at $300^{o}$C. The catalyst was packed in between quartz wool pack and sandwiched between silica beads. The reactor was placed inside a temperature controlled furnace with a thermocouple to measure the reaction temperature. In a typical reaction, a mixture of phenol and methanol in an optimized ratio was fed into the reactor at a specific flow rate using a syringe pump at a preset reaction temperature. The products were condensed and collected in an ice trap .and analyzed by a Chemito 8610 GC with an FID detector and an OV-17 column. The products are confirmed by GC-MS analysis. The conversion was expressed in terms of phenol reacted and the product selectivity was expressed as the ratio of amount of particular product to total amount of products multiplied by 100.

Gas chromatographic analysis conditions are given in Table2.6.

**Table 2.6 GC analysis conditions of various reactions**

| Reaction | GC | Temperature($^{o}$C) | | Programme of analysis |
|---|---|---|---|---|
| | | Injector | Detector | |
| Cumene cracking | GC1000, SE-30 Capillary column, FID detector | 230 | 230 | 70$^{o}$C-2min-10$^{o}$C/min-250$^{o}$C-2min |
| Ethylbenzene oxidation | GC1000, SE-30 Capillary column, FID detector | 250 | 250 | 60$^{o}$C-2min-10$^{o}$C/min-125$^{o}$C-2min-2$^{o}$C/min-140 $^{o}$C-1min-150$^{o}$C-200$^{o}$C -1min |
| Benzylation | GC1000, SE-30 Capillary column, FID detector | 250 | 250 | 60$^{o}$C-4min-10$^{o}$C/min-110-4min-10$^{o}$C/min-170-1min |
| Acetalization-deacetalization | GC1000, SE-30 Capillary column, FID detector | 100 | 100 | 75$^{o}$C-1min-5$^{o}$C/min-125$^{o}$C-1min-10$^{o}$C/min-200$^{o}$C-1min |
| Phenol methylation | Chemito8610 GC OV-17Column, FID detector | 250 | 250 | 60$^{o}$C-1min20$^{o}$C/min-140-1min-10$^{o}$C/min-170-2min |

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Chapter 3

# PHYSICO – CHEMICAL CHARACTERIZATION

Contents

Transition metals incorporated mesoporous ceria catalysts were prepared by the soft templated method using the neutral surfactant hexadecyl amine (HDA). A detailed investigation of physico-chemical characterization of the catalytic systems was performed by techniques such as wide and low angle XRD, BET surface area, pore volume and pore distribution by sorption studies of nitrogen gas, EDX, ICP-AES, SEM, TEM, TG/DTA, UV-Vis DRS, FT-IR and temperature programmed reduction-hydrogen (TPR-$H_2$). Surface acidic properties of the systems were obtained from TPD of ammonia, and the results were tested by the test reaction of vapour phase cumene cracking.

## 3.1 Introduction

Porous materials have attracted the attention of chemists and material scientists due to commercial interest in their application in chemical separations and heterogeneous catalysis as well as scientific interest in the challenges posed by their synthesis, processing and characterization in heterogeneous catalysis. Catalysis and catalytic surfaces are needed to be characterized with reference to their physical properties and thereby investigating their actual performance as catalysts. The most important physical properties are those relating to the surface because catalytic performance is determined by the surface parameters. A complete knowledge on the exact location, structure and electronic ground state of the active site in the catalysts is essential to establish a basic understanding about the structure- activity correlations and to improve the efficiency of the catalyst for higher selectivity and stability [1]. Again variation in the conditions of preparation and pre-treatment very much alters the surface properties and the catalytic behaviour of the catalysts.

In recent years a considerable amount of interest has been shown in materials with grain size in nano scale. Preparation of nano size mesoporous cerium oxide was done by surfactant method and transition metals incorporated mesoporous cerium oxide catalysts were prepared by wet impregnation method. After catalyst preparation, the removal of surfactant from calcined sample was confirmed by FT-IR. FT-IR also give knowledge about surface functional groups. The surface morphology was obtained from SEM and TEM. Surface areas of the systems were measured by BET surface area measurement. Pore volume, pore size distribution and mesoscopic nature were investigated by sorption studies of nitrogen gas at liquid nitrogen temperature. Phase formation and mesoscopic nature of ceria crystals and modified samples were tested by wide and low angle XRD. Thermal stability of the systems were analysed by thermo gravimetric analysis. XRD study was performed to understand chemical structure of the prepared systems. UV-Vis-Diffuse reflectance spectrum gives idea about the metal ion co-ordination. Temperature programmed desorption of ammonia was carried out to understand the amount, distribution and strength of the acid sites of the prepared systems. Acidity thus obtained was tested by vapour phase cumene cracking reaction.

## 3.2 Physico - Chemical Characterization

The catalyst samples prepared were characterized by adopting various physical methods such as BET Surface area, pore diameter, pore distribution and pore volume measurements by BJH sorption studies of nitrogen, low and wide angle XRD, FT-IR, SEM, EDX, TEM, TG/DTA, ICP–AES, TPR in $H_2$ and UV-Vis DRS. The observations and explanations are given below.

### 3.2.1 Energy Dispersive X-ray Analysis (EDAX)

The knowledge of solid chemical composition must be the starting point of every investigation. A lot of literature results cannot be evaluated because of lack of composition data. It is noteworthy to remember that: (i) catalyst composition at the end of preparation can be different from that calculated from the weight of reagents; this is frequently observed in co-precipitation, hydrothermal synthesis, calcination of solids containing volatile compounds; (ii) composition reproducibility is a very common problem in catalyst preparation, so frequent experimental checks are necessary; (iii) impurities can always be present; their origin is extremely variable as they can come from polluted reagents, previous preparation residues, release of substances from vessels, etc. (iv) exposure to the reaction atmosphere changes almost every time the catalyst composition because of loss of volatile compounds, deposition of organic substances, reactions between solid and environment.

Energy dispersive X-ray spectroscopy (EDX) measurements and qualitative elemental analysis made on the calcined samples show the expected primary metal element signals which confirm that the inorganic walls consist of predominantly metal-oxygen networks. The elemental composition of the manganese doped and chromium doped samples were determined using EDX analysis and the results for a few samples are given in Fig.3.1.

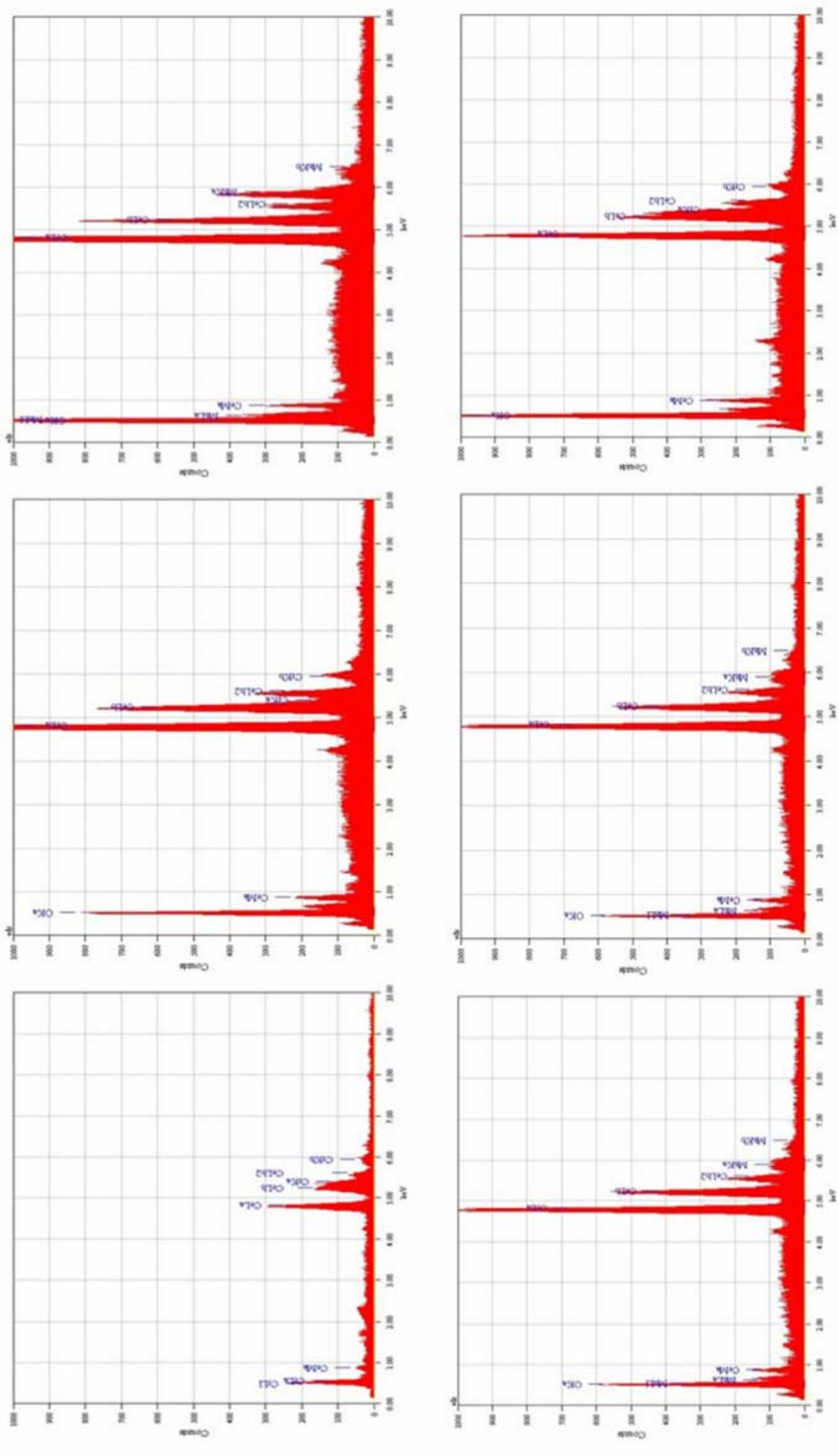


Fig. 3.1 EDX data for Manganese and Chromium modified catalyst systems

### 3.2.2 Elemental Analysis – ICP-AES Analysis

**Table 3.1 Composition (Atom %) of prepared samples**

| Catalysts | Composition (Atom %) | | | |
|---|---|---|---|---|
| | Ce | | Metal | |
| | Theoretical | experimental | Theoretical | experimental |
| CeCr (2%) | 93.7 | 94.7 | 6.3 | 5.3 |
| CeCr (4%) | 87.8 | 86.6 | 12.2 | 13.4 |
| CeCr (10%) | 73.1 | 76.3 | 26.9 | 23.7 |
| CeFe (2%) | 94.1 | 93.6 | 5.9 | 6.4 |
| CeFe (4%) | 88.6 | 87.9 | 11.4 | 12.1 |
| CeFe (10%) | 74.5 | 74 | 25.5 | 26 |
| CeMn (2%) | 94 | 93.2 | 6 | 6.8 |
| CeMn (4%) | 88.4 | 87.1 | 11.6 | 12.9 |
| CeMn (10%) | 74.4 | 73.4 | 25.6 | 26.6 |
| CeCo (2%) | 94.4 | 94 | 5.6 | 6 |
| CeCo (4%) | 89.1 | 89.2 | 10.9 | 10.8 |
| CeCo (10%) | 75.5 | 75.3 | 24.5 | 24.7 |
| CeCu (2%) | 94.7 | 94.6 | 5.3 | 5.4 |
| CeCu (4%) | 89.9 | 89.2 | 10.1 | 10.8 |
| CeCu (10%) | 76.9 | 76 | 23.9 | 24 |
| CeNi(2%) | 94.3 | 94.5 | 5.7 | 5.5 |
| CeNi (4%) | 89.1 | 89.1 | 10.9 | 10.9 |
| CeNi (10%) | 75.5 | 75.5 | 24.5 | 24.5 |

Various transition metal modified mesoporous ceria with various percentages of metals were synthesized and elemental analysis was done using ICP-AES. The data shown in the Table 3.1 gives the amount of $CeO_2$ and the different metals present in each samples. It is observed that the experimental atom percentage is close to the theoretical values. It can be concluded that the method of preparation adopted is effective for the preparation of metal modified ceria catalysts with required composition.

### 3.2.3 Surface area and pore volume measurements

The BET surface area ($S_{BET}$) and pore volumes measured for mesoporous ceria calcined at different temperatures are given in the Table 3.2.

**Table 3.2 Surface area and pore volumes of mesoporous ceria**

| catalyst | $S_{BET}$($m^2$ $g^{-1}$) | Pore volume ($cm^3$ g-1) | Pore diameter(nm) |
|---|---|---|---|
| Ce-250 | 61 | 0.26 | 4.8 |
| Ce-350 | 164 | 0.29 | 4.6 |
| Ce-400 | 134 | 0.17 | 4.8 |
| Ce-500 | 108 | 0.15 | 5.2 |
| Ce-550 | 105 | 0.19 | 4.7 |
| Ce-600 | 79 | 0.18 | 5.2 |

* Pore volume measured at $p/p_0$ of 0.997

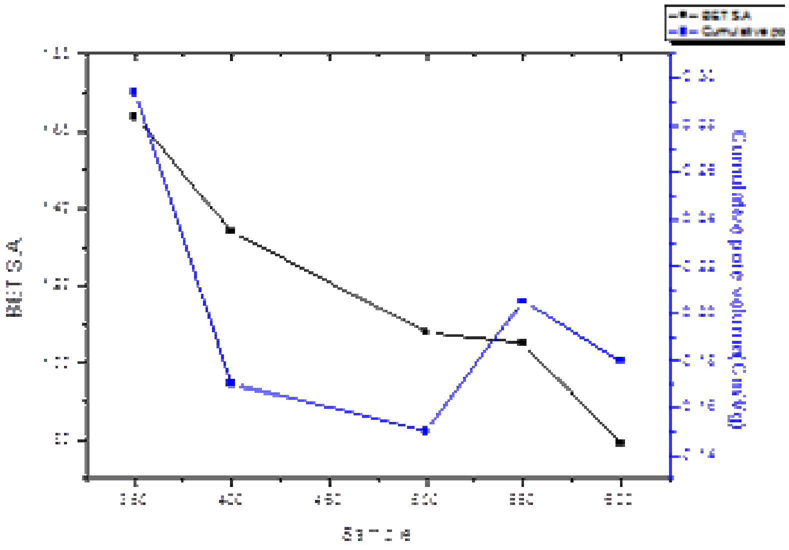


**Fig.3.2 Variation of surface area and pore volume with calcination temperature**

From the Table 3.2 it can be observed that as the calcination temperature increases the surface area decreases. There is change in the pore volume with calcination temperature. The material showed a high (BET) surface area of 164 $m^2g^{-1}$. In the literature, most of the publications report ceria with specific surface areas below 100 $m^2g^{-1}$ and only in a few cases was values around 200 $m^2g^{-1}$ were obtained [2].

**Table 3.3 Surface area and pore volume of metal incorporated mesoporous ceria systems**

| **Catalyst** | **$S_{BET}$($m^2$ $g^{-1}$)** | **Pore volume ($cm^3$ g-$^1$)** | **Pore diameter(nm)** |
|---|---|---|---|
| Ce-350 | 164 | 0.29 | 4.6 |
| CeCr (2%) | 123 | 0.2 | 5.4 |
| CeCr (4%) | 120 | 0.18 | 5.6 |
| CeCr (10%) | 96 | 0.14 | 3.8 |
| CeFe (2%) | 100 | 0.18 | 4.5 |
| CeFe (4%) | 99 | 0.17 | 5.2 |
| CeFe (10%) | 52.6 | 0.12 | 4.6 |
| CeCo (2%) | 135 | 0.22 | 4.59 |
| CeCo (4%) | 124 | 0.19 | 4.99 |
| CeCo (10%) | 108 | 0.17 | 4.69 |
| CeMn (2%) | 121 | 0.23 | 4.71 |
| CeMn(4%) | 119 | 0.22 | 4.92 |
| CeMn(10%) | 109 | 0.18 | 4.5 |
| CeCu (2%) | 82 | 0.18 | 4.4 |
| CeCu (4%) | 80 | 0.17 | 5.2 |
| CeCu (10%) | 72 | 0.15 | 4.3 |
| CeNi (2%) | 96 | 0.18 | 4.6 |
| CeNi (4%) | 89 | 0.15 | 4.4 |
| CeNi (10%) | 85 | 0.14 | 3.8 |

* Pore volume measured at $p/p_0$ of 0.997

The surface areas decrease with metal loading and increase in basicity (atomic weight) of the metal in most of the cases. It is partly due to an increase in the effective weight of the catalyst due to the large amount of deposited metal oxides, these values are also lower than that of pure $CeO_2$. The decrease in surface area is attributed to the 'dissolution' of the surface by the metals during impregnation, and pore filling by the metal oxides.

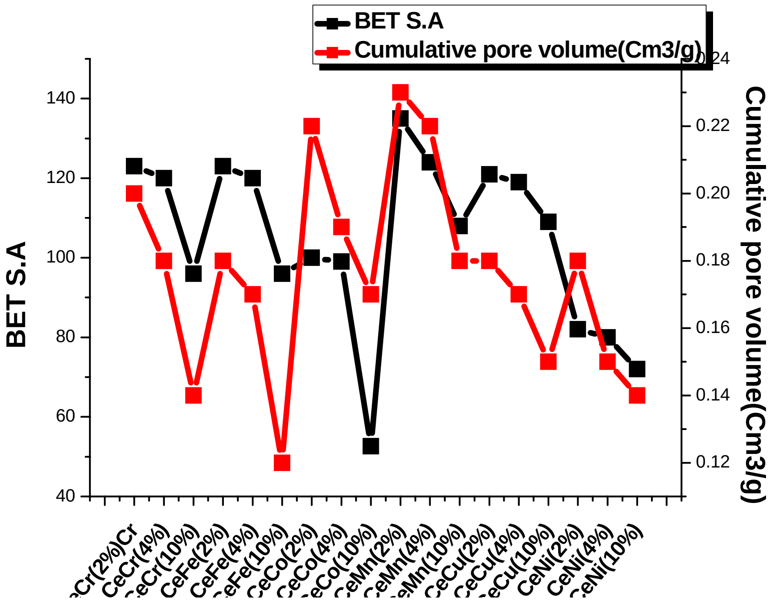


**Fig. 3.3 Variation of surface area and pore volume with metal doping**

## a) Iron incorporated systems

From the Table 3.3 it can be observed that the surface area of the support decreases with the introduction of iron. Surface area decreases on incorporation of 2, 4 & 10 weight% iron into pure ceria. By the incorporation of 10% iron, the surface area is decreased from 100 to 52.6 $m^2/g$. Pore volume also shows a similar trend when iron is added to pure ceria. The result indicates a negative effect in the surface area on incorporation of iron. It can be inferred that when iron is incorporated into mesoporous ceria by wet impregnation method, the metal is homogeneously distributed in the system occupying the surface vacant site.

### b) Chromium incorporated ceria systems

Table 3.3 shows the effect of chromium doping into mesoporous ceria. The increasing the percentages of chromium, the surface area and pore volume decreases in a similar manner. This also shows the homogeneous distribution of chromium metal into the surface vacant site attained by wet impregnation method.

### c) Cobalt incorporated systems

The effect of incorporation of cobalt metal into mesoporous ceria is shown in the Table 3.3. Similar to iron and chromium, cobalt incorporation also decreases the surface area and pore volume with increase in metal %. With increase in the composition of Co from 2 to 10%, the surface area changes from 135 to 108 ($m^2g^{-1}$).

### d) Copper incorporated systems

From Table 3.3 the effect of incorporation of copper into mesoporous ceria can be observed. Though the pore volume and surface area decreases with increase in the percentage of copper, the pore diameter increases initially with metal incorporation, then it decreases when concentration exceeds a certain limit.

### c) Manganese incorporated systems

For Mn incorporation the surface area and pore diameter decrease steadily, but the change in the pore volume is not showing the same trend.

### e) Nickel incorporated systems

In the case of modification with nickel surface area, pore volume and pore diameter decrease with metal concentration.

### 3.2.3.1 Nitrogen adsorption isotherm

Fig. 3.4 shows adsorption isotherms of ceria calcined at different temperatures which resemble Type IV of IUPAC classification [3] with a hysteresis loop which is characteristic of mesoporous solids. This hysteresis loop is due to the capillary condensation, in the mesopores. Adsorption at lower relative pressures ($p/p_0$) is due to the formation of monolayer of nitrogen molecules on the walls of mesoporous material. At low values of $P/P_0$ the isotherm is similar to Type II, but then adsorption increases rapidly at $P/P_0$ above 0.5, where pore condensation takes place. This sharp inflection is due to the capillary condensation within the mesopores. From the sharpness of the step corresponding to the filling of the mesopores, once can expect a uniform pore size distribution. The relative pressure corresponding to the inflection point is related to the diameter of the mesopores. In all these cases, the nature of the isotherm at lower relative pressures is same. Though the point of inflection corresponding to the capillary condensation within the mesopores differs, still it is not very significant. In general, for mesoporous materials the presence of hysteresis loop was taken as the confirmation for the presence of mesopores in the material. The $N_2$ adsorption-desorption isotherms provide information about the mesoscopic nature of the samples.

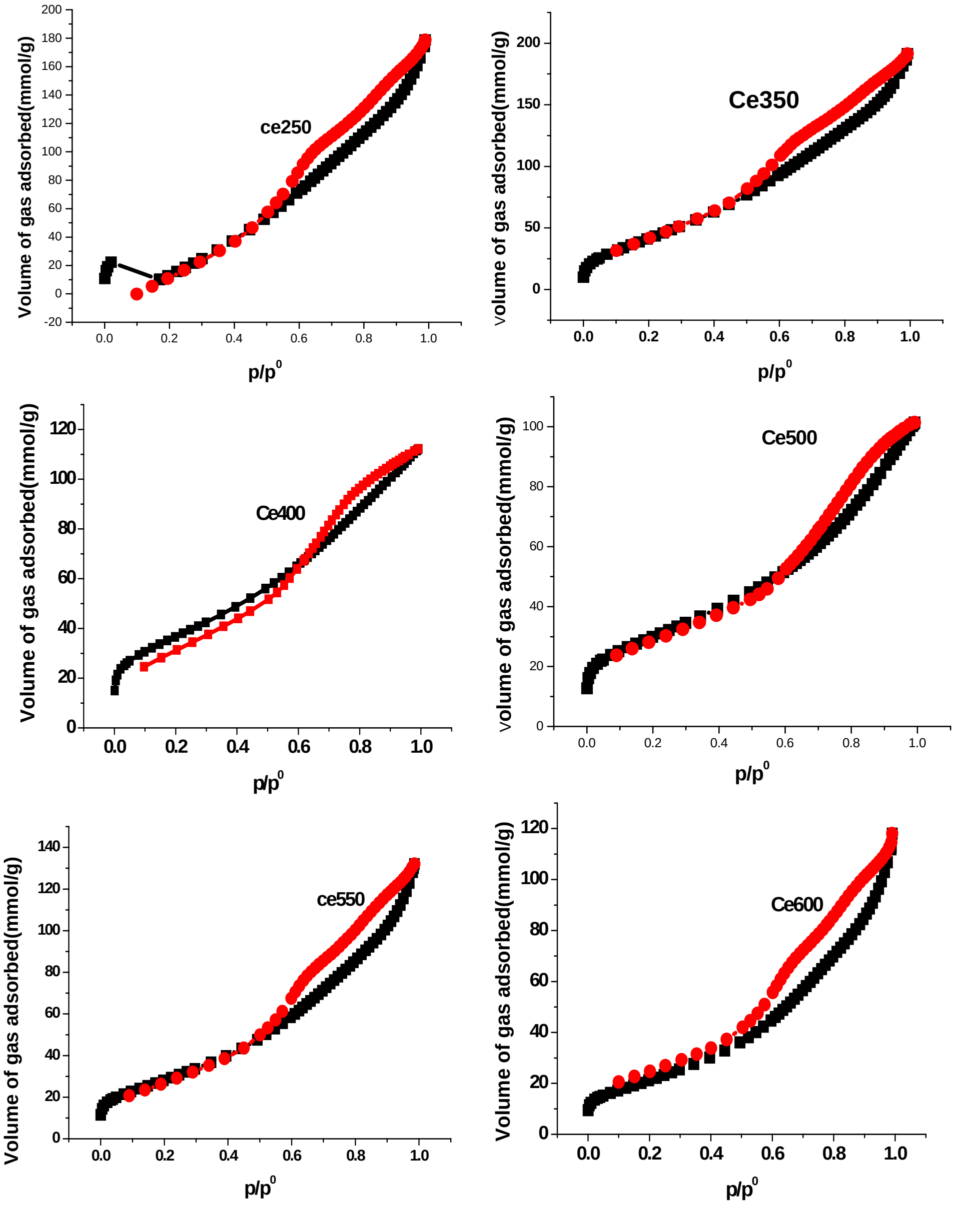
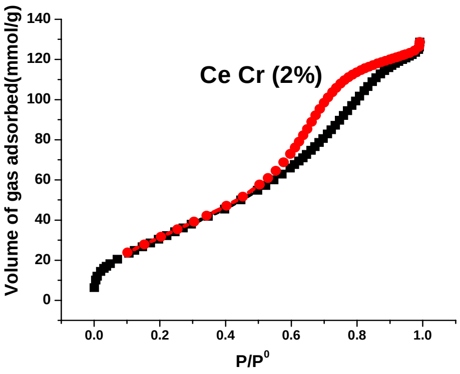
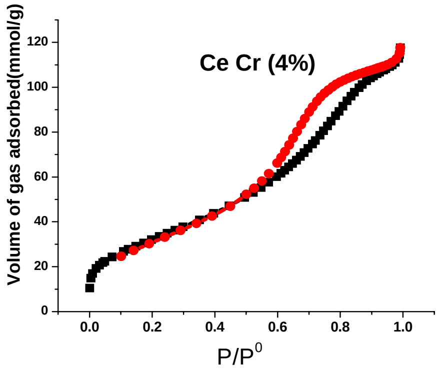
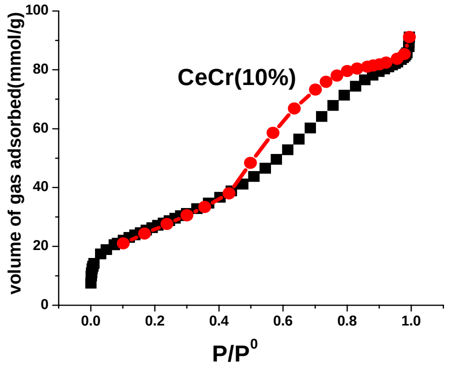
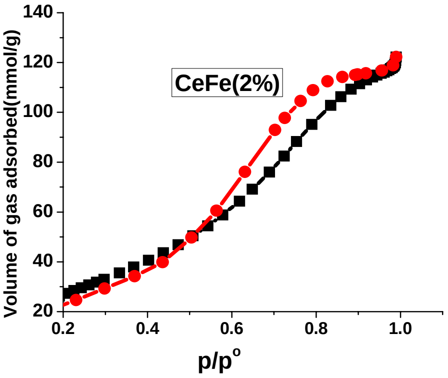


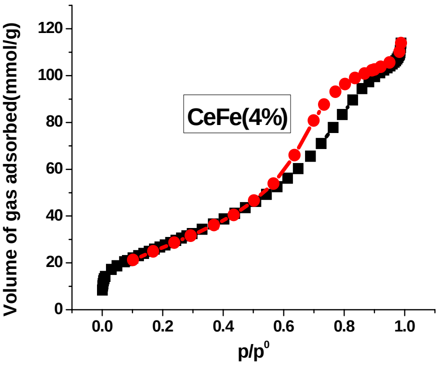
Fig. 3.4. Adsorption isotherms of ceria calcined at different temperatures

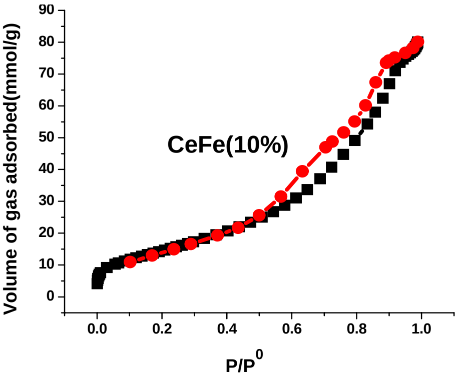

Ce Cr (2%)
Volume of gas adsorbed(mmol/g)
0
20
40
60
80
100
120
140
0.0
0.2
0.4
0.6
0.8
1.0
P/P⁰

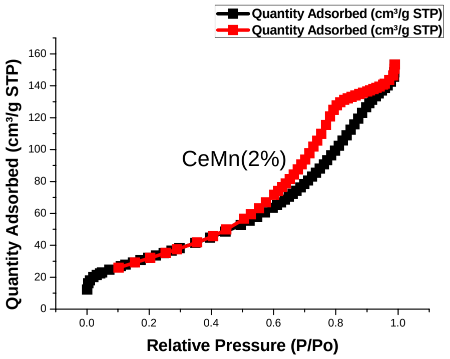

Ce Cr (4%)
Volume of gas adsorbed(mmol/g)
0
20
40
60
80
100
120
0.0
0.2
0.4
0.6
0.8
1.0
P/P⁰

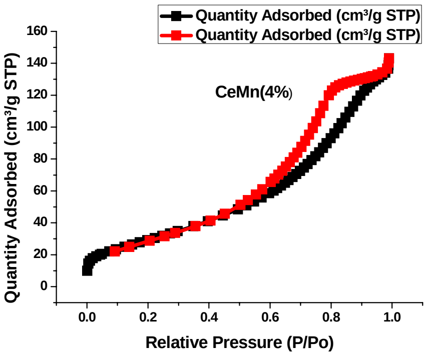

CeCr(10%)
volume of gas adsorbed(mmol/g)
0
20
40
60
80
100
0.0
0.2
0.4
0.6
0.8
1.0
P/P⁰


CeFe(2%)
Volume of gas adsorbed(mmol/g)
20
40
60
80
100
120
140
0.2
0.4
0.6
0.8
1.0
p/p°


CeFe(4%)
Volume of gas adsorbed(mmol/g)
0
20
40
60
80
100
120
0.0
0.2
0.4
0.6
0.8
1.0
p/p⁰


CeFe(10%)
Volume of gas adsorbed(mmol/g)
0
10
20
30
40
50
60
70
80
90
0.0
0.2
0.4
0.6
0.8
1.0
P/P⁰


Quantity Adsorbed (cm³/g STP)
Quantity Adsorbed (cm³/g STP)
CeMn(2%)
Quantity Adsorbed (cm³/g STP)
0
20
40
60
80
100
120
140
160
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/Po)


Quantity Adsorbed (cm³/g STP)
Quantity Adsorbed (cm³/g STP)
CeMn(4%)
Quantity Adsorbed (cm³/g STP)
0
20
40
60
80
100
120
140
160
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/Po)

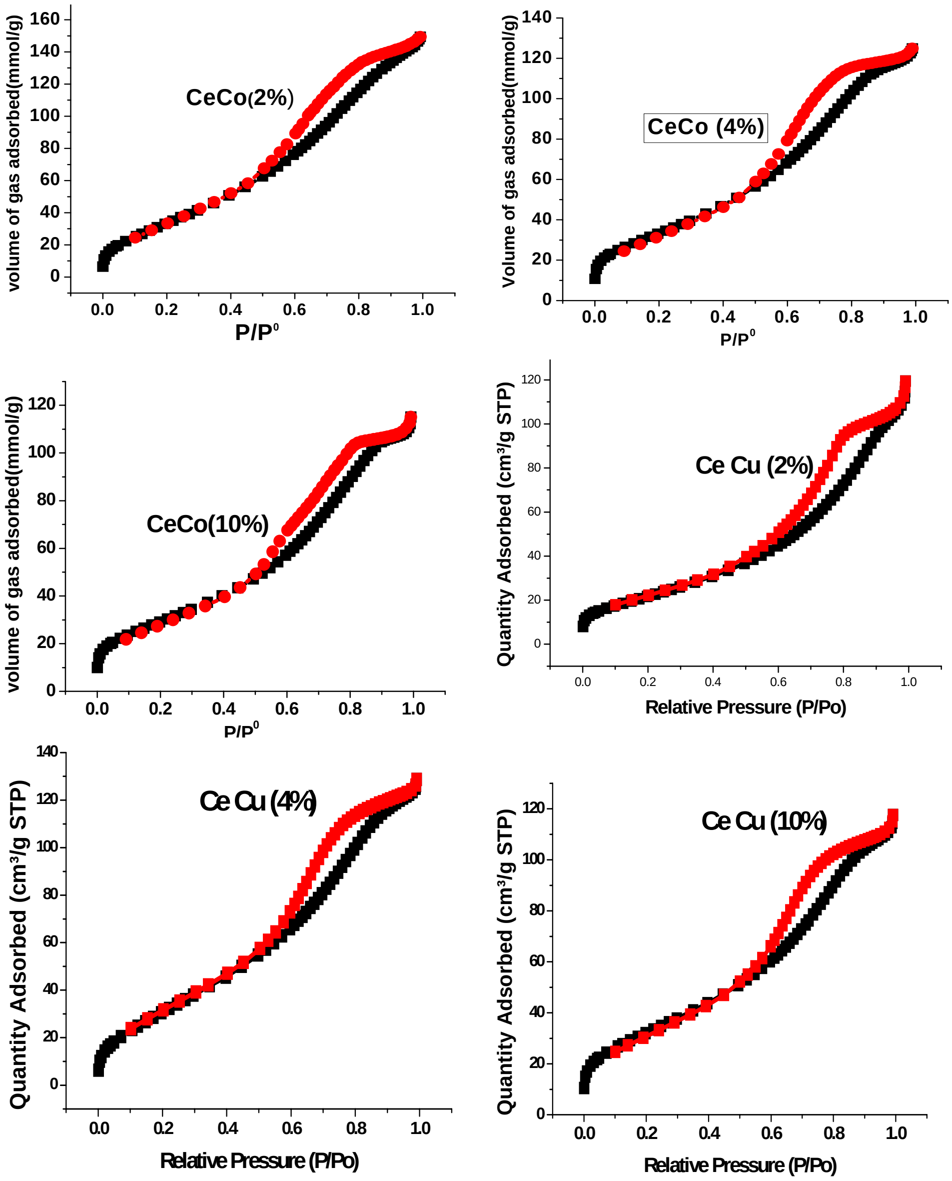


Fig. 3.5. Adsorption isotherms of ceria modified with different metals

### 3.2.3.2 Pore size distribution

Pore size distribution of calcined mesoporous ceria at different calcination temperatures are shown in Fig.3.6. The values of pore diameter of mesoporous ceria calcined at different temperatures are given in Table3.2. The data show that the pore size is increased when the calcination temperature is increased from 350 to 500°C, and then it is decreased. This may be due to the rupture of the pore when the temperature is increased. The narrow pore size distribution shows uniformity of the pores.

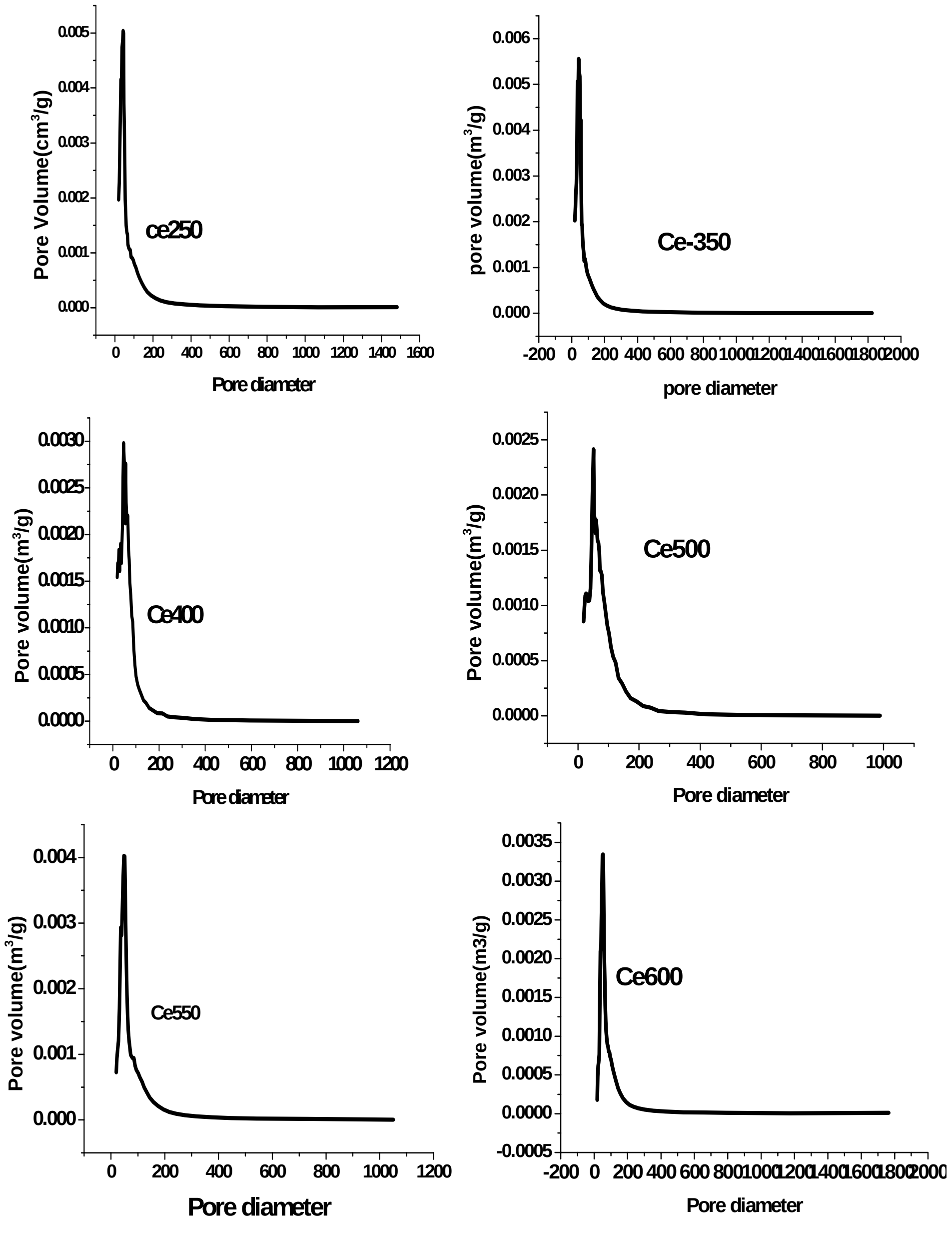


**Fig. 3.6. Pore size distribution of mesoporous ceria calcined at different temperatures**

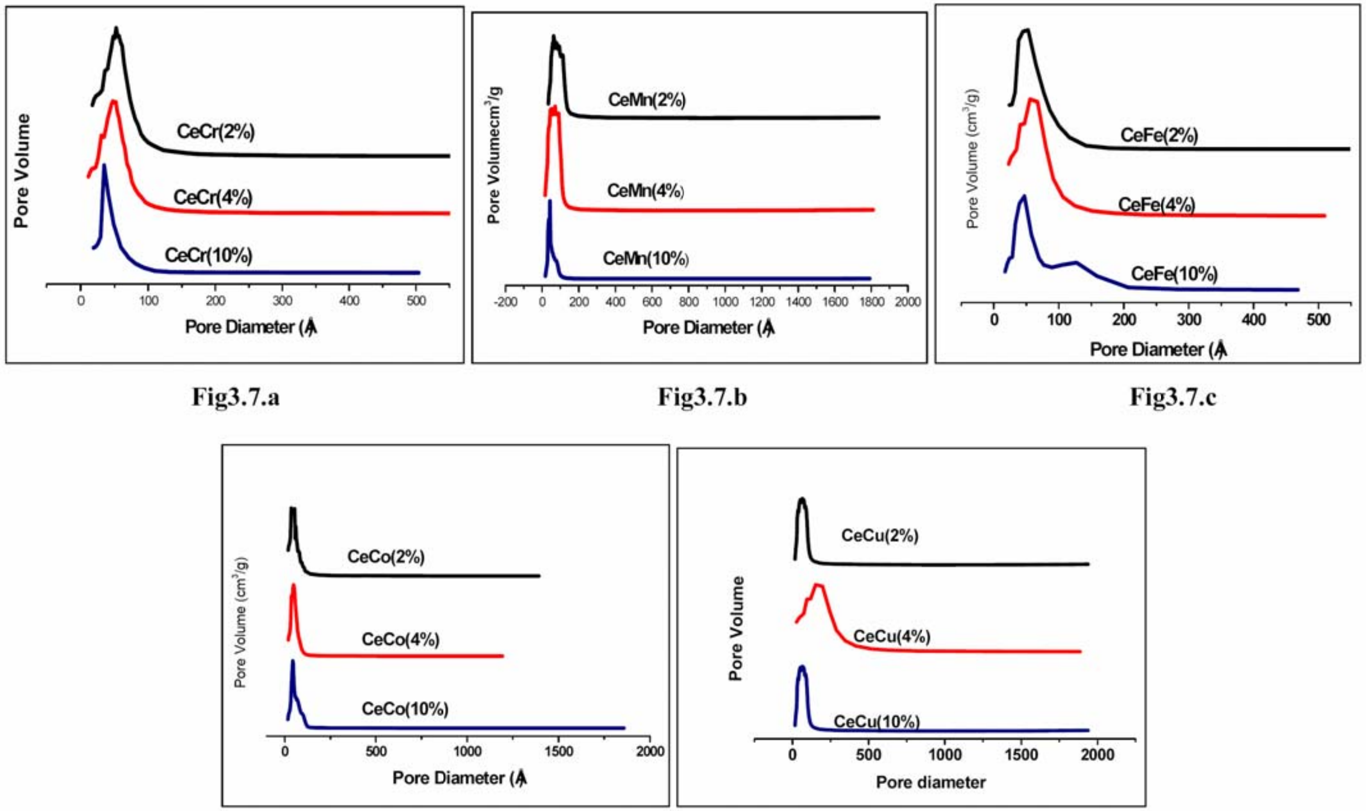


Fig3.7.a

Fig3.7.b

Fig3.7.c

Fig3.7.d

Fig3.7.e

**Fig3.7** **Pore size distribution of mesoporous ceria modified with transition metals 3.7a. - 2, 4&10% Cr; 3.7b. 2, 4&10% Mn; 3.57c. 2, 4&10% Fe 3.7.d. 2, 4&10%Co; 3.7.e - 2, 4&10%Cu**

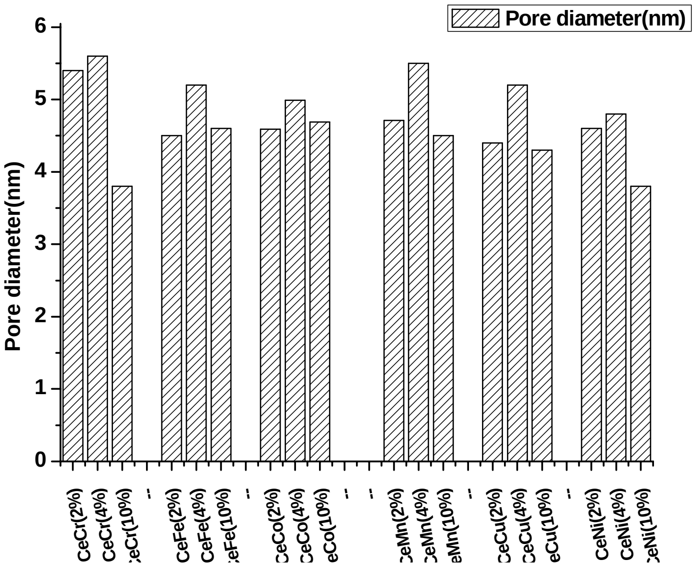


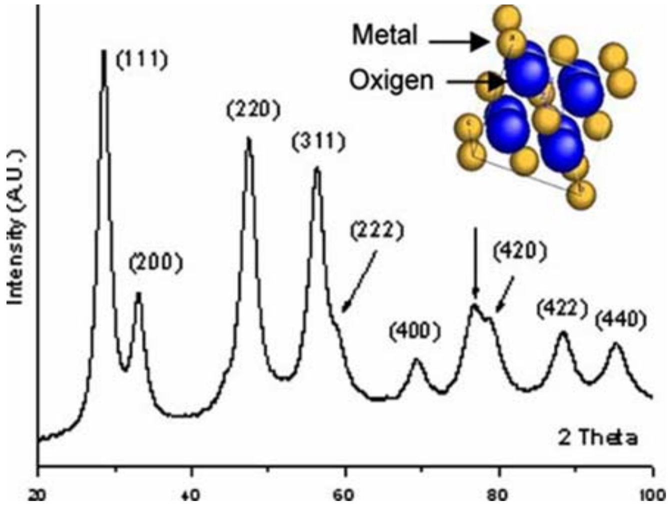
**Fig. 3.8 Correlation of metal loading with pore diameter**

In Fig.3.8 the pore diameter is correlated with the % metal loading. The pore diameter is increased with metal loading in the sample but only up to a certain percentage. When metal % exceeds a limit the pore diameter decreases.

### 3.2.4 Wide Angle XRD Analysis.

### 3.2.4.1 Mesoporous ceria

Fig.3.9.1 illustrates the XRD spectrum indexed from JCPDS database (75-0162). The typical peaks corresponding to the planes (111), (200), (220) and (311) are observed at $2\theta = 28.5, 33.0, 47.5, 56.5(^{o})$ respectively (space group Fm3m) [4]. Fluorite structure is shown as an inset in the figure. X-ray diffraction within the range of 20-70($^{o}$) of calcined ceria at 350$^{o}$C is also shown. XRD spectra of the prepared ceria consists of all the peaks corresponding to the cubic fluorite structure as is given in the JCPDS file, confirming the cubic crystal structure for ceria prepared by this method.



**XRD spectrum indexed from JCPDS database 75-0162). Fluorite structure is shown as an inset shown as an inset**

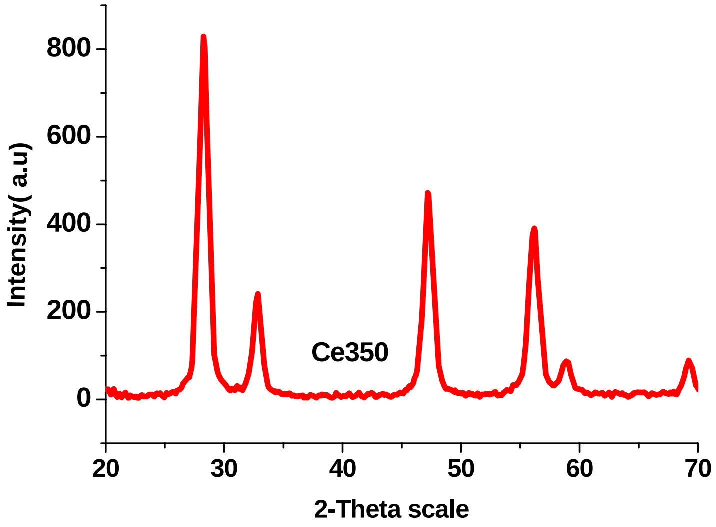


**Fig. 3.9.1 XRD spectrum of Ce-350**

Fig 3.9.2 represents X-ray diffractograms of ceria calcined at 350°C and pre calcined sample. During the pre-calcination stage itself the phase is formed.

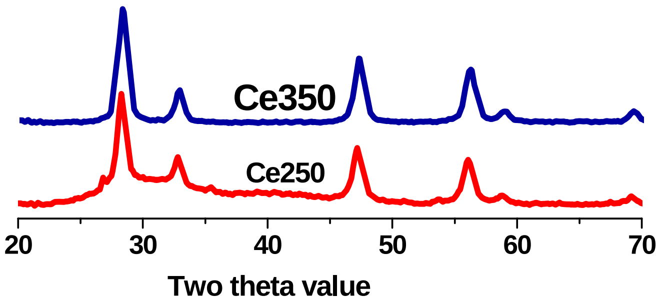


**Fig. 3.9.2 X-ray diffractograms of pure $CeO_2$: Sample pre calcined at 250°C and after calcination at 350°C.**

The unit cell parameter is calculated from the d-spacing value using the formula

$$a_0 = d_{111} (h^2 + k^2 + l^2)^{1/2}.$$

**Table 3.4 XRD data of ceria calcined at different temperatures**

| Sample | Average crystallite size (nm) | Lattice parameter(nm) | d-spacing(nm) |
|---|---|---|---|
| Ce250 | 5.6 | 5.4 | 3.127 |
| Ce350 | 12.8 | 5.45 | 3.15 |
| Ce550 | 10.6 | 5.46 | 3.15 |

Table 3.4 shows the values of crystallize size, and lattice parameters. The increase in the lattice parameter and d-spacing are attributed to the reduction of $Ce^{4+}$ ions (ionic radius 0.97A°) to $Ce^{3+}$ (ionic radius 1.17A°). Average crystallite size is greater for ceria calcined at 350°C.

### 3.2.4.2 Metal doped samples

The XRD data of the prepared systems agree well with the standard values given in the JCPDS data cards (4 -593) confirming fluorite structure. The mesoporous ceria could effectively induce a good spreading of active phase at its surface, inhibiting the crystallite formation when the metal loading is lower except for Mn. Though in wide angle XRD pattern characteristic peaks of metal except for Mn are found at higher loading, the intensity of peaks are very low. The absence of peaks of metal oxides indicates that the guest $MO_x$ has been highly dispersed in the support frame work of mesoporous ceria. The typical peaks corresponding to the planes (111), (200), (220) and (311) are observed at $2\theta=28.5, 33.0, 47.5, 56.5(^{o})$ respectively (space group Fm3m) [4]. After metal incorporation, the presence of all the peaks indicating that the addition of the metal did not destroy the characteristic crystal fluorite structure of ceria. The average crystallite size was calculated using Scherrer equation. For the metal doped samples also the unit cell parameter is calculated from the d-spacing value using the formula

$$a_0 = d_{111} (h^2 + k^2 + l^2)^{1/2}.$$

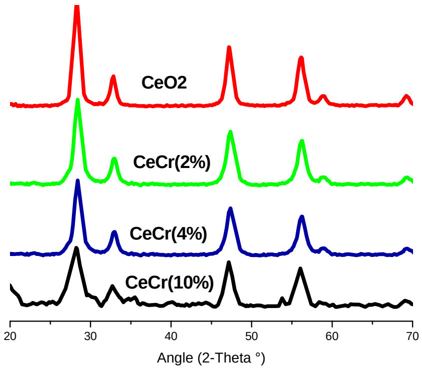


Fig. 3.9.3a

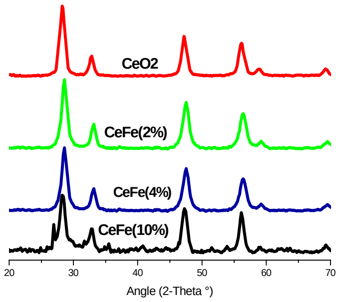


Fig. 3.9.3b

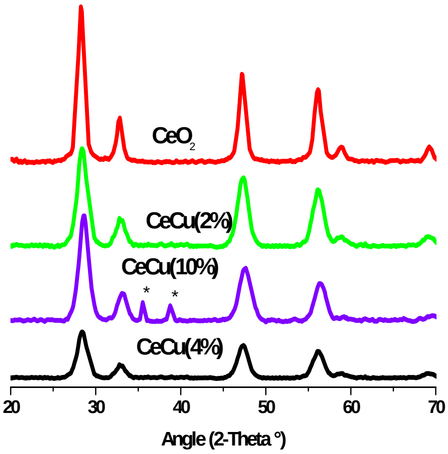


Fig. 3.9.3c

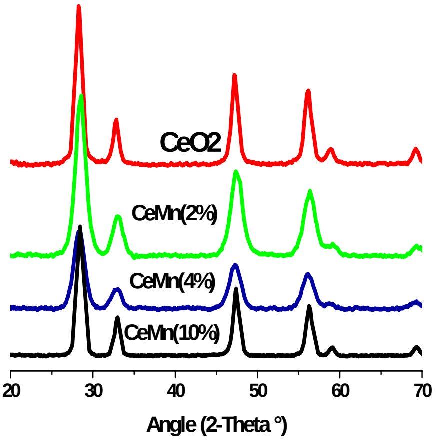


Fig. 3.9.3d

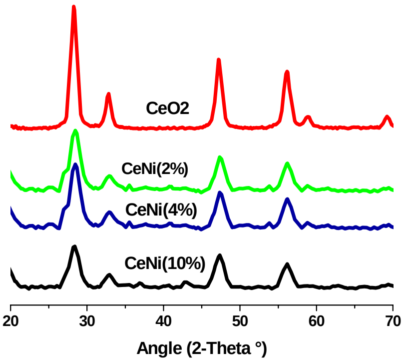


Fig. 3.9.3e

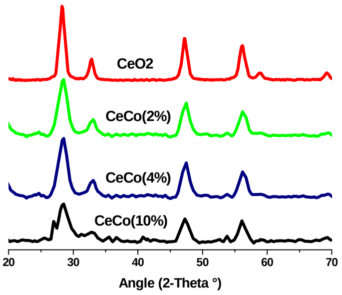


Fig. 3.9.3f

Fig. 3.9.3 XRD patterns of ceria samples of modified with metals

a) **Cr incorporated systems.** The XRD patterns of the modified systems show the peaks corresponding to ceria only (fcc with a = 0.54nm). Cubic fluorite structure of ceria remained intact even after the modification with chromium. The characteristic peak of crystalline chromium oxide is absent in all these cases. It is reported that in the case of metal oxides there is a critical value called dispersion capacity, below which the oxide might become highly dispersed on the support without the formation of its crystalline phase [5]. Since no characteristic peaks corresponding to chromium species is present, it can be concluded that the chromium loading is below the dispersion capacity. According to Viswanath et al., the absence of chromia phase in the diffraction pattern for the supported catalysts may be attributed to the fact that chromium species are randomly dispersed and crystalline size may be smaller than the detection limit [6]. But with higher loading, peaks characteristics of $Cr_2O_3$ can be found along with the fluorite peaks of $CeO_2$. Peaks corresponding to $2\theta = 24$, 33 & 36 are characteristics of $Cr_2O_3$ species [7]. But in the present case up to 10% loading no chromia crystalline phase is not formed.

b) **Iron incorporated ceria systems.** The powder X-ray diffractograms of the pure and iron doped systems calcined at 350°C is given in Fig. 3.9.3.b. The XRD pattern of pure ceria gives sharp peaks characteristics of the fluorite structure (fcc with a = 0.5435 nm) of ceria, which remained intact after modification with 2, 4 & 10% iron oxide. The characteristic peak of crystalline iron oxide is absent in lower loading. This points to the fact that the iron species are highly dispersed or exist as microcrystalline material below the XRD detection limit as discussed in the case of chromium. But when the loading is higher than detection limit the peaks corresponding to $Fe_2O_3$ (2θ = 33, 35 & 54) may be found [8].

c) **Copper incorporated ceria systems.** Table 3.9.3 represents the XRD data indexing results for copper-doped systems. Here the crystallite size increased with modification. The crystal structure is fcc in all catalytic systems. Fig.3.9.3.c represents the X-ray diffractograms of different % of Cu doped mesoporous ceria. In the samples modified with 2 & 4% Copper, no peaks corresponding to crystalline CuO appear. In 10% Cu containing catalyst two peaks corresponding to crystalline CuO were observed (2θ = 35.4, 38.8$^{o}$) [9]. So if Cu concentration is higher than 10%, additional CuO crystals will be formed.

d) **Manganese incorporated ceria systems.** Fig. 3.9.3.d. represents XRD spectra of manganese modified systems. It is reported that the replacement of $Ce^{4+}$ crystallites by $Mn^{3+}$ in the fluorite structure is possible by their structural similarity [10]. Manganese oxide crystallisation takes place only when Mn content is greater than 50%. Hence $MnO_x$ are efficiently dispersed on the surface of the catalyst. The addition of manganese ions to ceria or vice versa could help to control crystallite growth and to maintain the pore system of the materials. Similar phenomena were observed in the cases of Mn-Ce catalysts prepared by co-precipitation [11, 12] and combustion method [13] originated from the solid solution formation between $Mn_2O_3$ and $CeO_2$, because of their structural similarities. It was well recognized that the dispersion of the active phase plays an important role in the oxidation reaction.

e) **Nickel incorporated ceria systems**. For Nickel modified catalysts, no nickel oxide peaks are seen at Ni loading as shown in Fig. 3.9.3.e. Higher Ni loaded catalyst may show NiO peak at 2θ = 37, 43.7 & $62.9^o$ [14].

f) Cobalt incorporated ceria systems. No formation of crystalline Co oxide was observed in the case of Co (2, 4 &10%) modified systems as shown in Fig. 3.9.3.f. Co loaded catalyst at higher loading may show $Co_3O_4$ peak at 2θ = 30, 35.5 [8].

**Table 3.5 XRD data of ceria modified with transition metals**

| Sample | Average crystallite size (nm) | Lattice parameter ($A^0$) | d-spacing (nm) | Scattering Domain size(nm) |
|---|---|---|---|---|
| Ce350 | 12.8 | 5.45 | 3.15 | 1.495 |
| CeCr (4%) | 9.9 | 5.43 | 3.13 | 0.789 |
| CeCr (10%) | 8.66 | 5.46 | 3.13 | 0.789 |
| CeFe (4%) | 10.26 | 5.39 | 3.12 | 0.790 |
| CeFe (10%) | 10.66 | 5.44 | 3.15 | 0.874 |
| CeMn (2%) | 6.27 | 5.39 | 3.12 | 1.054 |
| CeMn (4%) | 6.27 | 5.39 | 3.14 | 0.894 |
| CeMn (10%) | 12.6 | 5.43 | 3.13 | 0.819 |
| CeCu (2%) | 6.93 | 5.41 | 3.13 | 0.843 |
| CeCu (4%) | 11.5 | 5.41 | 3.13 | 1.372 |
| CeCu (10%) | 6.93 | 5.38 | 3.11 | 1.380 |
| CeNi (2%) | 7.1 | 5.45 | 3.12 | 0.691 |
| CeNi (4%) | 6.93 | 5.44 | 3.14 | 1.235 |
| CeNi (10%) | 6.3 | 5.44 | 3.15 | 0.785 |
| CeCo (2%) | 6.9 | 5.41 | 3.13 | 1.293 |
| CeCo (4%) | 7.0 | 5.41 | 3.13 | 1.273 |
| CeCo (10%) | 6.93 | 5.41 | 3.13 | 1.228 |

The results obtained on indexing the XRD pattern are given in the Table 3.5. The (h k l) values indicate the fluorite structure of $CeO_2$. The crystallite sizes obtained from Scherrer equation shows a decrease with metal incorporation. It is clear that with incorporation of heteroatom in the framework of ceria, a slight decrease in the $d_{111}$ spacing is observed, indicating the presence of the heteroatom within the framework. The cell parameter was calculated using the following equation,

$$a = d_{(111)} \sqrt{h^2+k^2+l^2}$$

One of the interesting features observed in the case of heteroatom incorporated ceria is that with incorporation of heteroatom, the reflections at higher 2θ are not affected. This might be due to the fact that with incorporation of heteroatoms in the framework, the crystallinity of ceria is not changed. This is also observed by various groups who dealt with the incorporation of the various transition metal ions into the framework of mesoporous materials. It is well documented in the literature that with this type of incorporation, the framework order of mesoporous solids decreases because of their semi crystallinity.

### 3.2.4.3 Low angle X-Ray Diffraction (XRD) Analysis

Small-angle X-ray scattering (SAXS) is a small-angle scattering (SAS) technique where the elastic scattering of X-rays (wavelength 0.1 ... 0.2 nm) by a sample which has inhomogeneity in the nm-range, is recorded at very low angles (typically 0.1-10°). This angular range contains information about the shape and size of macromolecules, characteristic distances of partially ordered materials, pore sizes, and other data. SAXS is capable of delivering structural information of molecules between 5 and 25 nm, of repeat distances in partially ordered systems of up to 150 nm. The mesoporous nature of the ceria samples is confirmed by the low angle XRD pattern (Fig.3.9.4). A Single well resolved peak corresponding to (1 0 0) plane characteristic of 2D hexagonal structure is obtained. The appearance of low-angle diffraction peaks indicates that mesoscopic order is preserved in the calcined metal oxide materials. For mesoporous materials reflexes are observed in X-ray powder patterns at low 2θ angles ($0.5 < 2\theta < 10^{o}$). These reflexes are due to the long-range order induced by the very regular arrangement of the pores. Because d-spacings are rather big for the mesopores, the reflexes appear at low angles.

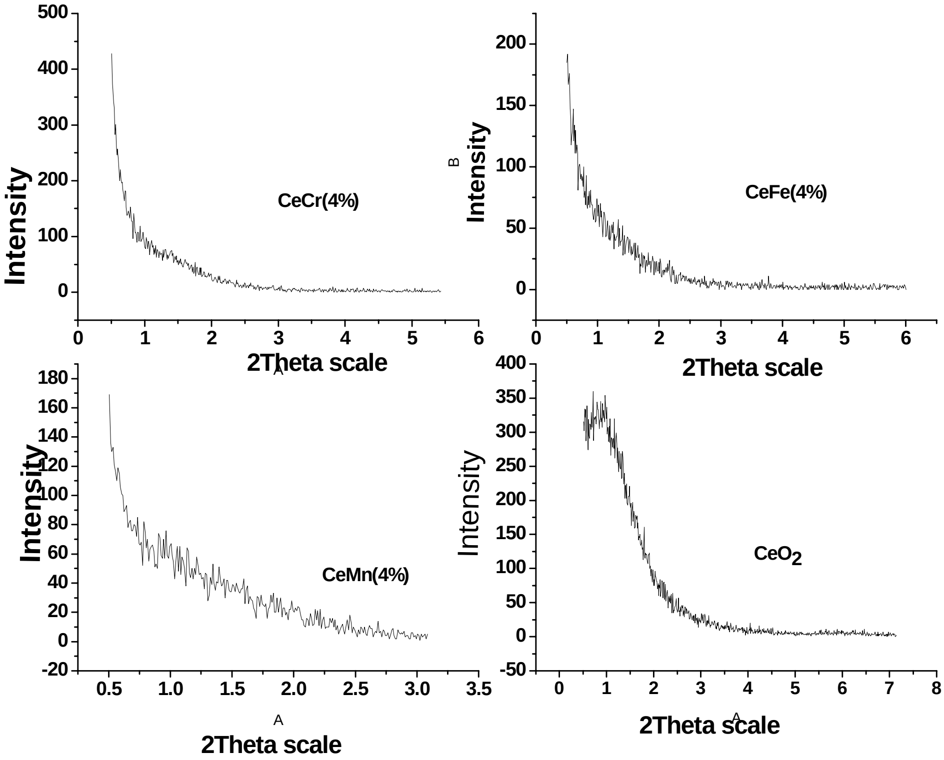
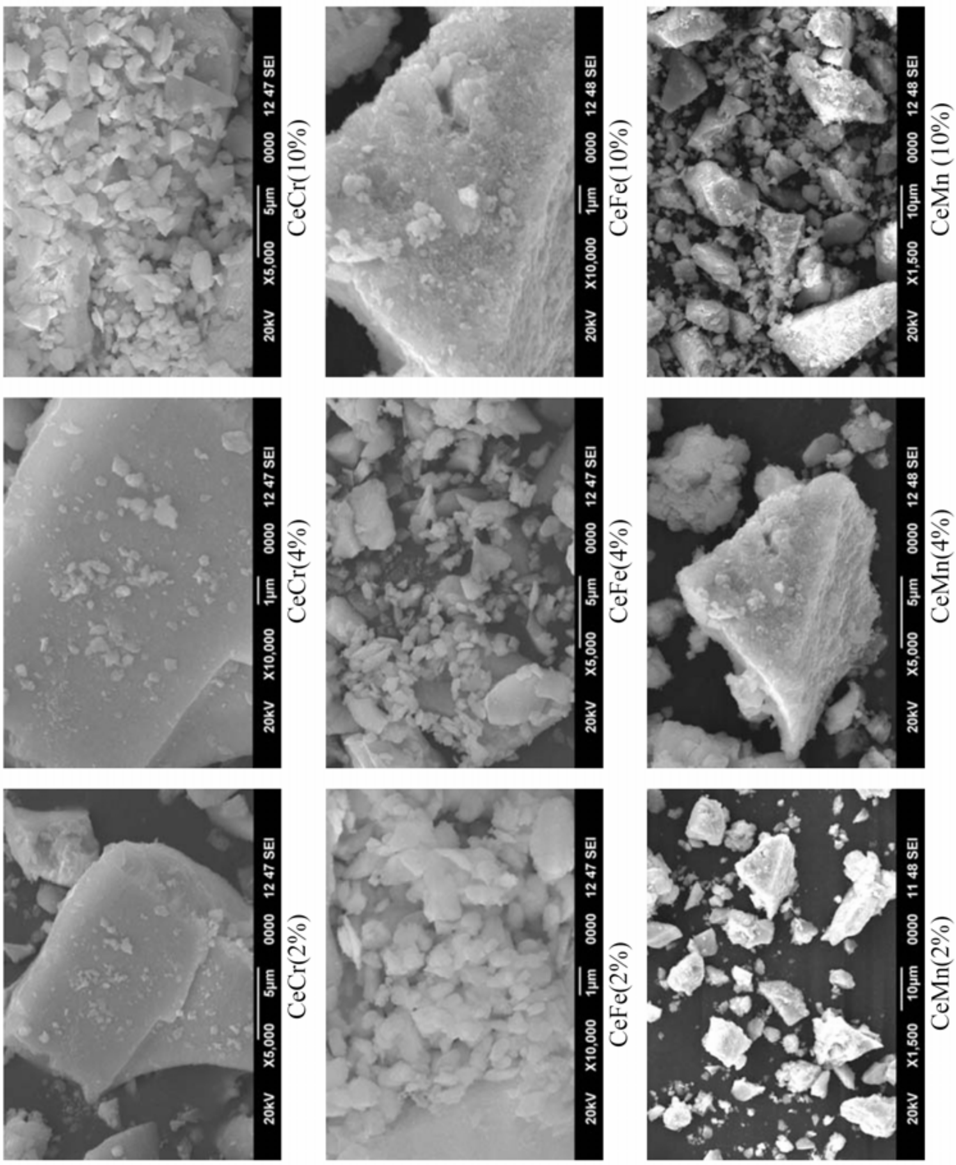


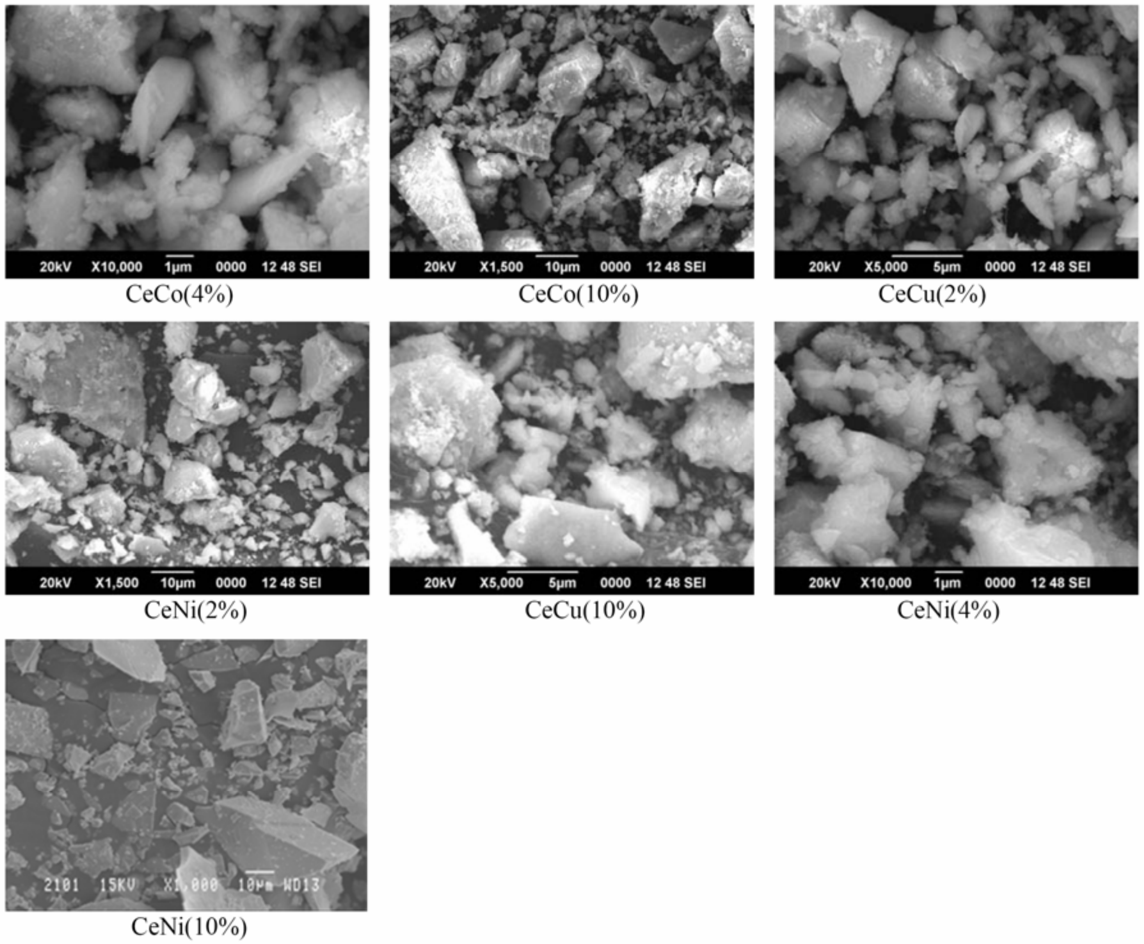
Fig. 3.9.4 Low angle XRD patterns of some representative samples

### 3.2.5 Scanning electron microscopy (SEM)

SEM analysis of the systems gives us the idea about the surface topography of the catalysts. Fig.3.10 presents the scanning electron micrographs of metal modified systems.



CeCr(2%)
CeCr(4%)
CeCr(10%)
CeFe(2%)
CeFe(4%)
CeFe(10%)
CeMn(2%)
CeMn(4%)
CeMn (10%)



CeCo(4%) CeCo(10%) CeCu(2%)

CeNi(2%) CeCu(10%) CeNi(4%)

CeNi(10%)

**Fig. 3.10. SEM pictures of pure and metal modified mesoporous ceria systems**

### 3.2.6 Thermo gravimetric Analysis (TG/DTA)

To examine the thermal stability of the prepared systems, thermal analysis was carried out and thermogram for pure ceria is shown in Fig 3.11. The mathematically obtained differential curve is also plotted in order to clarify the weight loss processes.

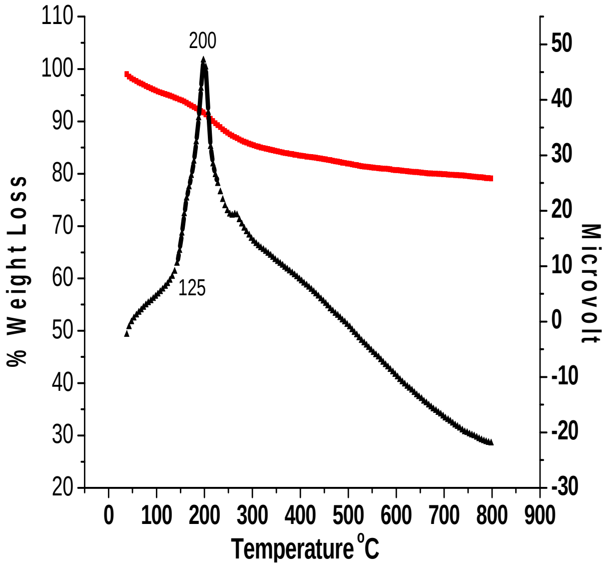


**Fig. 3.11 Thermo grams of as prepared ceria**

The TG curves of pure ceria show weight loss near 100°C which is due to the loss of physisorbed water as well as water held on surface of the catalyst [15, 16]. The second weight loss around 125-315°C could be due to the elimination of surfactant which is occluded in the mesopores through oxidation process [17]. The TG diagram of the sample shows a decrease of the weight of about 4% up to 100°C and a rapid and continuous weight loss from 125°C to 310°C (nearly 10%). No phase transition is observed indicating the stability of cerium oxide fluorite phase. Very small weight loss due to surfactant indicates the removal of most of the surfactant during the washing process. Only a small amount of the surfactant is remaining which is to be removed by calcination. This prevents the rupture of crystalline phase and loss of surface area during the high temperature calcination process. No further weight loss is observed confirming the structural stability of the catalyst systems. Mesoporous solids have been associated with severe problems like surfactant removal which in turn reflected on the thermal stability of the final material. In most of the cases, it has been observed that after the removal of the surfactant the pore looks worm-like rather cylindrical (17a). Most important aspect to be considered for the successful synthesis of mesoporous material is the removal of the surfactant. Moreover, compositions other than silica are often more susceptible to hydrolysis, redox reactions or phase transformations, accompanied by thermal breakdown of the structural integrity, which makes it more difficult to remove the template. Here no change is observed indicating the stability of cerium oxide fluorite phase after the surfactant removal.

### 3.2.7 Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis-DRS)

The diffuse reflectance UV-Vis spectroscopy is known to be a very sensitive technique for the identification and characterization of metal ion co-ordination. The UV-Vis DR spectra of metal doped ceria systems are helpful in identifying the structures of metal species dispersed on ceria surfaces. The UV-Vis DR spectra of various metal modified systems are shown in Fig.3.12a & 3.12b.

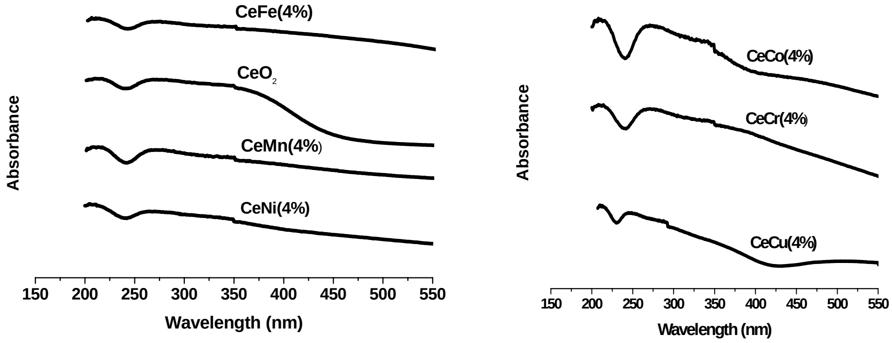


**Fig. 3.12a & 3.12b UV-Visible spectra of pure and metal modified mesoporous ceria systems.**

The spectrum clearly shows that a single band arising from ceria species around 270 nm is found in all cases. No additional bands are observed by the addition of metals. Since the absorption bands are around 270 nm it is assumed that the $Ce^{4+}$ species are in the tetra co-coordinated environment. The 5d-4f transitions occur prominently in the UV region (~200–270 nm) for isolated $Ce^{3+}$ ions on the surface or in other oxide. Several studies confirm the absence of extra framework bulk oxide species through UV-Vis by the absence of a band around 350 nm, which is due to the forbidden d-d transitions. In all the samples, the bands corresponding to d-d transitions are absent indicating the absence of extra framework bulk metal oxide species. This is confirmed by XRD results.

From Fig 3.12a & b it is evident that a single characteristic band around 250 nm is present in all cases. No additional bands are observed by the incorporation of metals. The position of ligand to metal charge transfer (LMCT, $O^{2-} \rightarrow Ce^{4+}$) spectra depends on the ligand field symmetry surrounding the cerium centre. The electronic transition around 270 nm is due to the tetra coordinated environment of $Ce^{4+}$ species.

### 3.2.8 Fourier Transform Infrared Spectroscopy (FT-IR)

For the mesoporous material, Fourier Transform Infrared spectroscopy (FT-IR) suggested that no organic species were present after calcination although the surface was covered by adventitiously adsorbed hydroxyl and carbonate species derived from ambient storage of the samples. No FT-IR evidence of superoxide or peroxide formation on the ceria surface, (characteristic vibrational frequencies of 1126 and 883 cm$^{-1}$, respectively), was found. FT-IR spectra of as prepared ceria and mesoporous ceria calcined at 350$^{o}$C are shown in Fig. 3.13. The broad absorption band located in the area from 3200 to 3600 cm$^{-1}$ approximately corresponds to the O-H stretching vibration, and the one located in the area from 400 to 750 cm$^{-1}$ to the $CeO_2$ stretching vibration. The absorption peaks at 1629 and 1062 cm$^{-1}$ correspond to the $H_2O$ bending vibration and Ce-OH stretching vibration respectively [18]. From IR spectra it was found that, the broad band in the range 3000-3500 cm$^{-1}$ is due to the v (O-H) vibrations of $H_2O$ absorbed by the powder sample.

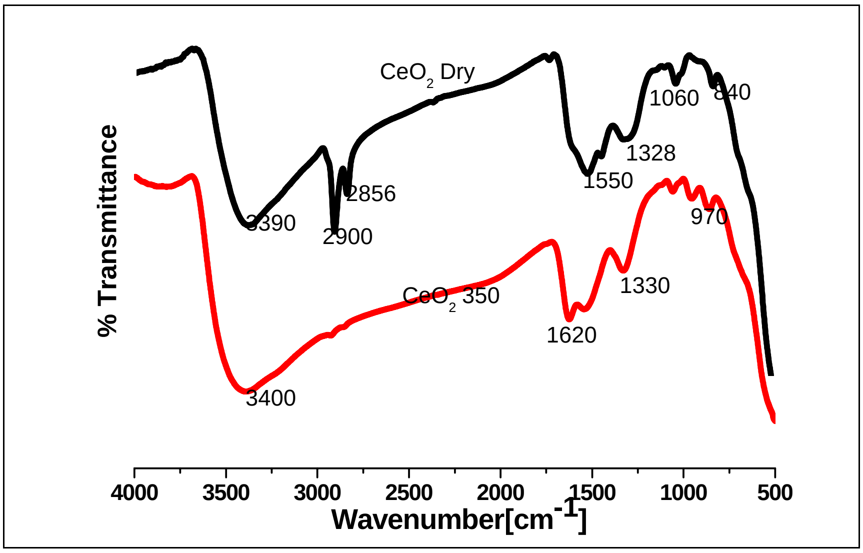


**Fig. 3.13 FT-IR spectra of dry and calcined ceria samples.**

The band at 1580 $cm^{-1}$ is due to the deformation vibration mode of water (δ-OH). Characteristic peak at 1075 $cm^{-1}$ is attributed to the vibrations of Ce-O-Ce bonding. Moreover no characteristic absorption peak is found at 1384 $cm^{-1}$. It means that, nitrates are completely removed during filtration and washing. In the spectra, we can find the absorption peaks at 860 $cm^{-1}$, 665 $cm^{-1}$ and 529 $cm^{-1}$which are due to stretching and bending mode of vibrations of metal-oxygen-metal bond. For the prepared mesoporous materials, Fourier Transform Infrared spectroscopy (FT-IR) suggested that no organic species are present after calcination, though the surface was covered by adsorbed hydroxyl and carbonate species derived from ambient storage of the samples. No FT-IR evidences of superoxide or peroxide formation on the ceria surface, with characteristic vibrational frequencies of 1126 and 883 $cm^{-1}$, respectively, were found.

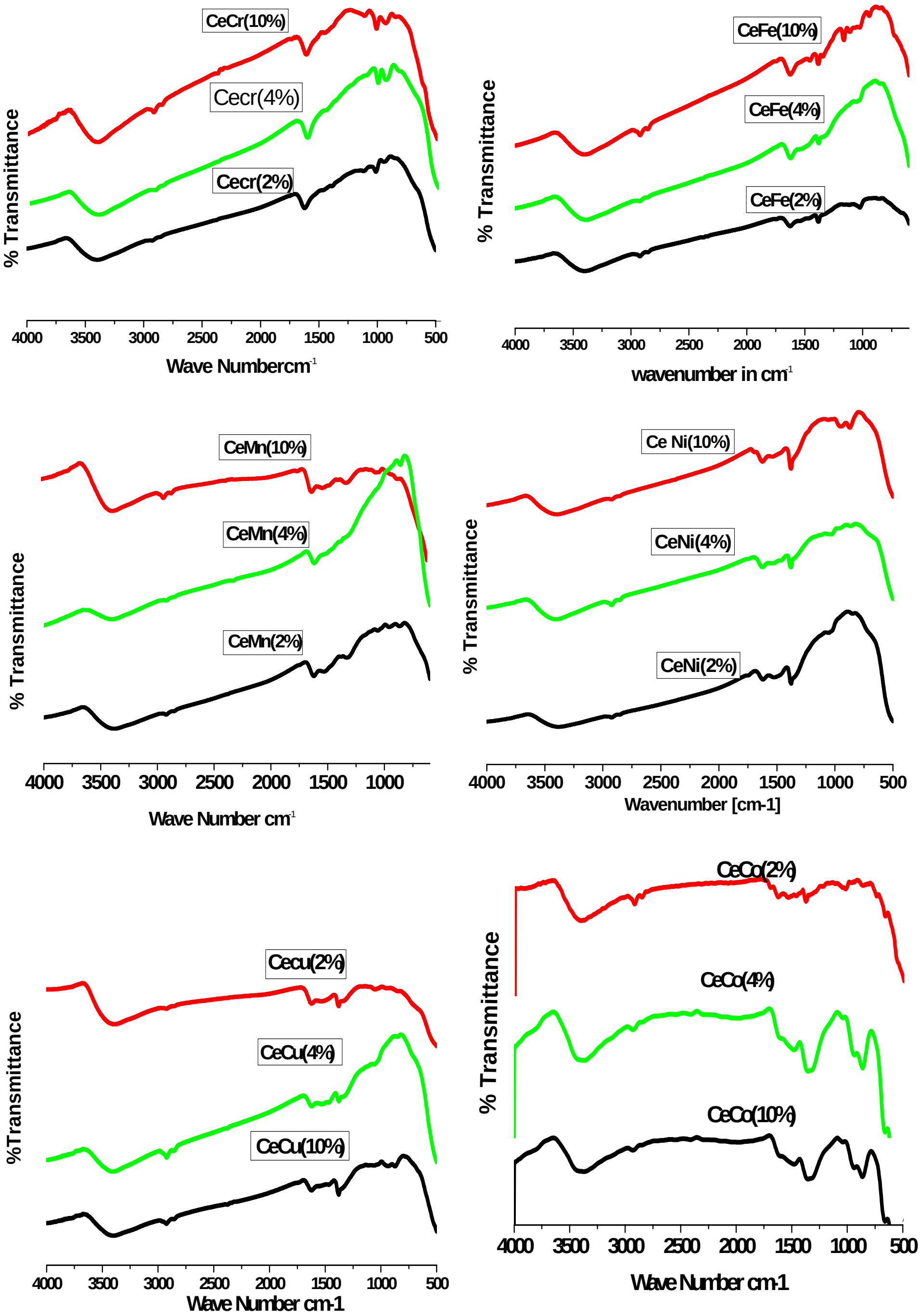


**Fig. 3.14. FT-IR spectra of metal doped mesoporous ceria samples.**

### 3.2.9 TEM

To investigate the morphology of the ceria sample the materials were examined by HR-TEM. Calcined sample consists of aggregated small crystallites of a few nanometres and very homogeneous in size. The observed crystallite size is consistent with the calculated value using the Scherrer equation. Also, the selected area electron diffraction (SAED) pattern (Fig. 3.15f) confirms the formation of the (111) surface plane. Ceria crystallizes in a cubic fluorite structure and exposes the thermodynamically most stable (111) surface. This surface is the oxygen termination of stoichiometric O–Ce–O trilayers stacked along the (111) direction and also represents the major fraction of the catalytic surface in the ceria nanocrystallites. Images show the presence of intracrystalline mesoporosities in the material (Fig.3.15a-d). The lattice fringes visible in the HR-TEM image displayed in Fig. 3.15.f are indicative of the high crystallinity of these particles. The indexing of the lattice parameters of the selected area electron diffraction (SAED) shown in Fig. 3.15.f would agree with the structure proposed from the XRD results. The average size of the mesopores between primary nanoparticles is also a few nanometres, which is in accordance with BJH pore size distribution confirms that the particles are single crystallites and not polycrystalline. It can be seen that the particle size of $CeO_2$ is about 10 nm, which is quite close to the value obtained from the Scherrer equation. The TEM images also reveal aggregates of primary particles.

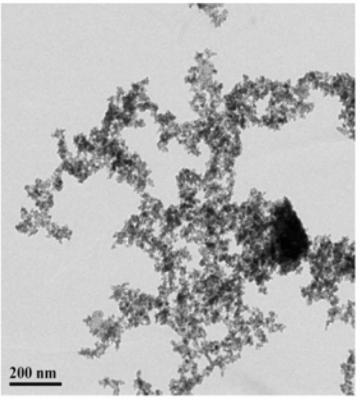


Fig.3.15a. Detailed image of the nanoparticle $CeO_2$-350 array

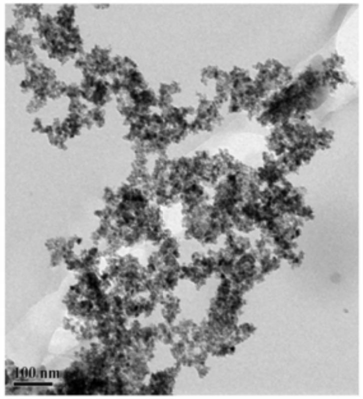


Fig.3.15b. Detailed image of the nanoparticle of $CeO_2$-350 array

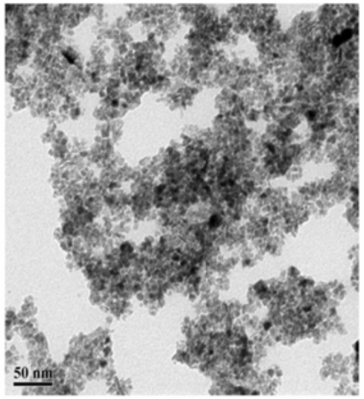


Fig.3.15c. Detailed image of the nanoparticle of $CeO_2$-350 array

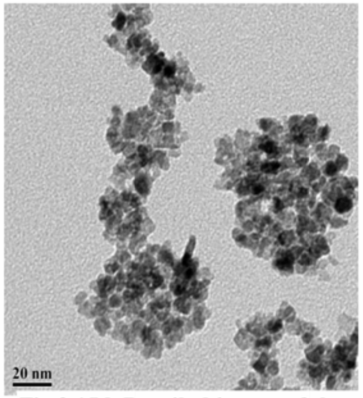


Fig.3.15d. Detailed image of the nanoparticle array

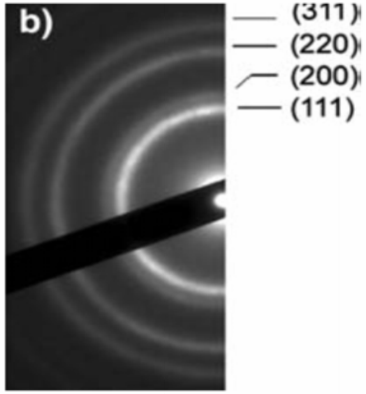


Fig.3.15e. SAED patterns indexed from JCPDS database (75-0162)

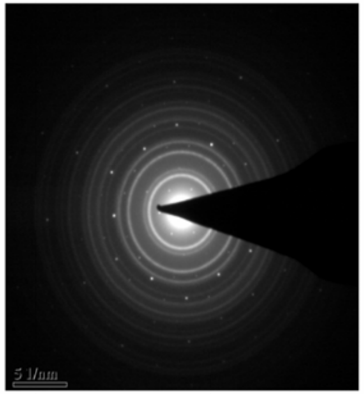


Fig.3.15f. SAED patterns of $CeO_2$-350

### 3.2.10 Temperature Programmed Reduction in $H_2$

(TPR) is unique to study the temperature dependence reduction behavior of ceria based materials. The reduction of ceria takes place essentially in two temperature regions. These two reduction regions are characteristics of ceria and are attributed to the surface and bulk reduction respectively. The coordinately unsaturated surface capping oxygen ions can be easily removed in the low temperature region. However, bulk oxygen requires to be transported to the surface before their reduction. Consequently, the bulk reduction takes place at higher temperature compared to the surface reduction. A linear correlation has been observed between the surface area and the hydrogen consumption at the low temperature region [18a]. The reducibility of the carrier of supported metal catalysts is a very important issue in connection with its ability to generate oxygen vacancies and transfer the oxygen onto the metal particles.

Temperature-programmed reduction (TPR) was carried out in a Micromeritics Instrument: Chemi Soft TPx V1.02 TPR system and 0.1725 mg sample was used for each measurement. Prior to the reduction, the sample was pretreated in an air stream at room temperature for 30 min. After that, $H_2$-$N_2$ mixture (5% $H_2$ by volume) was switched on and the temperature was increased linearly at a rate of $10^oC\ min^{-1}$. A thermal conductivity cell detected the consumption of $H_2$ in the reactant stream.

Another important aspect to be noticed from figure 3.16 is that the hydrogen consumption in the low temperature region increases with the surface area of the ceria sample. A linear correlation has been observed between the surface area and the hydrogen consumption at the low temperature region. The presence of a variety of surface capping oxygen ions can be expected in a small crystallite of ceria. A small crystallite surface may contain $O^{2-}$ ions at different positions with different coordination numbers. For example, the oxide surfaces can have imperfections such as steps, kinks, and corners projecting $O^{2-}$ ions of different coordination number. The variety and population of such surface $O^{2-}$ ions may increase with surface area [18a].

The promoting effect of solid solutions in a catalyst for catalytic reaction is based on the improving reducibility of catalyst and the high dispersion of metal oxide on the surface of support, thus accounting for the enhanced catalytic activity of the modified catalyst. There is a correlation between the catalytic properties of catalyst with the reducibility of metal oxide and $CeO_2$.

It is apparent that the reduction peak shifted towards lower temperature for modified catalysts shows improvement in the reducibility and the area under the peak indicates that large amount of oxygen existing in the catalyst which will be advantageous for the complete oxidation reaction.

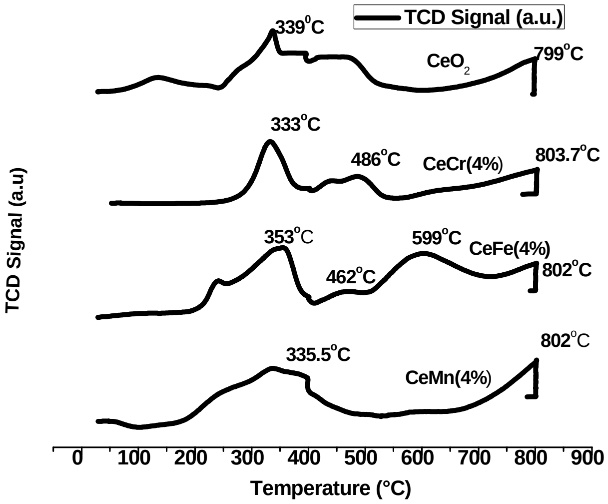


**Fig.3.16 TPR profiles of mesoporous $CeO_2$ and some modified samples**

## 3.3 Surface Acidity Measurement-TPD of ammonia

Metal Oxides due to their ability to take part in the exchange of electrons, protons and oxide ions are used as catalysts in the redox and acid-base catalysis. The acid site is due to the charge imbalance arising between host metal ion and doped metal ions and the basic sites are due to the presence of surface lattice oxide ions. The TPD of ammonia was used to characterize the acid site distribution and furthermore to obtain the quantitative amounts of the acid sites in the specified temperature range [19]. Ammonia is an excellent probe molecule as it allows the distribution of both the protonic and cationic acid centers. In this method, the interaction of acid sites and basic probe molecule ($NH_3$) is studied to determine the amount and strength of the acid sites [20]. The acid site distribution pattern can be classified into weak (desorption at 100-200$^{o}$C), medium (201-400$^{o}$C), and strong (401-600$^{o}$C) acid sites. The amount of ammonia desorbed at 100$^{o}$C may contain some amount of physisorbed ammonia too.

**Table 3.6 Distribution of acid sites of pure ceria and transition metals incorporated ceria.**

| Sample | Weak [mmol/g] (100-200℃) | Medium [m mol/g] (201-400℃) | Strong [mmol/g] (401-600℃) | Medium + strong | Total [mmol/g] (100-600℃) |
|---|---|---|---|---|---|
| Ce | 0.10 | 0.02 | **Nil** | 0.021 | 0.12 |
| CeFe(2%) | 0.09 | 0.07 | 0.01 | 0.08 | 0.17 |
| CeFe(4%) | 0.11 | 0.02 | 0.03 | 0.05 | 0.16 |
| CeFe(10%) | 0.09 | 0.02 | 0.02 | 0.04 | 0.13 |
| CeCr(2%) | 0.11 | 0.05 | 0.03 | 0.09 | 0.19 |
| CeCr(4%) | 0.13 | 0.02 | 0.02 | 0.04 | 0.17 |
| CeCr(10%) | 0.37 | 0.02 | 0.01 | 0.03 | 0.40 |
| CeMn(2%) | 0.07 | 0.02 | 0.01 | 0.03 | 0.10 |
| CeMn(4%) | 0.05 | 0.01 | 0.01 | 0.023 | 0.07 |
| CeMn(10%) | 0.08 | 0.02 | 0.01 | 0.03 | 0.11 |
| CeCo(2%) | 0.1 | 0.01 | 0.01 | 0.02 | 0.12 |
| CeCo(4%) | 0.07 | 0.015 | 0.01 | 0.022 | 0.09 |
| CeCo(10%) | 0.05 | 0.05 | 0.02 | 0.07 | 0.12 |
| CeNi(2%) | 0.13 | 0.03 | 0.02 | 0.05 | 0.18 |
| CeNi(4%) | 0.09 | 0.01 | 0.003 | 0.013 | 0.10 |
| CeNi(10%) | 0.16 | 0.01 | 0.01 | 0.02 | 0.18 |
| CeCu(2%) | 0.15 | 0.01 | 0.002 | 0.01 | 0.16 |
| CeCu(4%) | 0.15 | 0.02 | 0.01 | 0.03 | 0.18 |
| CeCu(10%) | 0.23 | 0.04 | 0.03 | 0.07 | 0.30 |

Table 3.6 gives the distribution of acid sites of pure and transition metals incorporated ceria samples. Total acidity is shown as the sum of amount of ammonia desorbed from the entire temperature range.

The table indicates that pure ceria possesses low surface acidity. Upon modification with metals, there is enhancement in the amount of weak, medium and strong acid sites. But within the series as the metal concentration increases though there is a change in the total acidity, for all the metals there is no steady increase in the acidity with increase in the concentration of the metals.

With iron doping the total acidity is decreased with increase of metal percentage. Tanabe et al. proposed a mechanism for the generation of acid sites by mixing two oxides [21-22]. They suggested that the acidity generation is caused by an excess of positive charge in a model structure of a binary oxide related to the co-ordination number of a positive element and a negative element.

Table 3.6 shows the acid strength distribution of the simple as well as chromium incorporated ceria systems. Here also pure cerium oxide exhibits lowest surface acidity among the different systems. Considerable enhancement of weak, medium, strong acidity is observed after chromium incorporation. Among chromium-modified systems, CeCr (10%) systems have the highest acidity. The TPD data of the chromium oxide doped ceria systems points to an increase of strong acid sites than the simple system. Among the different metals loaded systems (Fe, Cr, Mn, Cu, Co & Ni), Cr doped systems have highest acidity.

For manganese doped systems, the total acidity decreases with increase of concentration of manganese up to 4% then it increases. With Co doping there is not much change in the acidity, but the acidity slowly increases with doping. When Cu is incorporated, the acidity increases in a linear manner with increase in concentration of Cu. With Ni modification, the trend is opposite to that of Mn. Up to 4% the acidity increases; afterwards it decreases with metal doping.

### 3.3.1 Vapour phase cumene cracking reaction

Vapour phase cumene cracking reaction is a model reaction for identifying the Lewis / Brönsted acid ratio of a catalyst. During cumene cracking over the acidic sites cumene is either dealkylated or dehydrogenated depending on the nature of the acid site present. The major reactions taking place during the cracking of cumene are dealkylation to give benzene and propene over BAS [23, 24] and dehydrogenation to give α-methyl styrene over LAS [25]. A comparison of the amount of dealkylated products and α-methyl styrene gives an idea about the BAS and LAS possessed by the catalyst [26]. It is possible to correlate the acidic properties of the catalysts with the conversion of cumene and with the product distribution of the reaction. The catalytic activity of solid acid catalysts is not only related to the surface concentration of acid sites, but also to their nature, that is being Lewis or Brönsted sites [27]. Vapour phase cumene cracking is a model reaction for identifying the Lewis and Brönsted acid sites present in a catalyst [28]. Fig. 3.17 represents the general scheme of the cumene cracking reaction. So cumene cracking enables a simultaneous determination of Brönsted and Lewis acidity of the catalysts.

In the present work, the vapour phase cumene cracking reaction was carried out in a fixed bed, down flow vertical glass reactor inside a double zone furnace. 0.25g of the catalyst activated at $350^oC$ for 1hr was immobilized inside the reactor with glass wool. The catalyst was loaded in the middle of the reactor and packed with glass beads. The temperature was measured by a thermocouple placed in the middle of the catalyst bed. Cumene was fed into the reactor at a flow rate of 4mL/h after optimization. The temperature of the reaction bed was kept at $500^oC$.

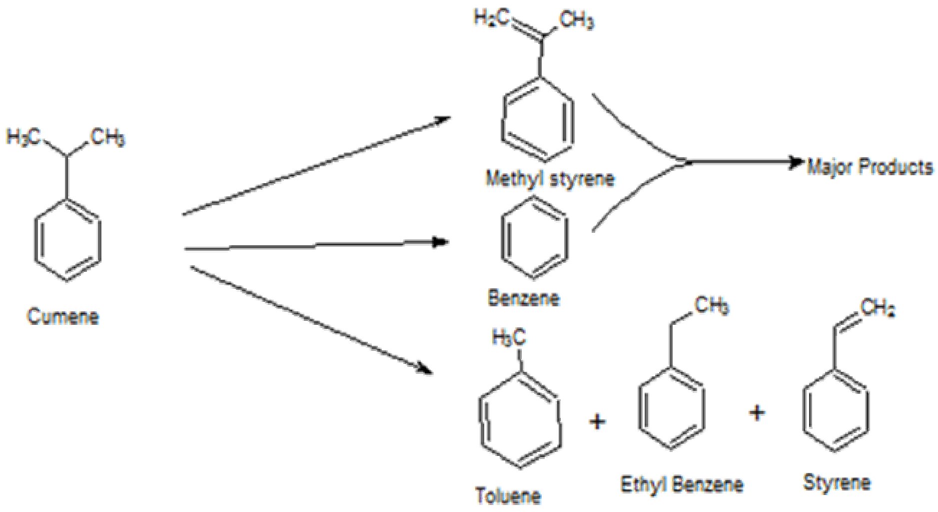


**Fig 3.17 Reaction scheme of vapour phase cumene cracking**

The product analysis was achieved by gas chromatography (Chemito GC 1000) by comparison with authentic samples. The analytical conditions are given in the table.

### 3.3.2 Optimization of reaction conditions

The influence of reaction conditions such as temperature, flow rate and time on stream on the conversion and selectivity is investigated. The results are given in the following sections.

#### 3.3.2.1 Effect of Temperature

For the optimization of reaction temperature, the catalytic activity was measured at different temperatures such as 350, 400, 450 and 500$^{o}$C with a constant flow rate of 4 mL/h for 2 hours.

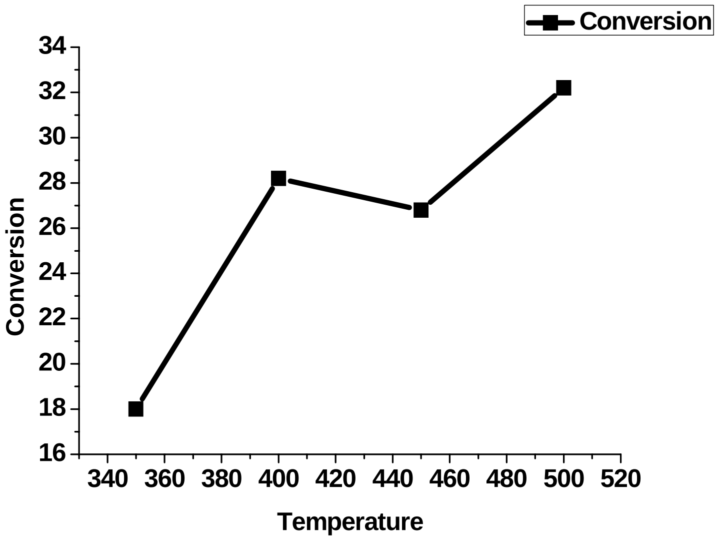


**Fig. 3.18 Effect of Temperature on cumene cracking**

*Reaction condition: Catalyst: 0.25g CeCr (10%), Flow rate 4mL/h, Time: 2h*

The result shows that as the temperature increases the cumene conversion also increases. At higher temperature the possibility of cracking of the carbon chain increases.

### 3.3.2.2 Effect of flow rate

The optimization of flow rate was done by performing the reaction at different flow rates like 4, 5, 6 and 7 mL/h at a constant temperature of 500°C for 1 hour. With regard to flow rate, higher flow rates were found to reduce the percentage conversion. This is because of the lower residence time of the reactants on the catalyst surface. It is reported that a decrease in the conversion is observed at higher flow rates due to smaller contact time, where the kinetics get affected [29].

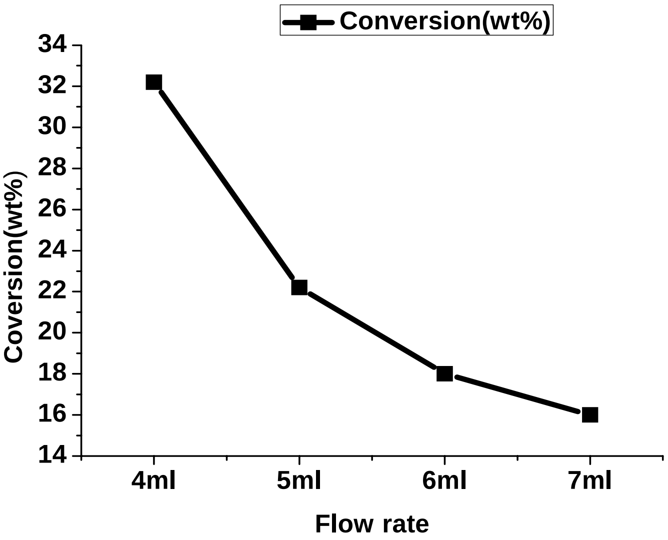


**Fig. 3.19 Effect of flow rate on cumene cracking**

*Reaction condition: Catalyst: 0.25gCeCr (10%), Flow rate 4mL/h, Time: 2h, Temperature: 500$^o$C*

### 3.3.2.3 Effect of time of flow

**Table 3.7 Effect of time of flow**

| Catalyst: CeCr (10%)<br>Temperature:500$^o$C<br>Weight: 0.25g<br>Flow rate:4mL | **Flow rate** | **Conversion (wt %)** |
|---|---|---|
| | 1hr | 31 |
| | 2hr | 32.2 |
| | 3hrs | 33 |
| | 4hrs | 28 |

To study the effect of time on stream, the reaction was carried out continuously for 4 hours over catalyst CeCr (10%) at a temperature of 500$^o$C and a flow rate of 4 mL/h. The effect of contact time on the conversion and selectivity towards dehydrogenation and cracking products is shown in Fig. 3.18. Although an increase in the percentage conversion of cumene can be seen in the beginning of the reaction, the conversion is found to decrease as time proceeds. It is a known fact that during organic reactions catalyzed by solid acid catalysts, the catalyst always suffers from strong deactivation due to formation and retention of heavy by products, so-called coke, which deactivates acid sites [30]. Wang and Manos [31] observed a similar decrease in product conversion with time during the reaction of 1-pentene over different zeolite catalysts. According to them, the drastic decrease in conversion seen during the reaction indicates a rapid coke formation, which takes place on acid sites catalyzing the reaction. Similarly, in the present reaction, the decrease in percentage conversion with reaction time may also be due to the blocking of the acid sites by the coke formed during the reaction. It is reported that the acid sites are strong promoters for coke deposition and deactivation of the catalyst [32].

**Table 3.8 Optimized Conditions**

| | |
|---|---|
| Temperature | 500$^o$C |
| Weight | 0.25g |
| Flow rate | 4mL |
| Temperature | 500$^o$C |

### 3.3.2.4 Effect of various catalysts on cumene cracking

Comparison of the catalytic activity of different systems was done at a temperature of 500$^o$C with a flow a rate of 4 mL/h for 1 hour. The products were identified using a gas chromatograph (GC 1000 Chemito with an SE- 30 capillary column). The injector and detector temperature of GC was maintained at 230$^o$C and the temperature programme for the column is set as 70$^o$C-2min-10$^o$C/min-250$^o$C-2min.

**Table 3.9 Comparison of catalytic activity of different samples on cumene cracking reaction**

| Sample | Cumene Conversion | α-methyl styrene selectivity | Dealkylated products selectivity | Lewis/ Bronsted acidity |
|---|---|---|---|---|
| CeFe (2%) | 18.5 | 74 | 26 | 2.8 |
| CeFe (4%) | 27 | 62.6 | 37.4 | 1.7 |
| CeFe (10%) | 14.2 | 57.2 | 42.8 | 1.3 |
| CeCr (2%) | 31.6 | 59.7 | 40.3 | 1.5 |
| CeCr (4%) | 22.5 | 58 | 42 | 1.4 |
| CeCr (10%) | 31.8 | 67.2 | 32.8 | 2.0 |
| CeMn (2%) | 24.8 | 65 | 35 | 1.9 |
| CeMn (4%) | 14.6 | 64.5 | 35.5 | 1.8 |
| CeMn (10%) | 25 | 68.2 | 31.8 | 2.1 |
| CeCo(2%) | 26 | 68 | 32 | 2.1 |
| CeCo (4%) | 28 | 67 | 33 | 2.0 |
| CeCo (10%) | 30 | 66.6 | 33.4 | 1.99 |
| CeNi (2%) | 33 | 68.2 | 31.7 | 2.1 |
| CeNi (4%) | 30 | 45.2 | 54.8 | 0.8 |
| CeNi (10%) | 20 | 49.5 | 50.5 | 1.0 |
| CeCu (2%) | 14 | 46 | 54 | 0.9 |
| CeCu (4%) | 24 | 75.9 | 24 | 3.1 |
| CeCu (10%) | 31 | 77 | 23 | 3.3 |

The results show the presence of both Lewis and Brönsted acid sites on the catalyst. α-methyl styrene is the major product along with some dealkylated products. Higher selectivity towards α-methyl styrene for the incorporated systems suggests the enhancement in Lewis acidity upon modification. Since the total acidity of the catalysts increases with incorporation, we can conclude that transition metal ion modification result in an increase in the Lewis acidity of pure ceria. The higher selectivity towards α-methyl styrene obtained during the reaction suggests the presence of more number of Lewis acid sites compared to the Brönsted acid sites.

### 3.3.3 Correlation of acidities from TPD of ammonia and cumene cracking reaction

The total acidity of the catalysts as determined by the temperature programmed desorption (TPD) of ammonia is found to influence the percentage conversion of cumene in the reaction. With transition metal ion impregnation, the total acidity of the catalysts was found to increase (as evident from TPD of ammonia) thereby increasing the total conversion of cumene in the reaction. Aberuagba et al. [33] also reported a similar dependence in cumene conversion with total acidity in the case of zirconia-alumina mixed oxides and magnesia-alumina mixed oxides. Since the total acidity of the catalysts increases with incorporation, we can conclude that transition metal ion modification result in an increase in the Lewis acidity of pure ceria.

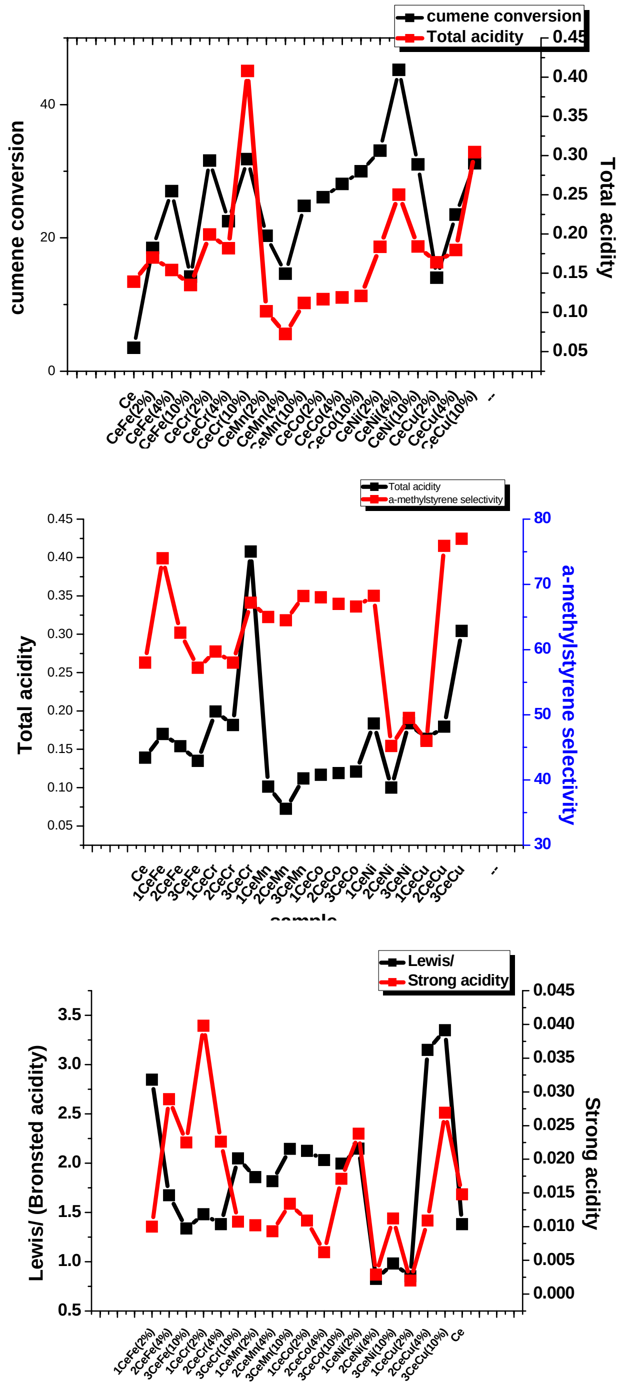


**Fig. 3.19.** **Correlation of acidities from TPD of ammonia and cumene cracking reaction**

In the study cumene conversion was found to depend on the surface acidity as obtained from TPD of ammonia. Modified systems are found to be more active than the simple system. Good correlation is observed for total acidity with cumene conversion, total acidity with α-methyl styrene selectivity, and Lewis to Brönsted acidity ratio with strong acidity obtained from TPD of ammonia. Strong acidity from TPD of ammonia may be taken as a measure of Lewis acid site. Lock and co-workers reported that desorption of ammonia in the moderate temperature range is due to potential Brönsted acid sites (BAS) [34]. This supports the generation of BAS through the hydrolysis of cations during temperature treatment.

## 3.4 Conclusions

The different surface characterization techniques and surface acidity studies may be concluded as:

- Mesoporous ceria modified with various transition metals can be successfully synthesised by template method using hexadecyl amine as surfactant. All the samples prepared have ordered pores.
- As the calcination temperature increases the surface area decreases. Also the surface area and pore volume of the support decrease with the introduction of transition metals. Adsorption isotherms of ceria calcined at different temperatures resemble Type IV of IUPAC classification which is characteristic of mesoporous materials. There is good correlation between surface area and pore diameter of the different sample. The narrow pore size distribution shows uniformity of the pore

- The XRD data of the prepared systems agree well with the standard values for the cubic fluorite structure of ceria. Except for 10% Cu no new characteristic phases where observed with the incorporation of transition metal oxides. This shows that metals are highly dispersed within the frame work structure.
- From FTIR and TG/DTA studies it can be concluded that the neutral surfactant can be successfully removed at a lower calcination temperature attaining maximum surface area.
- The acidity studies interpreted the total acidities of samples with the cumene cracking conversion. Good correlation was obtained between the acidities obtained by vapour phase cumene cracking and Temperature programmed desorption of ammonia. Acidity studies confirm the enhancement of surface acidity in particular strong acidity, upon modification with transition metals.

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Chapter 4

# FRIEDEL – CRAFTS BENZYLATION OF TOLUENE, O-XYLENE AND ANISOLE

Contents

Friedel-Crafts alkylation enables the introduction of alkyl chains to aromatic rings where alkyl chlorides, alcohols and alkenes being the commonly employed alkylating agents and hence is a key reaction in organic chemistry. The liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride and benzyl alcohol is an important process for the production of diphenyl methane and substituted diphenyl methanes which are industrially important. Benzylation using benzyl alcohol requires Brönsted acidity while benzyl chloride requires Lewis acidity for the catalysts. The present chapter deals with the liquid phase benzylation of toluene, o-xylene and anisole using benzyl chloride as benzylating agent. Here in this chapter, conversion of the reactant in terms of benzyl chloride is correlated with the acidities of the prepared catalysts. The various reaction parameters like temperature, molar ratio of substrate to benzyl chloride, weight of catalyst and time of the reaction were optimized using iron loaded catalyst for toluene benzylation. o-Xylene and anisole were also benzylated in the same optimized condition.

## 4.1 Introduction

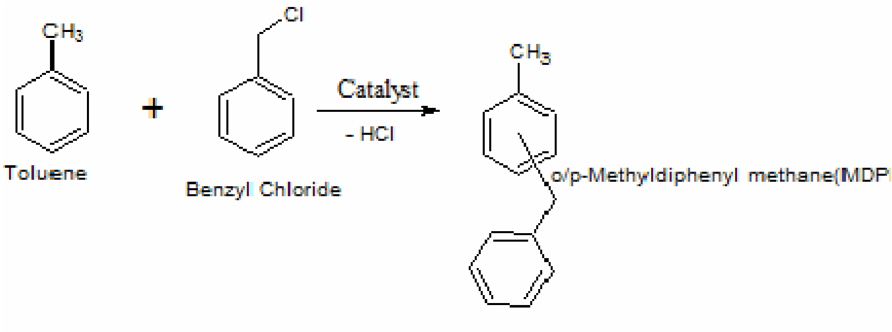
The development of sciences and technologies has resulted in a substantial improvement of our lifestyles. These almost unbelievable achievements have, however, led to some impacts on the global environment and public awareness. In particular, chemistry has been contributing to this evolution. Through the combination of knowledge on molecular reactivity, design and other sub disciplines of chemistry and chemical engineering, green chemistry has been looked upon as a sustainable science which accomplishes both economic and environmental goals, simultaneously. With this objective, we developed an alternative process to obtain the industrially important benzyl aromatics by benzylation of aromatics using benzyl chloride, catalysed by solid mesoporous acids. Friedel and Crafts first reported the alkylation of benzene with alkyl chlorides in the presence of aluminium chloride in 1877 [1]. Their historical discovery initiated an unimaginable flow of new synthetic processes. Over the past century, overwhelming number of compounds has been synthesized through the modification of the original approach, a field now commonly referred to as Friedel-Crafts chemistry. The Friedel-Crafts alkylation of aromatic substrates is an industrially important synthetic transformation. Friedel-Crafts alkylation enables the introduction of alkyl chains to aromatic rings where alkyl chlorides, alcohols and alkenes being the commonly employed alkylating agents and hence is a key reaction in organic chemistry. The liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride and benzyl alcohol is an important process for the production of diphenyl methane and substituted diphenyl methanes. Benzyl aromatics are key intermediates in the multifaceted angle of industrial applications. They are industrially important compounds used as pharmaceutical intermediates, heat transfer fluids, aromatic solvents, fragrances, monomers for polycarbonate resins and fine chemicals [2]. Dimethyl diphenyl methane is used as a synthetic intermediate for the production of dielectric fluids [3]. Despite more than 120 years of history, the Friedel–Crafts alkylation and acylation reactions are still in the forefront of organic synthesis research. The catalysts used in these reactions are often homogeneous catalyst such as HF, $H_2SO_4$, $AlCl_3$ and $BF_3$. Though readily available and inexpensive, these catalysts have numerous drawbacks, which include violent decomposition with water, liberating HCl, its corrosive nature and poor selectivity leading to undesired poly substituted and isomerized by-products. During the reaction workup, the catalyst is destroyed not only generating large volumes of gaseous effluent (HCl), but also generating Al-rich acidic effluents, which are difficult to deal with. These traditional catalysts have difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity etc. Moreover, these catalysts are highly moisture-sensitive and hence require moisture-free solvent and reactants and anhydrous conditions, and also dry atmosphere for their handling [4]. In addition, the catalysts are added in stoichiometric amounts which add the cost of the reaction. These catalysts also catalyse undesirable side reactions due to alkyl isomerizations, trans alkylation, and poly alkylation reactions. In order to reduce these reaction products the reactions are generally done at very low temperature (below -10$^{o}$C) and in solvents like carbon disulphide and nitro methane. Unfortunately, they do not fulfill the current requirements of environmental protection and safety standards. The work up procedure for the reaction using traditional catalysts involve a water quench which prevents the acid from being reused and on subsequent neutralization leads to the formation of salt waste. These drawbacks become a major disadvantage in the times of environmental concern emphasizing the need to develop an alternative to the conventional homogeneous Lewis acid catalyst. Replacing homogeneous catalytic systems with heterogeneous ones is advantageous mainly because of easy catalyst recovery, reusability and work-up of reaction products. During the past decade, much attention has been paid to the replacement of homogeneous catalysts by solid acid catalysts such as zeolites sulphated $ZrO_2$ or $Fe_2O_3$, sulphated $Al_2O_3$–$ZrO_2$ or $TiO_2$, clays, metal oxides and modified silica. Recently, ceaseless search for greener chemical process has become one of the most important tasks of today's chemical researchers [5]. There are lots of methods to achieve this goal such as alternative feed stocks, reagents, solvents, products, catalysts and so on. An important issue in these environmentally conscious days is the choice of suitable acid catalyst [6]. The environmental concern and the drive towards a 'clean technology' urge the replacement of the liquid acids by eco-friendly solid acid catalysts. In the past, benzylation of benzene has been carried over different iron containing mesoporous materials like Fe containing mesoporous silicate catalysts [7] and FeSBA-15 [8]. Introduction of iron into the mesoporous material by wet impregnation technique showed high redox property than tetrahedrally coordinated $Fe^{3+}$ located in the skeleton of the materials [9] which would be highly beneficial for the title reaction as it follows redox mechanism as confirmed by earlier report [7]. Mesoporous materials as support [10] and iron loaded mesoporous materials [11] as catalysts have proved to be highly active and efficient in previous studies. The use of iron loaded mesoporous materials as catalyst can also eliminate the hurdles like pore size constraint, recyclability, thermal and hydrothermal stability etc. Benzylation of o-xylene with benzyl chloride, which is a typical example of Friedel-Crafts alkylation, is generally known to proceed over a homogeneous Lewis acid catalyst $AlCl_3$ [12]. Catalytic behaviour of rare earth oxides has been explored for many reactions and a wide variety of catalytic properties have been known [13]. These oxides can be used in Friedel-Crafts reactions, too [14]. Benzylation of toluene with either benzyl alcohol or benzyl chloride (B-Cl) has extensively been studied previously. For example, alkylation of toluene with BC in presence of Al-SBA-15 as catalyst has been carried with 31% conversion and 88% para-selectivity [8]. A similar reaction catalyzed by Fe-SBA-15 afforded the corresponding para-alkylated product with 66% conversion and 100% selectivity [15]. Utilization of benzyl alcohol in the presence of Ga-Al-MCM-41 has converted 78% of toluene to a mixture of ortho and para during 6 hours [16]. Catalytic activities of niobium phosphate in the benzylation of toluene with benzyl alcohol have also been reported [17, 18]. In most cases, reactions either need long reaction times or are carried out at relatively high temperatures. More importantly, they mostly end up with a mixture of ortho and para-alkylated products [18, 19, 20]. After the induction period the toluene benzylation proceeds rapidly almost at the same rate in all these cases. This clearly shows that the catalyst is modified during the induction period creating new active sites on the catalyst, probably by the HCl formed in the reaction, and due to this process, the catalyst activation is enhanced [21]. The fundamental concept is to identify new, stable and recyclable catalysts as replacements for the conventional liquid acids, and ultimately develop environmentally safe industrial processes. Herein we report a recyclable, easily separable, eco-friendly and highly effective catalytic system of mesoporous ceria modified with transition metals (Fe modification giving maximum activity) for the benzylation of toluene with benzyl chloride (B-Cl), a typical example of Friedel Crafts alkylation.

A Friedel – Crafts reaction mixture involves many components:

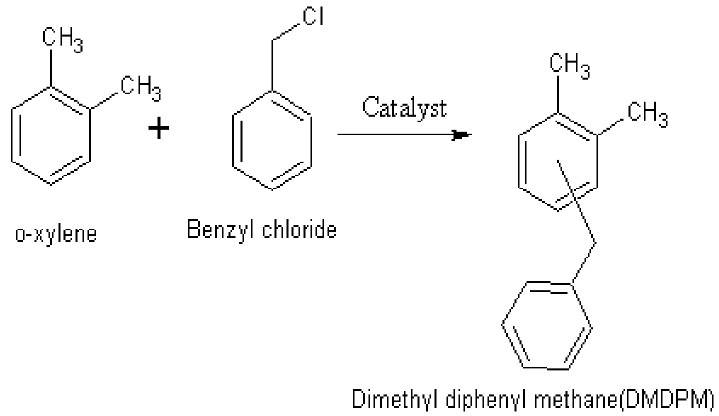
- The substance to be substituted
- A reagent that supplies the substituent
- A catalyst which may be a Lewis acid type or a proton acid as in Brönsted –Lowry concept
- A solvent which are generally non-ionizing type like $CS_2$, $CCl_4$ etc. or with high dielectric constant like nitrobenzene, nitro methane etc.
- The product formed in the reaction
- The by-product and conjugate acid formed in the reaction.

The combinations of these components give rise to complexity to the result of the reaction.

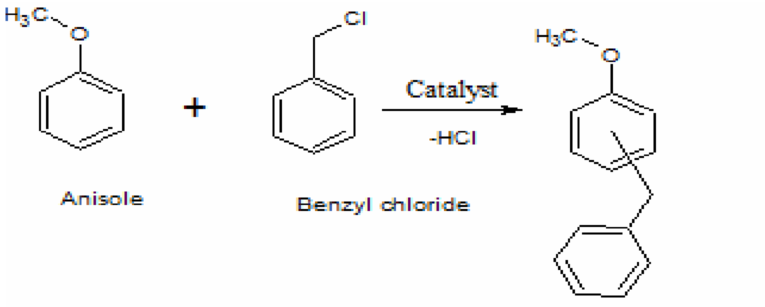
The Friedel-Crafts benzylation of aromatics using benzyl chloride catalysed by solid mesoporous acids is of significant interest in the field of organic chemistry. Acidic mesoporous heterogeneous catalysts, having Brönsted or Lewis acid centres are capable of replacing traditional homogeneous acids. Here we studied the liquid phase benzylation of toluene using benzyl chloride as benzylating agent over transition metal (Fe, Mn, Cr, Co, Cu & Ni) modified mesoporous ceria. The general scheme of Friedel-Crafts benzylation of toluene, o-xylene & anisole are shown in Figure 4.1.



Benzylation of Toluene



Benzylation of o-xylene



Benzylation of Anisole

**Fig.4.1 The general scheme of Friedel-Crafts benzylation of Toluene, o-Xylene & Anisole**

The reactions were carried out in a double necked round bottom flask fitted with are flux condenser. In a typical run, appropriate amounts of toluene /o-xylene / anisole, benzyl chloride and the catalyst were allowed to react at specified temperatures under magnetic stirring. The reaction mixtures were analysed periodically using 8610 GC equipped with SE-30 column and FID detector. As toluene /o-xylene /anisole taken in excess, the yield of the reaction was expressed as the total percentage of benzyl chloride transformed. The product formed was identified as o/p methyl diphenyl methane /dimethyl diphenyl methane/ methoxy diphenyl methane for toluene, o-xylene & anisole respectively.

## 4.2 Influence of reaction conditions

Generally for any reaction, the conversion and selectivity to a desired product depends on various reaction parameters such as temperature, mole ratio of the reactants, catalyst weight, and time of the reaction. Before testing the catalytic activities of different catalytic systems prepared, it is necessary to optimize the reaction parameters.

### 4.2.1 Effect of temperature

In a typical reaction, to a definite amount of toluene taken in the RB flask, required amount of catalyst was added and heated for 25 minutes with stirring. Then required amount of benzyl chloride was added at a particular temperature. The influence of temperature on benzylation of toluene was tested in a temperature range from $60^oC$ to $90^oC$. The observations are represented in Fig. 4.2.

At low temperatures below $80^oC$ there was no reaction taking place. The reaction was found to be 100% selective towards methyl diphenyl methane (MDPM) at 80$^{o}$C with 100% conversion of benzyl chloride. Hence for the benzylation temperature is an important factor.

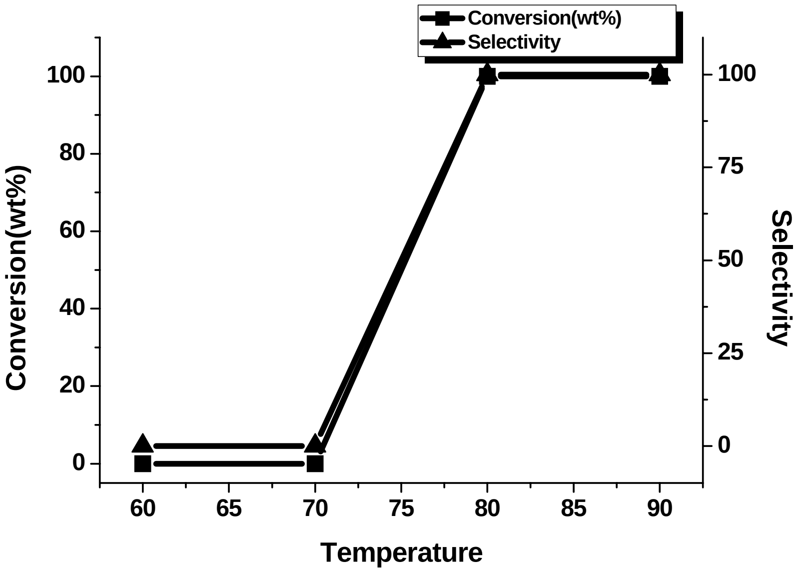


**Fig.4.2 Effect of temperature on benzylation of toluene.**

*Reaction conditions: catalyst CeFe (10%), Time-4hrs, Toluene: benzyl chloride (mole) – 13:1, Weight of catalyst-0.1g*

### 4.2.2 Effect of catalyst weight

To study the effect of catalyst weight on reaction, the weight was varied from zero (absence of catalyst) to 100mg. The reaction was conducted with CeFe (2%). In the run 13 moles of toluene with definite weight of the catalyst was heated for 25 minutes to activate the catalyst. Then 1 mole of benzyl chloride was added and the reaction was allowed to proceed for 2 hours. The results obtained with different weights of catalyst are given below in Fig.4.3.

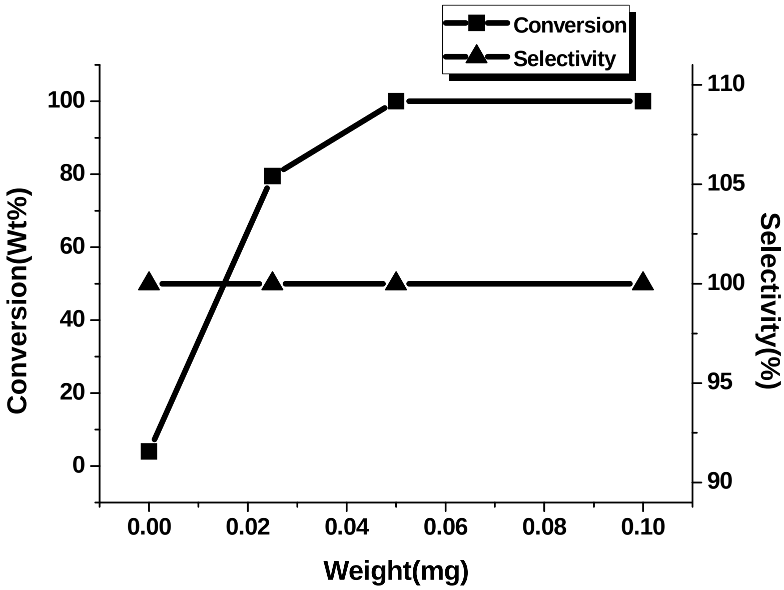


**Fig.4.3 Effect of catalyst weight on benzylation of toluene.**

*Reaction conditions: catalyst CeFe (2%), Time-2hrs, Toluene: benzyl chloride – 13:1*

The presence of catalyst has pronounced effect on the benzylation reaction. In the absence of any catalyst there was no reaction taking place. This shows that the reaction proceeds through the formation of benzyl carbonium ion in the presence of the catalyst. As the catalyst weight is increased the conversion of benzyl chloride increases and reaches 100% at a catalyst weight of 50mg. The selectivity is also 100% at all conversions producing only mono alkylated product. The increase in the conversion with increase in the catalyst weight shows that the reaction is truly heterogeneous in nature. On increasing the catalyst concentration the number active sites on the surface increases which in turn increases the catalyst activity.

### 4.2.3 Effect of substrate to benzyl chloride ratio

The influence of substrate to benzyl chloride molar ratio was investigated by changing the molar concentration of the substrate, keeping the amount of benzyl chloride constant. The reaction was done at a temperature of 80°C, by adding 50 mg of CeFe (2%) for 2hours. The result is shown in the Fig. 4.4.

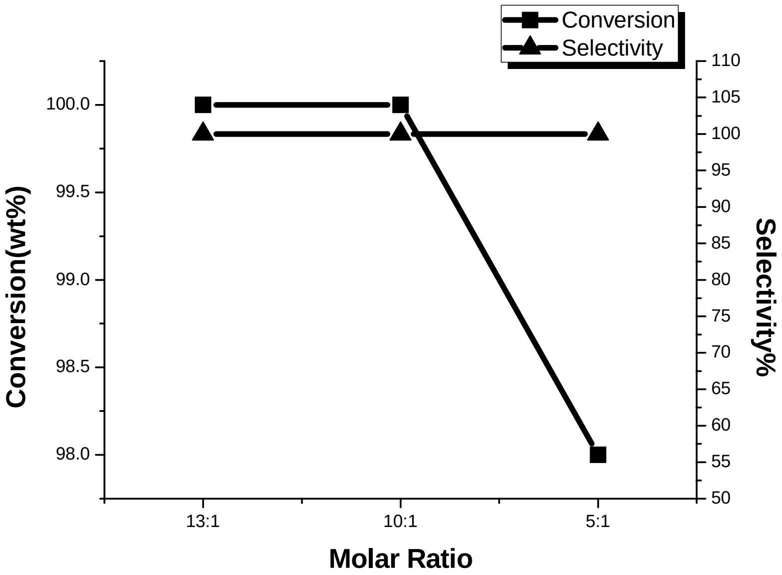


**Fig.4.4 Effect of molar ratio of substrate to benzyl chloride on benzylation of toluene.**

*Reaction conditions: catalyst CeFe (2%), catalyst weight 50mg, Time-2hrs, Temperature: 80°C*

As depicted from the figure, the ratio of the substrate to benzyl chloride is optimised to be 5:1 considering the conversion of benzyl chloride and also atom economy of the reactants. When ratio changes from 5:1 to 10: 1 the change in conversion is only 2%. Selectivity is always 100% to mono alkylated product.

### 4.2.4 Effect of Time

The reaction was carried out for 2 hrs to study the effect of time on conversion and selectivity. Results are shown in the Fig.4.5. The reaction was done with 50 mg of CeFe (2%) at a temperature of 80°C with toluene to benzyl chloride molar ratio of 5. When the reaction was conducted for 30 minutes the conversion was only 5.4 indicating an induction period essential for the reaction to proceed. After the induction period the conversion increases steadily to above 95%. Then it changes slowly. This clearly shows that the catalyst is modified during the induction period creating new active sites on the catalyst, probably by the HCl formed in the reaction, and this process of the catalyst activation is enhanced [21]. The temperature effect and the existence of an induction period indicate the possibility of redox or free radical mechanism.

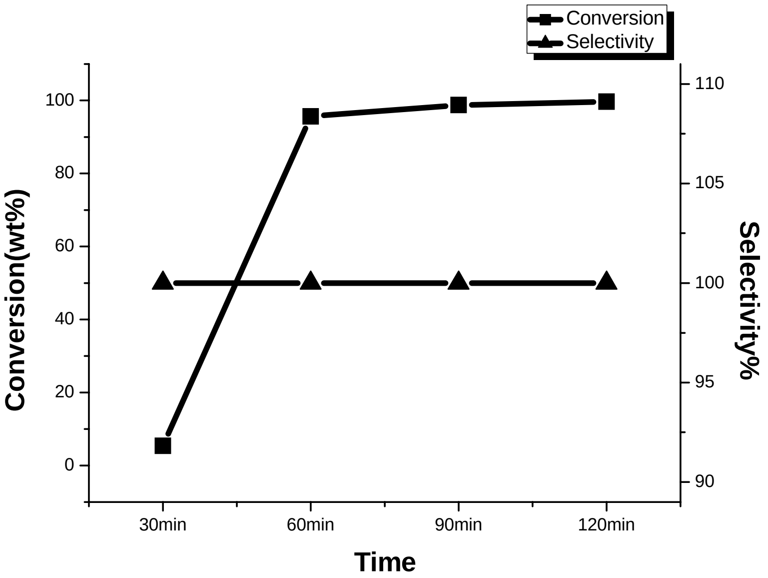


**Fig.4.5 Effect of Time on benzyl chloride conversion in benzylation of toluene**

*Reaction conditions: catalyst CeFe (2%), Catalyst weight 50mg, Temperature80°C, Ratio 5:1*

### 4.2.5 Optimised conditions

From the results of the studies on various parameters on benzylation of toluene by benzyl chloride, the optimized parameters are given in Table 4.1

**Table 4.1 Optimized Reaction conditions**

| Parameters | Optimized conditions |
|---|---|
| Weight of the catalyst | 50mg |
| Temperature | 80°C |
| Time | 2hrs |
| Substrate to B-Cl ratio | 5:1 |

## 4.3 Comparison of Catalysts

After the optimization studies, under the optimized conditions the catalytic activities of all the prepared systems were studied for the benzylation of toluene using benzyl chloride as the reagent. Under the same optimized conditions o-xylene and anisole are also benzylated using benzyl chloride. The results are given in the Table 4.2.

Table 4.2. Benzylation over transition metal modified ceria systems.

| Catalyst | Toluene | | o-Xylene | | Anisole | | |
|---|---|---|---|---|---|---|---|
| | Benzyl chloride conversion (Wt%) | | Benzyl chloride conversion (Wt%) | | B-Cl Conversion (Wt%) | %Selectivity | |
| | | | | | | o-pdt | p-pdt |
| **Without catalyst** | **4** | **% Selectivity** | **nil** | **% Selectivity** | **nil** | **-** | |
| Ce | 4.3 | 100 | 21 | 100 | 22 | 45 | 55 |
| CeFe(2%) | 99.7 | 100 | 100 | 100 | 93.9 | 46.8 | 53.2 |
| CeFe(4%) | 100 | 100 | 100 | 100 | 100 | 47.3 | 52.7 |
| CeFe(10%) | 100 | 100 | 100 | 100 | 100 | 47.3 | 52.7 |
| CeCr(2%) | 38.4 | 100 | 21.1 | 100 | 26.9 | 41.8 | 58.2 |
| CeCr(4%) | 45.2 | 100 | 15.9 | 100 | 47.5 | 43.5 | 56.5 |
| CeCr(10%) | 68.3 | 100 | 19 | 100 | 61.7 | 49.5 | 50.5 |
| CeMn(2%) | 42.3 | 100 | 18.1 | 100 | 38.1 | 51.2 | 48.7 |
| CeMn(4%) | 24 | 100 | 23.3 | 100 | 19.4 | - | 100 |
| CeMn(10%) | 27.5 | 100 | 16 | 100 | 28.7 | 47.5 | 52.5 |
| CeNi(2%) | 23.4 | 100 | 30.2 | 100 | 29.5 | 42.8 | 57.2 |
| CeNi(4%) | 39.8 | 100 | 25.8 | 100 | 27.7 | 44.3 | 55.7 |
| CeNi(10%) | 27.3 | 100 | 21 | 100 | 35.6 | 48.1 | 51.9 |
| CeCo(2%) | 32 | 100 | 15.7 | 100 | 39.1 | 29.8 | 70.2 |
| CeCo(4%) | 24 | 100 | 21 | 100 | 35.8 | 46.3 | 53.7 |
| CeCo(10%) | 24.5 | 100 | 33 | 100 | 23.4 | 43.7 | 56.3 |
| CeCu(2%) | 14.6 | 100 | 21 | 100 | 27.7 | 41 | 59 |
| CeCu(4%) | 28.3 | 100 | 26 | 100 | 35.6 | 43.4 | 56.6 |
| CeCu(10%) | 35.7 | 100 | 28.5 | 100 | 38.6 | 46.9 | 53.1 |

To determine the role of catalyst, the same reaction was carried in the absence of the catalyst. The desired product was not observed even after 40-45 minutes, which indicates that the catalysts exhibit a high catalytic activity in this transformation. Pure ceria gave low conversions than various metal modified samples. The metal modification improves the %conversion to a great extent. The increase in % conversion and activity may be attributed to the increase in the acid sites up on metal modification. The catalytic activities of the samples vary with variation in the metal percentages. In the case of each metal, as the metal percentage increases, the benzyl chloride conversion and the catalytic activity also changes. The same trend is observed for all the metals. This trend is illustrated in the Fig.4.6.1 to 4.6.3.

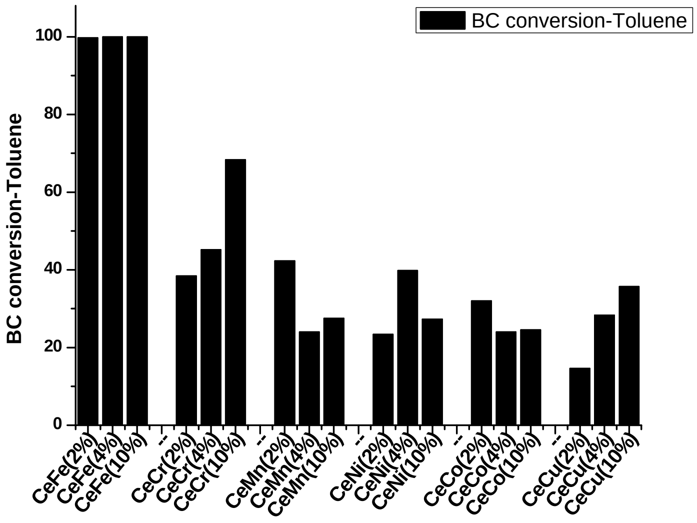


**Fig.4.6.1 B-Cl Conversion in benzylation of Toluene by different systems**

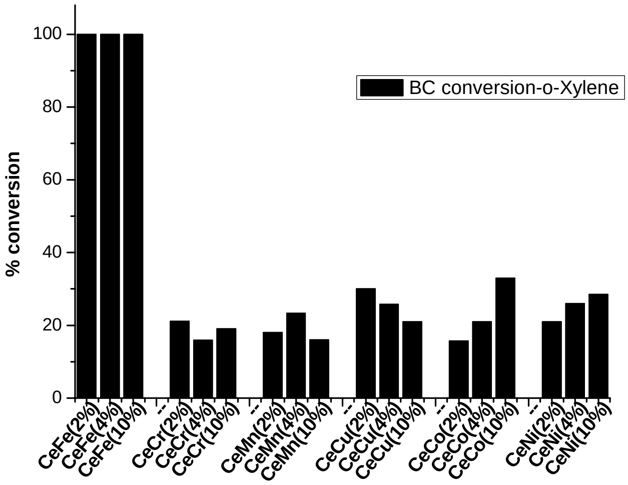


Fig.4.6.2 B-Cl Conversion in benzylation of o-xylene by different systems

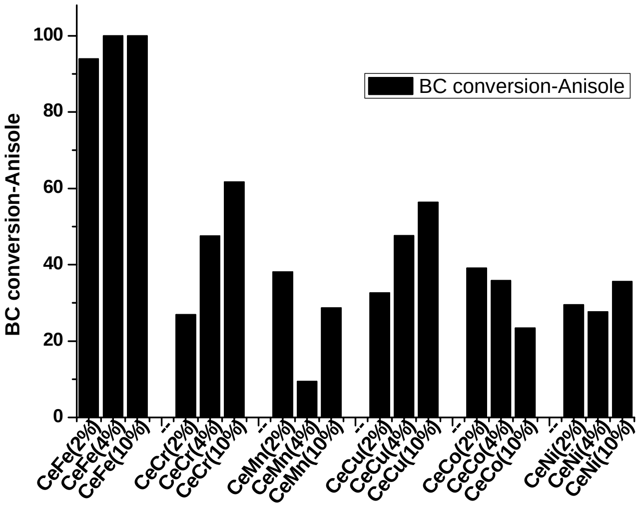


Fig.4.6.3 B-Cl Conversion in benzylation of Anisole by different systems

From Table 4.2, it is understood that among the various transition metals studied, Fe modified samples gave maximum conversion for toluene, o-xylene and anisole. This catalytic activity of Fe samples are greater than other metals like Cr, Ni, Cu etc. which have total acidity and α-methyl styrene selectivity (which is an indication of Lewis acidity) greater than that of Fe. Hence the high activity of Fe systems cannot not be explained on the basis of their Lewis acidity alone. This hike in the conversion points to the fact that benzylation activity of iron loaded systems cannot be explained on the basis of usual carbocation mechanism for alkylation reaction. It is reported that catalysts containing reducible cations like $Fe^{3+}$, $Cu^{2+}$ etc. exhibit high alkylation activity regardless their Lewis acidity [22]. When a redox mechanism is operating there will be homolytic fission of carbon- chlorine bond of the alkylating agent (benzyl chloride). The radicals so formed are powerful reductants, which would be readily oxidised to carbocations in the presence of reducible metallic $Fe^{3+}$. The mechanism is depicted in Fig.4.13. It may be assumed that the below 80°C, the energy for the homolytic rupture of carbon-chlorine bond may not be attained and therefore no reaction occurs below this temperature [23]. This may be the reason for no conversion at temperatures below 80°C.

Good correlation is obtained for benzyl chloride conversion and total acidity obtained from TPD of ammonia for benzylation of toluene, o-xylene & anisole. The results are illustrated in Fig4.7.1 to 4.9.2

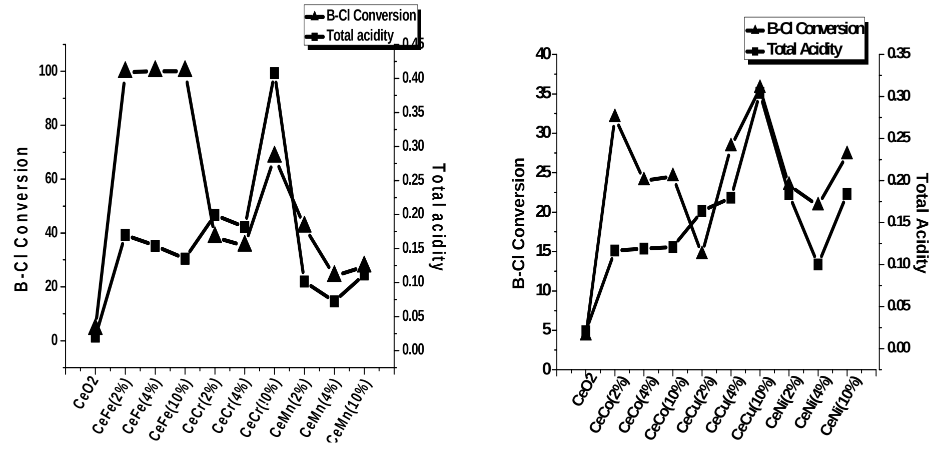


**Fig. 4.7.1 and 4.7.2 Correlation between total acidity from TPD of ammonia & B-Cl conversion in toluene benzylation**

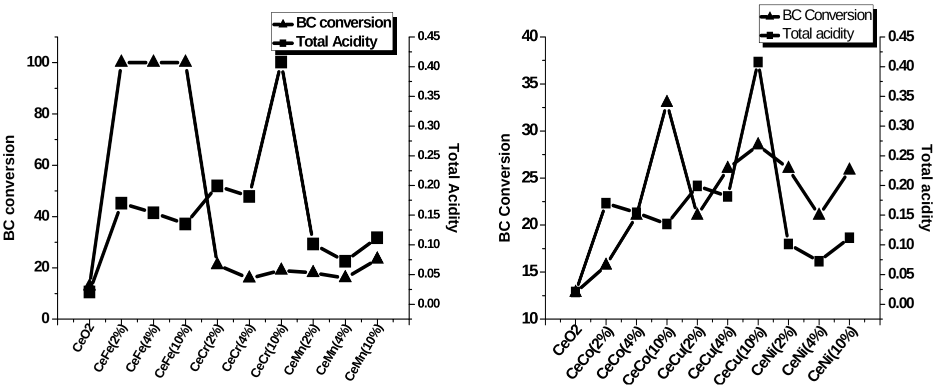


**Fig. 4.8.1 and 4.8.2** Correlation between total acidity from TPD of ammonia & B-Cl conversion in o-xylene benzylation

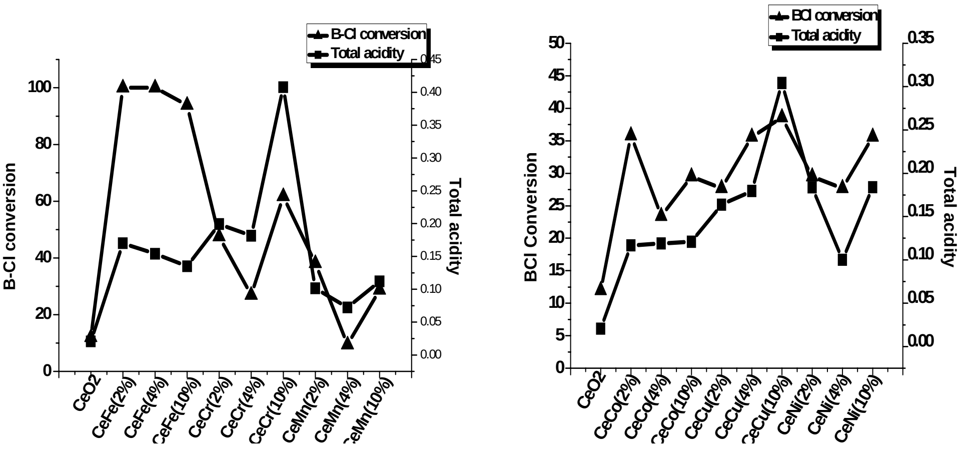


**Fig. 4.9.1 and 4.9.2** Correlation between total acidity from TPD of ammonia & B-Cl conversion in anisole benzylation

All prepared samples show high selectivity towards α-methyl styrene in vapour phase cumene cracking test reaction on acidity which is an indication of Lewis acid site availability on the catalyst surface. The involvement of Lewis acid sites in carbocation generation is well established. The correlation between the benzyl chloride (B-Cl) conversion in benzylation of toluene, o-xylene, and anisole with α-methyl styrene selectivity in vapour phase cumene cracking reaction are given in Fig.4.10.1 to 4.12.2

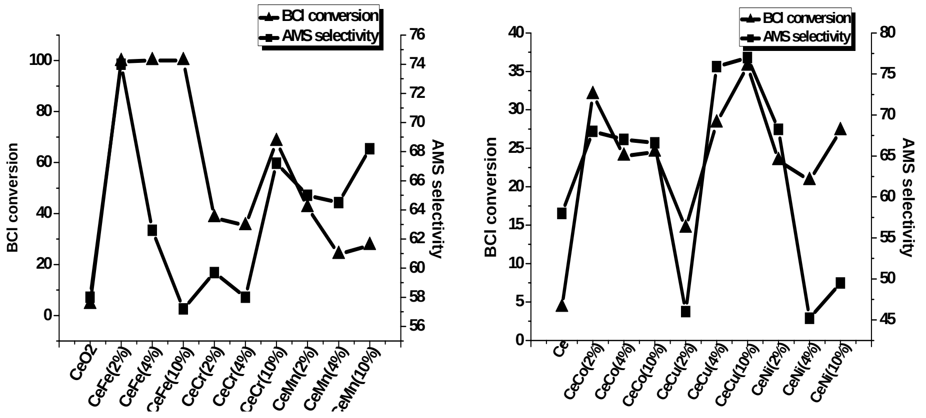


**Fig. 4.10.1 and 4.10.2 Correlation between α-methyl styrene selectivity from cumene cracking reaction & B-Cl Conversion in Toluene benzylation**

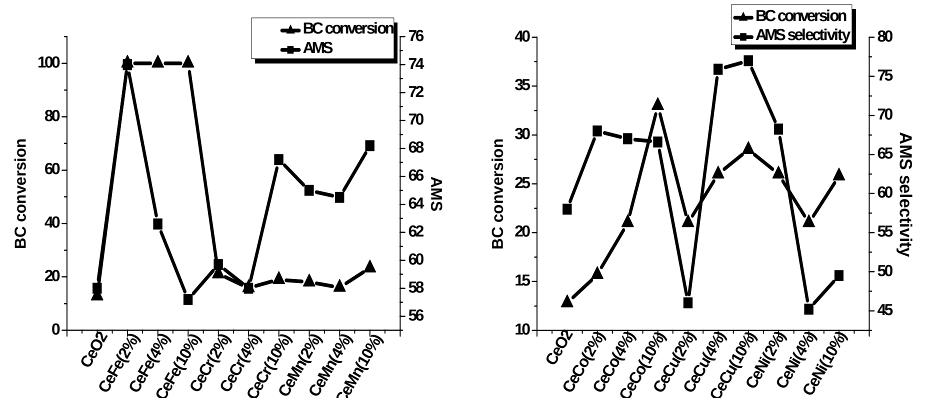


**Fig.4.11.1 and 4.11.2 Correlation between α-methyl styrene selectivity from cumene cracking reaction & B-Cl conversion in o-xylene benzylation**

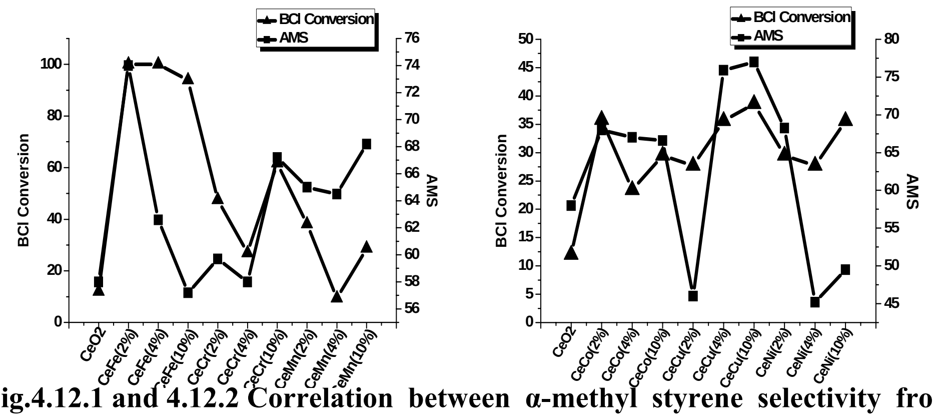


**Fig.4.12.1 and 4.12.2 Correlation between α-methyl styrene selectivity from cumene cracking reaction& B-Cl conversion in anisole benzylation**

The productivity of a catalyst can be described by the turn over number (or TON) and the catalytic activity by the turn over frequency (TOF), which is the TON per time unit. Catalyst activity = mmoles of reactant reacted/ Surface area of catalyst/time. The TON, TOF and catalyst activities of the prepared samples in liquid phase benzylation of toluene, o-xylene and anisole are given in the Tables 4.3 to 4.5.

**Table 4.3 Turn overs of different samples in the benzylation of toluene**

| Catalysts | Toluene | | |
|---|---|---|---|
| | TON[a] | TOF[b] ($h^{-1}$) | Catalyst Activity ($mmol/m^2/h$) |
| CeFe (2%) | 47800 | 23900 | 0.043 |
| CeFe (4%) | 24000 | 12000 | 0.043 |
| CeFe (10%) | 9600 | 4800 | 0.077 |
| CeCr (2%) | 17100 | 8550 | 0.013 |
| CeCr (4%) | 10100 | 5050 | 0.016 |
| CeCr (10%) | 12100 | 5150 | 0.03 |
| CeMn (2%) | 20000 | 10000 | 0.015 |
| CeMn (4%) | 5500 | 2750 | 0.008 |
| CeMn (10%) | 2500 | 1250 | 0.010 |
| CeCu (2%) | 12500 | 6250 | 0.007 |
| CeCu (4%) | 4020 | 2010 | 0.015 |
| CeCu (10%) | 3010 | 1505 | 0.0215 |
| CeCo (2%) | 16200 | 8100 | 0.010 |
| CeCo (4%) | 6078 | 3039 | 0.008 |
| CeCo (10%) | 2480 | 1240 | 0.0098 |
| CeNi (2%) | 7380 | 3690 | 0.011 |
| CeNi (4%) | 7160 | 3580 | 0.019 |
| CeNi (10%) | 3610 | 2305 | 0.014 |

*TON* = *(mmoles of reagent reacted/ mmoles of metal added) x 100*

*TOF* = *TON /hour*

*Catalyst activity* = *mmoles of reactant reacted/ Surface area of Catalyst / time*

The catalyst activities of the samples in benzylation of various aromatics are correlated with total acidity and are shown in the Fig. 4.13. The catalyst activities have good correlation with the total acidities of the samples calculated by temperature programmed desorption of ammonia. There is change in the catalyst activity and TON of the samples with change in metal concentration.

**Table 4.4 Turn overs of different samples in the benzylation of o-xylene**

| catalyst | o-Xylene | | |
|---|---|---|---|
| | TON[a] | TOF[b]($h^{-1}$) | Catalyst Activity ($mmol/m^2/h$) |
| CeFe (2%) | 50588 | 25294 | 0.043 |
| CeFe (4%) | 24571 | 12285.5 | 0.043 |
| CeFe (10%) | 9662 | 4831 | 0.082 |
| CeCr (2%) | 9550 | 4775 | 0.0074 |
| CeCr (4%) | 3707 | 1853.5 | 0.0057 |
| CeCr (10%) | 1729 | 864.5 | 0.0088 |
| CeMn (2%) | 8600 | 4300 | 0.006 |
| CeMn (4%) | 5566 | 2783 | 0.0085 |
| CeMn (10%) | 1528 | 764 | 0.006 |
| CeCu (2%) | 17200 | 8600 | 0.01 |
| CeCu (4%) | 7396 | 3698 | 0.014 |
| CeCu (10%) | 2408 | 1204 | 0.017 |
| CeCo (2%) | 7942 | 3971 | 0.0050 |
| CeCo (4%) | 5311 | 2655.5 | 0.0073 |
| CeCo (10%) | 3338 | 1669 | 0.0013 |
| CeNi (2%) | 10623 | 5311.5 | 0.013 |
| CeNi (4%) | 6526 | 3263 | 0.012 |
| CeNi (10%) | 3770 | 1885 | 0.01 |

**Table 4.5 Turn overs of different samples in the benzylation of anisole**

| catalyst | Anisole | | |
|---|---|---|---|
| | TON[a] | TOF[b]$(h^{-1})$ | Catalyst Activity $(mmol/m^2/h)$ |
| CeFe (2%) | 47500 | 23750 | 0.04 |
| CeFe (4%) | 25290 | 12645 | 0.043 |
| CeFe (10%) | 10120 | 5060 | 0.032 |
| CeCr (2%) | 12180 | 6090 | 0.0095 |
| CeCr (4%) | 10750 | 5375 | 0.017 |
| CeCr (10%) | 5585 | 2792.5 | 0.028 |
| CeMn (2%) | 18200 | 9100 | 0.014 |
| CeMn (4%) | 4630 | 2315 | 0.007 |
| CeMn (10%) | 2740 | 1370 | 0.011 |
| CeCu (2%) | 15880 | 7940 | 0.015 |
| CeCu (4%) | 10200 | 5100 | 0.02 |
| CeCu (10%) | 4426 | 2213 | 0.023 |
| CeCo (2%) | 19780 | 9890 | 0.0125 |
| CeCo (4%) | 9055 | 4527.5 | 0.0125 |
| CeCo (10%) | 2367 | 1183.5 | 0.0093 |
| CeNi (2%) | 14920 | 634.5 | 0.013 |
| CeNi (4%) | 7006 | 3503 | 0.014 |
| CeN i(10%) | 3601 | 1800.5 | 0.018 |

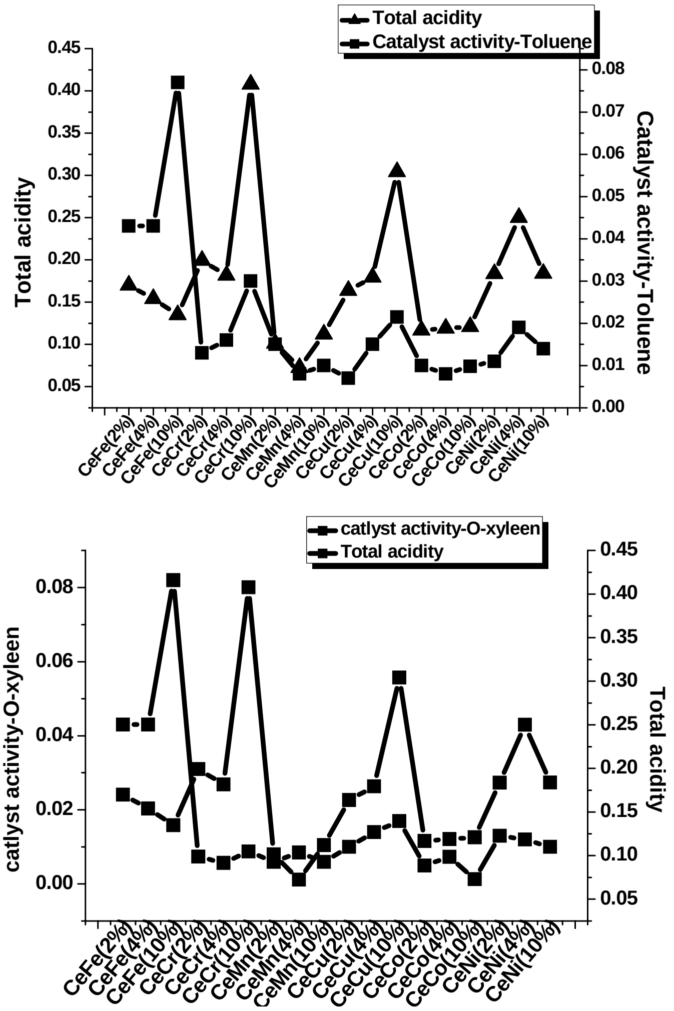


**Fig. 4.13 Correlation between catalyst activity and total acidity**

## 4.4 Mechanism of benzylation reaction

The reaction appears to proceed by an electrophile, which involves the reaction of benzyl chloride with the acidic oxide catalyst. The oxide catalyst polarizes the benzylating agent and in turn, produces an electrophile ($C_6H_5$–$CH_2^+$) [24, 25, 26)]. Thus the generated electrophilic species attacks the xylene ring, resulting in the formation of 3, 4-dimethyl diphenyl methane. Even though the catalysts have very low surface area and pore volume, the presence of strong as well as weak acid sites on the catalyst surface appears to be very important for the polarization of benzyl chloride into an electrophile ($C_6H_5$-$CH_2^+$) which then attacks the benzene ring resulting in the formation of dimethyl diphenyl methane [27]. Non-polar nature of the substrate molecules also supports the formation of the electrophilic species by adsorption of B-Cl molecule on the catalyst surface. A plausible mechanism for the reaction can be represented schematically as shown in Fig.4. 13.

The percentage conversions obtained in the case of iron loaded systems were much higher than that expected from its Lewis acidity. The high activity of iron systems, which does not commensurate with the acidity values, can be attributed to the redox or free radical mechanism (Fig.4.14). Choudary et al. [28] suggested the possibility of a redox mechanism for reducible cations when B-Cl was the alkylating agent. Considering all the aspects, we propose the existence of a redox or a free radical mechanism in the case of Fe loaded samples side by side with the involvement of Lewis acid sites. Radicals are powerful reductants, which can readily be oxidized to cations in the presence of reducible metal cations. Thus the high activity associated with these reducible cations involves the initiation of the reaction by the homolytic cleavage of the carbon-chlorine bond followed by the oxidation of the radical to the corresponding ion [29].

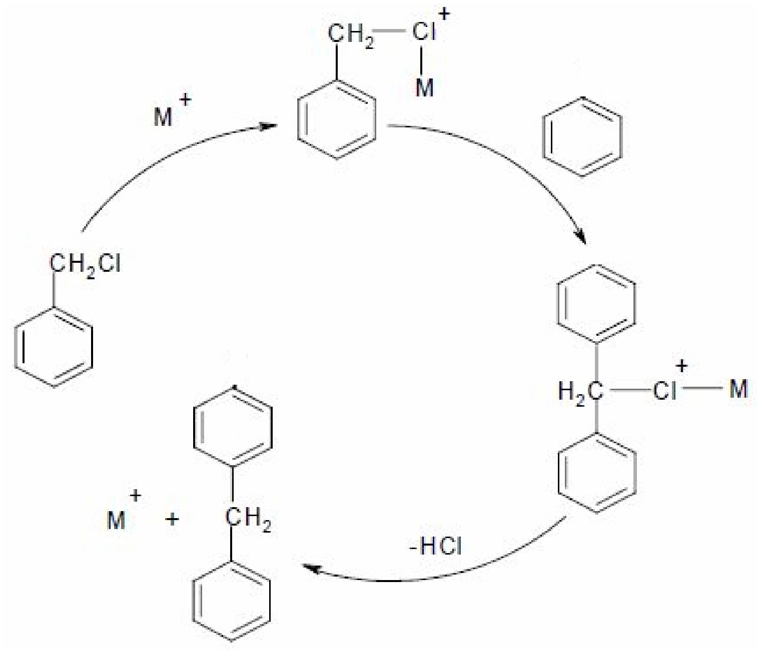


**Fig. 4.14 Mechanism of Friedel-Crafts benzylation using benzyl chloride showing the active involvement of Lewis acid site.**

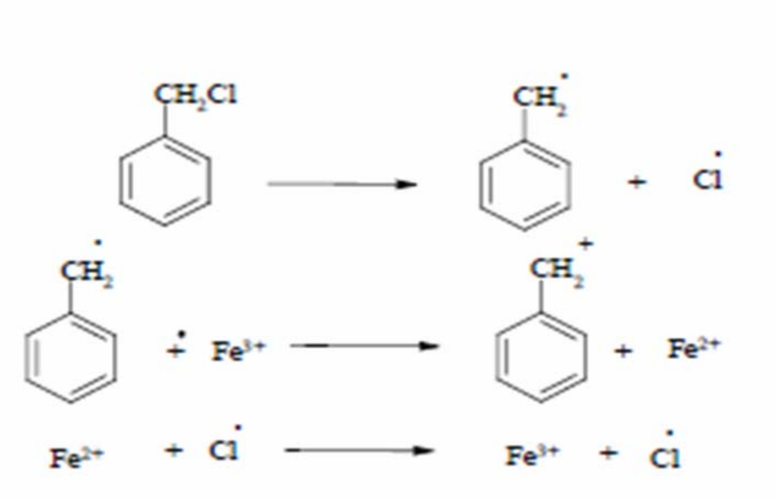


**Fig. 4.15 Free radical mechanism for benzylation of arenes.**

## 4.5 Metal Leaching studies

In the case of heterogeneous catalyst systems, metal leaching studies are essential because in some systems some metal ions will leach out from crystal lattice of catalyst and will homogeneously catalyse the reaction. For the leaching studies, the reaction was carried for a particular time and after that the catalyst was hot filtered off and the reaction was continued for another period without catalyst. Under optimized condition, in the presence of the catalyst (CeFe10%) the reaction was allowed to proceed for 30 minutes. Then the catalyst is filtered off and the reaction was allowed to proceed for 2 hours. The result of leaching studies is given in Table 4.3.

**Table 4.6 Results of leaching study**

| Catalyst | Time | % Conversion |
|---|---|---|
| CeFe (10%) | 30Min | 25.3 |
| | 2Hrs | 28 |

***Reaction conditions: catalyst CeFe (10%), catalyst weight 50mg, Temperature80$^o$C, Ratio 5:1***

Not much increase in the conversion was noticed after the removal of the catalyst confirming that there is no leaching of the metal ions during the reaction to the reactant system. This suggests that reaction proceed in a true heterogeneous manner.

## 4.6 Reusability

To study the reusability, the catalyst was removed from the reaction mixture after the reaction by filtration. It was thoroughly washed with acetone and dried in an air oven and activated for 3 hours. The same catalyst was used again for carrying out another reaction under the same reaction condition. The reaction was repeated up to 3 cycles. Fe catalyst was tested for the reusability and the results are given in Table 4.7.

**Table 4.7 Results of reusability study**

| Catalyst | No.of Cycle | % Conversion |
|---|---|---|
| CeFe (10%), | I | 100 |
| | II | 100 |
| | III | 98 |

*Reaction conditions: Catalyst CeFe (10%), Catalyst weight 50mg, Temperature 80$^o$C, Ratio 5:1*

From the results it is obvious that the catalyst is reusable. The catalyst can be regenerable and can be used again. This reusability regenerability, high selectivity, 100% conversion, moderate reaction temperature, and absence of solvent, etc. make this heterogeneous reaction an environment friendly one. Hence this solid acid catalyst can be used in efficient green chemical process for the manufacture of industrially important compounds used as pharmaceutical intermediates, heat transfer fluids, aromatic solvents, fragrances, monomers for polycarbonate resins and fine chemicals. Thus this Fe modified ceria catalyst gives a solution for the ceaseless search for greener chemical process which has become one of the most important tasks of today’s chemical researchers.

## 4.7 Conclusions

From the present study it can be concluded that

- On modification of mesoporous ceria with transition metals, the catalyst activity is very much improved. The catalyst activity& Turn over numbers which indicate the catalytic activity and productivity have good correlation with the total acidities of the samples.
- They are suitable solid acid catalysts for the liquid phase benzylation reaction. The most efficient catalysts among the prepared samples are iron modified ones. Exceptionally high activity in the case of iron systems proposed a free radical mechanism, which was confirmed by the effect temperature as well as the presence of an induction period for the reaction.
- The catalysts are regenerable and can be used again. This reusability regenerability, high selectivity, 100% conversion, moderate reaction temperature, and absence of solvent, etc. make these catalyst to use in a truly heterogeneous manner and makes the benzylation reaction an environment friendly one. Hence this solid acid catalyst can be used in efficient green chemical process for the manufacture of industrially important compounds.

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Chapter 5

# ACETALIZATION OF CYCLOHEXANONE

Contents

The synthesis of dimethyl acetals of carbonyl compound such as cyclohexanone has successfully been carried out by the reaction between cyclohexanone and methanol using different solid acid catalysts. The strong influence of the textural properties of the catalysts such as acid amount and adsorption properties (surface area and pore volume) determine the catalytic activity.

## 5.1 Introduction

Acids are the catalysts which are used most in industry, including the fields of oil refining, petrochemicals and chemicals. They are responsible for producing more than 1 $\times 10^8$mt/year of products. Among the first acid catalysts, the most commonly used were HF, $H_2SO_4$, $HClO_4$ and $H_3PO_4$ (in liquid form or supported on Keiselguhr). Solid acids have many advantages such as simplicity in handling, decreasing reactor and plant corrosion problems, and environmentally safe disposal [1]. Also, wastes and by-products can be minimized or avoided by developing cleaner synthesis routes [2]. On the other hand, any reduction in the amount of sulphuric acid needed and/or any simplification in handling procedures is required for risk reduction, economic advantage and environment protection. In addition, there is current research and general interest in heterogeneous systems because of the importance of such systems in industry and in developing technologies [3]. Very recently, many others have demonstrated that heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and minimization of chemical wastes as compared to the liquid phase counterparts [4]. The acetalization reaction is a process that is widely used in organic synthesis to protect the carbonyl group of aldehydes and ketones [5]. Afterward, acetals became important reactants for synthesis of enantiomerically pure compounds which were widely used as steroids, pharmaceuticals, and fragrances [6]. The title reaction is many times a requirement to protect carbonyl groups specifically during the manipulation of multifunctional organic molecules since dimethyl acetals display higher stability towards strong bases, Grignard reagent, lithium aluminium hydride, strong oxidants and esterification reagents than their parent carbonyl compounds [5]. 1, 2-Diacetals are efficient protecting groups for vicinal 1, 2-diol units in carbohydrates [7, 8]. In particular, protection of monosaccharide units as cyclohexane 1, 2-diacetals (CDA) offers rapid access to important building blocks for oligosaccharide synthesis [9]. S.V. Ley, Grice and co-workers reported the preparation, structure, and derivatization and NMR data of cyclohexane 1, 2-diacetal protected carbohydrates [7a, 10]. Previously, the catalysts used in the acetalization reactions were generally proton acids, Lewis acids, and a number of transitional metal complexes including Rh, Pd and Pt [11]. Although good results were obtained, the separation of the products from the catalyst system after the reaction was still difficult to overcome and the noble metal catalysts used were quite expensive and usually unstable [12]. Although many efficient and reliable reactions for the conversion of carbonyl compounds to their corresponding acetals have been reported, there are, however, some drawbacks such as long reaction times, tedious work-up and separation of catalyst, toxic metal waste, unwanted side reaction and nonselectivity regarding these methods. Therefore, design and synthesis of a catalytic system that may be stable, easily separable, and reusable has long been pursued. Furthermore, the basic requirements for achieving high catalytic activity, as it was reported in previous literature, were the presence of sufficient acidity and the existence of two adjacent acid sites to have the reactants in a mutually cis position [12] and all these studies offered us the possibility of designing suitable catalysts for this reaction. Zeolites, clays, sulphated metal oxides, and mesoporous materials provide a convenient catalytic route for protecting the carbonyl groups during organic synthesis.

Besides the interest of acetals as protecting groups of carbonyl compounds during organic synthesis, many of them have found direct applications as fragrances in cosmetics, food and beverage additives, pharmaceuticals, and polymer chemistry, medicinal and drug design chemistry. This reaction is extensively used in the synthesis of enantiomerically pure compounds [13] which find practical application in the fields of synthetic carbohydrates, food and beverage additives [14] steroids [15], pharmaceuticals and fragrances [16] among others. The methyl and ethyl acetals of n-octanal and n-decanal, for example, find widespread applications in perfume and flavour industries [17]. Sometimes, several acetals named as 'potential fragrances' are introduced into the different formulations and, at the time of contact with the skin, the products are hydrolysed and odorous compounds are released. The conversion of a carbonyl compound to its acetal alters its vapour pressure, solubility and aroma characteristics, and often results in flavour attenuation. For example, the propylene dioxy derivative of vanillin is commonly used as a vanilla flavour since it causes flavour attenuation [18].

The most general method for the synthesis of acetals is the reaction of carbonyl compounds with an alcohol or an ortho ester in the presence of acid catalysts [19]. The synthesis of dimethyl acetals of carbonyl compound cyclohexanone has successfully been carried out by the reaction between cyclohexanone and methanol using different solid acid catalysts. The commonly used acid catalysts include corrosive protic acids such as HCl, $H_2SO_4$ and Lewis acids such as $ZnCl_2$ and $FeCl_3$ [20, 21]. Homogeneous acid catalysts ranging from $Mg(ClO_4)_2$ [22], p-toluene sulphonic acid [23], and a series of cationic diphosphine Lewis acidic complexes of Pt (II), Pd (II), and Rh (III) [12a, 24] etc. have also been employed successfully for the generation of acetals. Gorla and Venanzi have described the basic structural requirements to achieve high activity of the catalysts [25].

However, acetalization procedures mentioned above require expensive reagents, tedious work-up procedure and neutralization of the strongly acidic media leading to the production of harmful wastes. Hence, these methods suffer limitations derived from high E-factors and low atom utilization as the catalysts are irreversibly lost. Furthermore, the formation of dimethyl acetals in homogeneous phase is often carried out by using trimethyl ortho formate as the reagent. Methanol is more desirable for this reaction. The choice of the catalyst is of prime importance in these environmentally conscious days. Green chemistry demands the replacement of highly corrosive, hazardous and polluting acid catalysts with eco-friendly and renewable solid acid catalysts. The use of heterogeneous solid catalysts in the organic synthesis and industrial manufacture of chemicals is interesting and important, since they provide green alternatives to homogeneous catalysts. This is particularly important in acid catalysis where solid acids are not only safe alternatives to hazardous and corrosive liquid acids, but also have many advantages, such as simplicity in handling, decreasing reactor and plant corrosion problems and environmentally safe disposal. Also, wastes and by-products can be minimized or avoided by developing cleaner synthesis routes. Any reduction in the required quantity of liquid acids and/or any simplification in treatment procedures are necessary for to reduce risk, create economic advantage and protect the environment. Environmentally benign solid acid catalysts such as various rare earths-exchanged Mg–Y zeolites, CeMg– Y and Ce-montmorillonite were revealed to be the most efficient catalysts for the acetalization reactions. Although significant progress has been achieved in improving the catalytic activity, selectivity, and reagent scope, in many cases, however, they require a high catalyst loading and suffer from catalytic activity losses during reuse. Therefore, there is still a need for a low loading, more economic, and environmentally benign solid catalysts [26]. Previously, the catalysts used in the acetalization reactions were generally proton acids, Lewis acids, and a number of transitional metal complexes including Rh, Pd, and Pt [11]. Although good results were obtained, the separation of the products from the catalyst system after the reaction was still difficult to overcome and the noble metal catalysts used were quite expensive and usually unstable [12a]. Therefore, to design and synthesize a catalytic system that may be stable, easily separable, and reusable has long been pursued. Furthermore, the basic requirements for achieving high catalytic activity, as it was reported in previous literature, were the presence of sufficient acidity and the existence of two adjacent acid sites to have the reactants in a mutually cis position [12a] and all these studies offered us the possibility of designing suitable catalysts for this reaction. Acetalization of cyclohexanone reached equilibrium within 60 min and the yields of acetal were 66.7% with CeMg–Y zeolite and 69.8% with $Ce^{3+}$ cation. Cyclohexanone reacted smoothly in methanol at room temperature with solid acid catalysts.

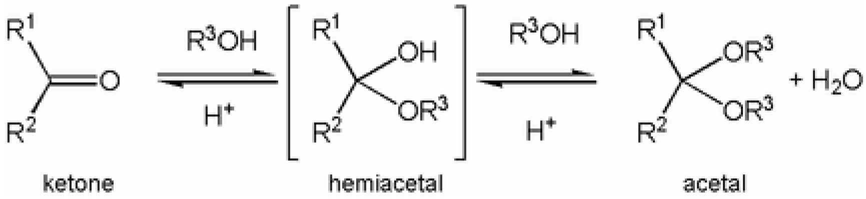

**Fig. 5.1 Pathways of acetalization of cyclohexanone**

## 5.2 Acetalization of ketones

Acetal or ketal formation is a reversible reaction, which proceeds by a two-step mechanism. Their formation is strongly affected by electronic and steric factors (12b).

The first step is the formation of hemiacetal, followed by the removal of a molecule of water. Formation of a cation from the protonated hemiacetal is the rate determining step of acetalization reactions. However, the protonation of hemiacetal is also a slow step and the reaction medium has to be sufficiently acidic to promote efficient protonation of hemiacetal. Also, the reaction medium must be polar enough to stabilize of the cation intermediate formed from hemiacetal.

In the mechanism presented below, cyclohexanone is first protonated by the Brönsted acid sites ($H^+$ ions of the catalyst) to produce the intermediate (2) which then combine with methanol to form the hemiacetal (4). Protonation of (4) leads to intermediate (5) which undergoes subsequent dehydration to give (6). Reaction of (6) with a molecule of methanol gives intermediate (7). Removal of a proton from (7) leads to the formation of the acetal (8).

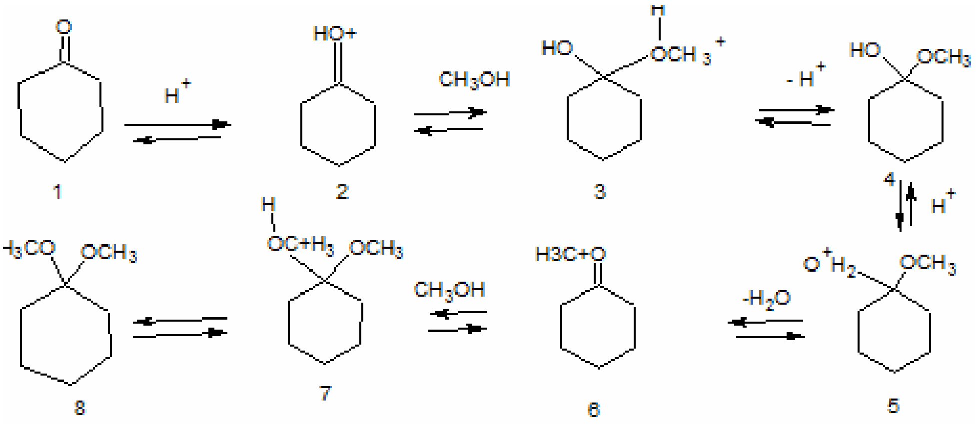

Fig. 5.2 Mechanism of acetalization of cyclohexanone

## 5.3 Reaction Procedure

In order to explore the influence of the modified mesoporous ceria catalyst on reaction, the reaction of cyclohexanone with methanol was chosen as a model reaction. Initially, the reaction was performed under catalyst free condition and no product formation was observed. Then, to obtain optimized reaction conditions, the acetalization reaction was performed with cyclohexanone and methanol using different amounts of modified mesoporous ceria catalyst at different temperatures. Cyclohexanone, purchased from Aldrich Chemical Company, USA and commercial-grade methanol (available from S. D. Fine Chemicals, India) were used as received. One-pot acetalization reactions of carbonyl compounds were carried out in a 50 mL glass batch reactor equipped with a magnetic stirrer, thermometer, water condenser and temperature controller. Samples were withdrawn every 30 minutes and at the end of the reaction and were analyzed with a Chemito GC1000 gas chromatograph equipped with a SE-30 capillary column (oven temperature 353–503 K, injector temperature 373 K and detector temperature 373 K). The products were further analyzed by GC-MS using a Shimadzu-5050 instrument provided with a 30 m HP-30 capillary column of cross linked 5% phenyl methyl silicone.

## 5.4 Optimization of Reaction Conditions

The reaction conditions play an important role in deciding the catalytic activity. The factors influencing the activity of catalyst in the reaction were studied by varying the reaction temperature, weight of the catalyst, molar ratio of cyclohexanone to methanol and time of reaction. The parameters were optimized and the best conditions were found.

### 5.4.1 Effect of Volume of methanol on cyclohexanone conversion

Fig.5.3. shows the effect of molar ratio of cyclohexanone to methanol on cyclohexanone conversion. A number of experiments were done to

study the effect of molar ratio of cyclohexanone to methanol. Molar ratio of the reactants plays a major role in the rate of reaction. The conversion of cyclohexanone increases with the increase in the molar volume of methanol. When volume of methanol is 10 ml conversion is maximum and then it is getting decreased. The conversion changes from 29% to 60.2 % when the molar ratio changes from 1: 05 to 1:10. Further increase in molar ratio causes a decrease in the conversion

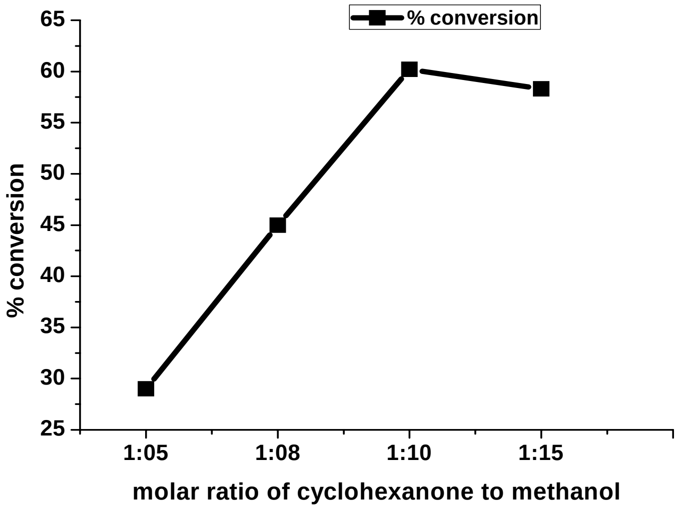

**Fig.5.3 Effect of molar ratio on conversion of cyclohexanone**

*Reaction conditions: Catalyst-0.05g CeFe (10%), Temperature-70$^o$C, Time -30min.*

### 5.4.2 Temperature

The conversion of cyclohexanone depends very much on temperature. At room temperature there was no reaction. As the temperature is increased and reached 70$^o$C the conversion became appreciable. Further increase in temperature caused an increase in the conversion and it reaches maximum at 80$^o$C but the boiling of methanol takes place. Beyond 80$^o$C the rate of reaction was decreased. So the temperature for the reaction was selected as

70°C. At all temperatures the sole product was dimethyl acetal. The result of the study of temperature dependence of the reaction is shown in Fig 5.4.

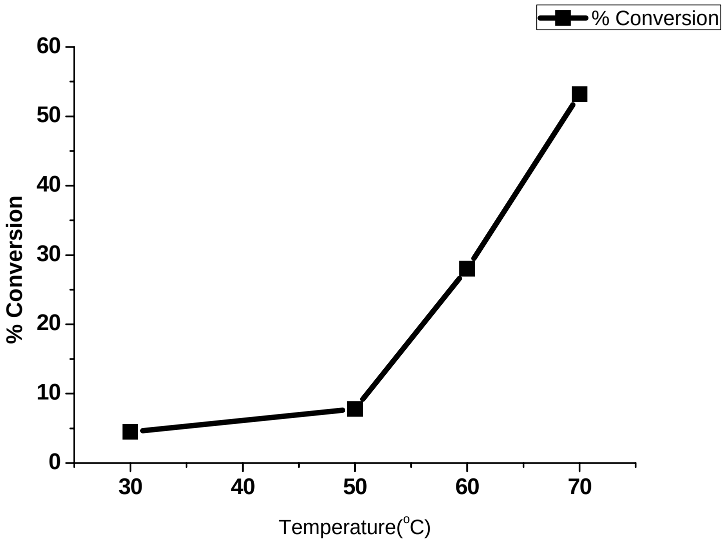

**Fig.5.4 Effect of Temperature on conversion of cyclohexanone**
*Reaction conditions: Catalyst-0.05 g CeFe (10%), Time -30min*

### 5.4.3 Weight of the catalyst

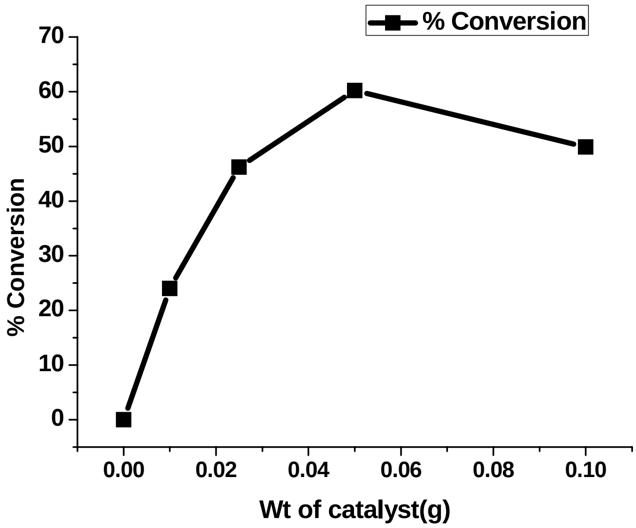

**Fig.5.5 Effect of wt. of catalyst on conversion of cyclohexanone**
*Reaction conditions: Volume of methanol-10ml,*
*Catalyst- CeFe (10%), Temperature- 70°C, Time -30min.*

In heterogeneous catalysis weight of the catalyst plays an important role in influencing the rate of a reaction. The acetalization of cyclohexanone was repeated with different weights of CeFe (10%) catalyst at 70°C, using 10 ml of methanol, to optimize the catalyst weight. The reaction was conducted for 30minutes and the product collected was analysed. Without the catalyst, reaction was at a negligible rate. As the weight of catalyst is increased the reaction rate is also increased. Conversion is maximum with 0.05 g of the catalyst and then it is decreased. So 0.05g of catalyst was used for further reaction. The Fig. 5.5 shows that there was no conversion in the absence of catalyst. As the amount of catalyst increases, the rate of reaction also increases. It is very much noticeable that very small amount of the mesoporous ceria based catalyst is enough the reaction rate to increase from zero to 60%. With 0.05g catalyst the rate reaches maximum but after that there is a small decrease when the weight of the catalyst is doubled to 0.1g. So the weight was optimized as 0.05g.

### **5.4.4 Time of reaction**.

To study the effect of reaction time on the reaction rate the reaction was done for 2hours at 70°C with 0.05g of CeCr (10%) using 1:10 molar ratio of cyclohexanone to methanol.

Fig. 5.6 shows that at 15 minutes the conversion of cyclohexanone was very low (48.5%). At 30 minutes it is increased to 53.5 %. Then it decreases till 1hour then it remains almost constant. Decrease in the catalytic activity after 30 minutes may be due to high adsorption of bulky reaction products and remain constant may be because of the lower diffusion rate of these bulky groups. The products may be adsorbed by the catalyst resulting in blocking of the pores or active sites leading to the loss of catalytic activity.

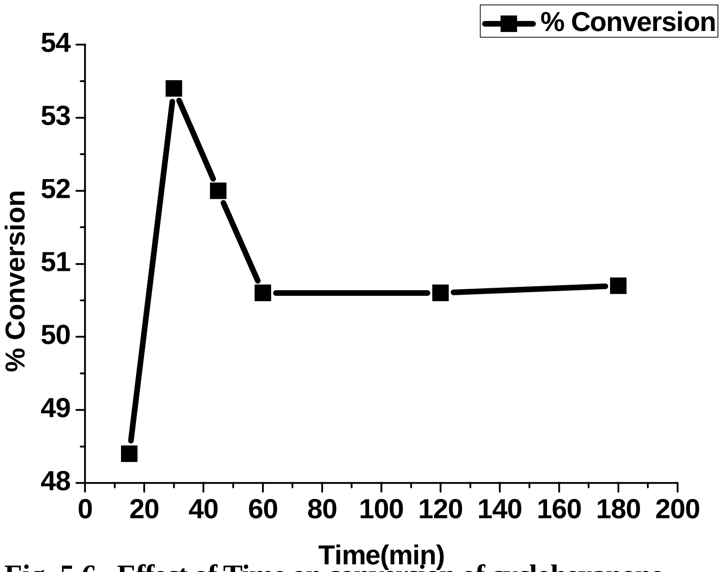

**Fig. 5.6 Effect of Time on conversion of cyclohexanone**

*Reaction conditions: Volume of methanol-10ml, Catalyst-0.05g CeFe (10%), Temperature- 70$^o$C.*

### 5.4.5 Leaching Test and Recycling

Metal leaching studies give the information about the nature of reaction. To test the heterogeneity of the catalytic system, the leaching test was performed. For this the catalyst was removed from the reaction mixture by filtration after a small interval after the reaction has proceeded. Then the reaction was allowed to proceed again without the catalyst and the % conversion of cyclohexanone before and after the filtration was analysed using GC. The reaction was carried out at 70$^o$C, using CeCr (10%) keeping the molar ratio of cyclohexanone to methanol 1:10 for 15 minutes. Then the catalyst is filtered off and again the reaction mixture was allowed to proceed under the same condition for 15 more minutes. It was found that after filtration of the catalyst, the filtration liquor reacted much more slowly and at a similar rate to the reaction taking place in the absence of the catalyst (Table5.1, Entry2), indicating that no leaching of the active catalytic species occurred during the reaction.

After filtration, the catalyst was washed with methanol and dried before the next cycle. The catalyst was found to be reusable for consecutive cycles without any significant loss of activity. The conversion was analysed. The result is given in the Table 5.3.

**Table 5.1 Influence of metal leaching in acetalization of cyclohexanone with methanol**

| Time (min) | Conversion (%) |
|---|---|
| 15 | 48.4 |
| 30* | 49 |

*Catalyst: 0.05g CeCr (10%), Temperature: 70$^o$C, Cyclohexanone to methanol molar ratio: 1:10*

*After filtration

**Table 5.2 Optimized Reaction conditions for acetalization of cyclohexanone**

| Parameters | Optimized conditions |
|---|---|
| Temperature | 70$^o$C |
| Cyclohexanone-Methanol Ratio | 1:10 |
| Catalyst Amount | 0.05g |
| Time | 30 min |

## 5.5 Catalytic Activity of prepared samples

**Table 5.3 Catalytic activities of different prepared catalysts**

| Catalyst | Conversion of cy. hexanone (%) | TON[a] | TOF[b] |
|---|---|---|---|
| $CeO_2$ | 12 | - | - |
| w.c | 4 | - | - |
| CeFe (2%) | 56.4 | 318.5 | 637 |
| CeFe (4%) | 57 | 160.9 | 321.8 |
| CeFe (10%) | 64 | 72.3 | 144.6 |
| CeCr (2%) | 28 | 141.5 | 283 |
| CeCr (4%) | 33.7 | 85.1 | 170.2 |
| CeCr (10%) | 53.4 | 53.9 | 107.8 |
| CeMn (2%) | 38.5 | 205.3 | 410.6 |
| CeMn (4%) | 20.7 | 55.2 | 110.4 |
| CeMn (10%) | 29.4 | 31.3 | 62.6 |
| CeCo (2%) | 39.6 | 223.6 | 447.6 |
| CeCo (4%) | 29.1 | 82.2 | 164.4 |
| CeCo (10%) | 34.5 | 26.4 | 52.8 |
| CeNi (2%) | 33.3 | 188 | 376 |
| CeNi (4%) | 32.5 | 91.8 | 183.6 |
| CeNi (10%) | 33.2 | 37.5 | 75 |
| CeCu (2%) | 36 | 230.4 | 460.8 |
| CeCu (4%) | 38.1 | 121.9 | 243.8 |
| CeCu (10%) | 35.7 | 45.7 | 91.4 |

*a- TON = (mmoles of reagent reacted/ mmoles of metal added) x 100*
*b- TOF = TON / time (h)*

Acetalization of cyclohexanone was carried out over all the prepared catalyst systems using methanol under the optimized conditions. In all the cases the corresponding diacetal was obtained as a single product with high yield. In a typical run, 10 ml of 1:10 mixture of ketone and methanol was stirred with 50 mg of pre-activated catalyst, at 70$^{o}$C for 30 minutes.

For a comparison of catalytic activity of mesoporous ceria modified by different transition metals as catalyst for acetalization of cyclohexanone, reaction was studied both in presence of catalysts and without catalyst. A comparative evaluation result obtained is given in the Table 5.3.

It is noticeable that a negligible conversion was obtained for blank reaction. Pure Mesoporous ceria gave very low conversion under the specified reaction conditions. Modification with different transition metals increases the activity in acetalization reaction. All the modified ceria catalysts produced dimethyl acetal as the only product during the reaction. The highest activity was shown by 10% iron incorporated mesoporous ceria system.

From the reaction mechanism, it appears that the reaction proceeds with the formation of very bulky intermediates and a microporous material like zeolite may be less reactive in comparison to a mesoporous material. It is not only the acidic structure of the catalysts which determine the acetalization ability to a greater extent but also the diffusional properties of the catalytic systems are the deciding factor in the acetalization reaction of ketones. The activity of catalyst towards the acetalization reaction does not require strong acidic sites [16a]. As pointed out by Corma and co-workers the pore diffusion limitation imposed by larger molecular sizes (0.75nm for cyclohexanone as determined by the energy minimization program) of the reactant played an important role during the acetalization reaction using solid acid catalysts [1, 27]. In the case of cyclohexanone; the distance between oxygen and the most distant hydrogen is 0.51 nm; the van der

Waals radius of oxygen is 0.14, and that of hydrogen is 0.1 nm leading to an effective end-to-end distance of 0.75 nm. Its volume is estimated at 38.351 $nm^3$ [28]. Enhancement in catalytic activity could be explained in terms of improvement in textural and structural properties. Enhancement in the total pore volume could provide a better diffusional pathway for the bulky acetals. It appears that the acid structural properties and the diffusional properties of the catalytic systems are the deciding factor in the acetalization reaction of ketones.

The enhancement in catalytic activity could be explained in terms of improvement in textural and structural properties. Enhancement in the total pore volume could provide a better diffusional pathway for the bulky acetals. The enhanced formation of acetal over transition metal modified mesoporous ceria could also be explained as follows. In general transition metal modified mesoporous ceria possess much more amounts of weak plus medium acid sites and an assembly of these weak acid sites may act as an effective/strong acid site. A reasonable hypothesis is that all the surface hydroxyl groups on the pore wall of the catalyst point to the centre of each pore, and thus they could work as a group. Such an assembly might induce efficient catalysis despite the low acidity of each -OH group [29]. In the case of modified samples, the surface hydroxyl groups provide most of the weak acid sites. The bigger pore size of catalyst samples over zeolites promotes the rate of diffusion of the bulky products through the channels. The rate determining step of acetalization is the formation of a cation from the protonated hemiacetal. Lin and co-workers proposed that the bulkiness of hemiacetal of acetophenone might prevent the bulky $CH^+$ $(OCH_3)$ from attacking its carbonyl carbon shifting the rate determining step during the acetalization with tri methoxy ortho formate [30]. Hence, we conclude that the comparative low activity of acetophenone and benzophenone might be due to two reasons: (1) the bulkiness of hemiacetal might prevent the attack of the $CH_3OH$ on the carbonyl carbon atom there by effecting a change in the rate-determining step (2). The electron withdrawing power of phenyl group reduces the easy release of the pair of electron on the carbonyl carbon during the reaction. But we cannot over emphasize the role of molecular size on reactivity since it is known that cyclohexanone is more reactive. The method developed by us does not involve additives and the catalysts can be recycled without loss of activity. Removal of water is not warranted in these reactions.

We have prepared 19 different catalyst samples. For the comparison of catalyst composition, from the product yield and considering the reaction as pseudo unimolecular, the intrinsic rate constants in the units of $\min^{-1}m^{-2}$ was determined for each catalyst sample using the formula,

$$k(\min^{-1}\ m^{-2}) = \frac{2.303}{twA}\log\frac{100}{100\text{-}\%\ \text{yield}}$$

Where

t: Time of the reaction in minutes,
w: Weight of the catalyst (g), and
A: BET surface area of the catalyst ($m^2/g$).

The rate constants of different samples are given in the Table 5.4.

**Table 5.4 Rate constants of acetalization of cyclohexanone using different catalyst systems**

| Catalyst | Rate constant x$10^{-3}$ ($min^{-1}m^{-2}$) |
|---|---|
| Ce | 0.05 |
| CeFe (2%) | 2.96 |
| CeFe (4%) | 3.32 |
| CeFe (10%) | 7.5 |
| CeCr (2%) | 1.77 |
| CeCr (4%) | 2.29 |
| CeCr (10%) | 4.37 |
| CeMn (2%) | 2.34 |
| CeMn (4%) | 1.28 |
| CeMn (10%) | 2.12 |
| CeCo (2%) | 2.48 |
| CeCo (4%) | 1.8 |
| CeCo (10%) | 2.59 |
| CeNi (2%) | 2.62 |
| CeNi (4%) | 2.89 |
| CeNi (10%) | 3.15 |
| CeCu (2%) | 3.62 |
| CeCu (4%) | 3.99 |
| CeCu (10%) | 4.08 |

The data reveal that the effect of modification of ceria with transition metals enhances its catalytic activity to a large extent. But the effect on catalytic activity by different metals is not alike. Different metals show different trend in the enhancement of catalytic activity. From the table it is evident that on incorporation of successive amounts of iron, chromium, copper and nickel the activity increases in a similar manner. For manganese and cobalt there is a decrease in activity initially upon loading then it is increased.

### 5.5.1 Correlation between acidity and cyclohexanone conversion

Acetalization reaction being an acid catalysed reaction, the difference in the activities of the catalysts can be attributed to their difference in the acidity values. Fig.5.7. shows that the conversion of cyclohexanone upon acetalization, using different systems are in agreement with sum of weak and medium acidity as measured by ammonia TPD studies. The strong influence of textural properties of the catalysts such as acid amount and adsorption properties (surface area and pore volume) determine the catalytic activity. The reaction requires active sites with considerable acid strength. In addition to the acid strength, the pore volume, pore sizes and their distribution in the catalyst are responsible for their activity in the reaction.

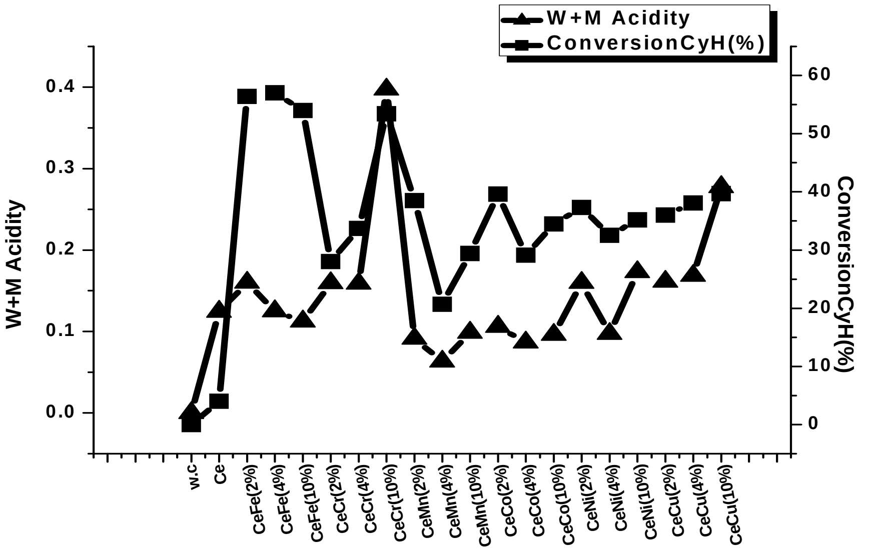

**Fig.5.7 Catalytic activity correlated with sum of weak and medium acid sites obtained from TPD of ammonia**

## 5.6 De-protection reaction (Hydrolysis of dimethoxy cyclohexanone)

The introduction and removal of protecting groups can play an important role in organic and natural product synthesis [31]. A major challenge in a multistep synthesis is to protect a carbonyl group from nucleophilic attack until its electrophilic properties of carbonyl can be exploited. Thus, regeneration of the parent carbonyl compound is a key step in such reactions. A number of acidic aqueous media, [32] acidic non-aqueous media [33] and non-acidic [34] methods have been reported for oxidative cleavage of acetals and ketals to the respective carbonyl compounds. However, some of the methods have limitations including severe reaction conditions, low yields of the products, unavailability and instability of the reagents, the requirement for aqueous reaction conditions and tedious work-up. Therefore, introduction of new methods and inexpensive reagents for such transformation is still in demand. De-protection is often performed by acid-catalyzed trans acetalization in acetone (in excess or as solvent), or hydrolysis in wet solvents or in aqueous acid. A convenient de-protection of acyclic and cyclic o, o -acetals and o, o-ketals is achieved in excellent yields within minutes under neutral conditions in the presence of a catalytic amount of iodine [35]. The electrophilicity of the carbonyl group is a dominant feature of its extensive chemistry. A major challenge in multistep synthesis is to shield a carbonyl from nucleophilic attack until its electrophilic properties can be exploited. For this reason the protection and deprotection of the carbonyl functional group remain crucial challenges to organic chemists. Experience shows that the critical parameters are generally the stability and the cleavage of the protecting group rather than its introduction. As with most of the protecting groups, many methods are available for the deprotection of acetals and ketals [36]. Now we wish to report a convenient method for deprotection of acetals or ketals. Hydrolysis of acetal was performed at $70^{o}C$ in the presence acetone-water mixture in the ratio 20:1. The reaction was conducted for 30 minutes by adding 10 ml of the acetone – water mixture.

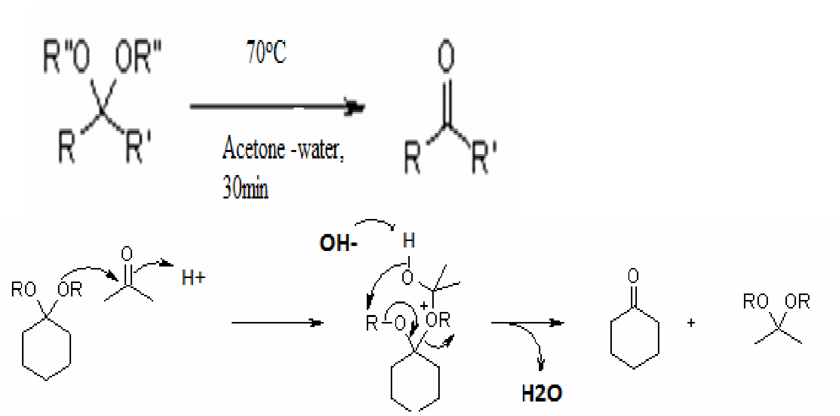

Fig.5.8 Mechanism of hydrolysis of dimethoxy cyclohexanone

## 5.7 Catalytic Activity of prepared samples in deacetalization of acetals

| Catalyst | %Deacetalization |
|---|---|
| CeFe (2%) | 100 |
| CeFe (4%) | 100 |
| CeFe (10%) | 100 |
| CeCr (2%) | 100 |
| CeCr (4%) | 98 |
| CeCr (10%) | 98.2 |
| CeMn (2%) | 98.3 |
| CeMn (4%) | 100 |
| CeMn (10%) | 98.9 |
| CeCo (2%) | 100 |
| CeCo (4%) | 100 |
| CeCo (10%) | 100 |
| CeNi (2%) | 100 |
| CeNi (4%) | 100 |
| CeNi (10%) | 100 |
| CeCu (2%) | 100 |
| CeCu (4%) | 100 |
| CeCu (10%) | 100 |

A cheap and easy procedure for the effective conversion of acetals and ketals to their corresponding carbonyl derivatives has been achieved here. The low cost and availability of the reagents, easy procedure and work-up make this method attractive for the large-scale operation. The high yields, the observed selectivity, the very gentle reaction conditions, and the almost neutral pH make this procedure particularly attractive for multistep synthesis.

## 5.8 Conclusion

In conclusion, we introduced a mild and selective reagent for the oxidative cleavage of acetals under aqueous and heterogeneous conditions. The stability, simple work-up and high yields of the products are among the advantages of this procedure which make it an attractive supplement to the present reported methods.

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Chapter 6

# OXIDATION OF ETHYL BENZENE

Contents

Recently there has been an increased interest in the development of clean and economical processes for the selective oxidation of ethyl benzene to the higher value added product acetophenone. The current industrial production of acetophenone is via the oxidation of ethyl benzene with molecular oxygen using cobalt cycloalkane carboxylate or cobalt acetate as catalyst in acetic acid solvent. This method suffers from its corrosive form and environmentally unfriendly nature. For the present investigation, oxidation of ethyl benzene was carried out in liquid phase using the mesoporous ceria and different transition metals modified ceria systems using tert-butyl hydroperoxide (TBHP) as the oxidizing agent. The reaction was studied at different temperatures to find out the kinetic parameters of the optimized catalyst.

## 6.1 Introduction

One of the foremost challenges currently facing the chemical industry is the need for alternative production technologies that are cleaner, safer, and environmentally friendly. Processes should be efficient both in terms of economy and energy consumption. Catalytic oxidation of hydrocarbons in general is employed in the manufacture of fine chemicals. The selective catalytic oxidation of organic compounds using environmentally friendly and cheap oxidants, such as molecular oxygen and aqueous $H_2O_2$, and a heterogeneous, easily recyclable catalyst is a challenging goal of the fine chemical industry [1]. Site isolation of discrete redox metal centres in inorganic matrices can afford oxidation catalysts with unique activities and selectivity by circumventing the oligomerization of the active monomeric species. One way of designing stable, solid catalysts with unique activities is through incorporation of redox metal ions or complexes into the framework or cavities of the molecular sieves.

Autoxidation reactions are very important milestones in the development of new petrochemical processes. These kinds of reactions use the most abundant and cheapest oxidant that minimizes the production and use of pollutants. The use of mesoporous materials is recommended highly if one oxidizes organic compounds of large molecular sizes with a bulky oxidant such as tert-butyl hydroperoxide (TBHP). Side chain oxidation of alkyl aromatics using cleaner peroxide oxidants catalysed by heterogeneous catalysts still attracts interest. Classical laboratory procedures preferably use stoichiometric oxidants such as permanganates and dichromate, which are hazardous [2]. Hence there has been an interest to develop eco-friendly catalysts for the oxidation of alkyl aromatics. As these reactions follow a complex radical mechanism, it is difficult to reach high selectivity at high conversion levels. The development of catalytic systems that allows good yields could be a great challenge in the “green chemistry”. Oxygenated products are the required intermediates for many chemical feed stocks, agrochemicals, fragrances, pharmaceuticals, and polymers, but traditional methods for their preparation often require stoichiometric amounts of Cr(VI), Mn(VII) or Os(VIII) that generate large quantities of toxic metal waste [3]. A substantial amount of research was focused on the homogeneous catalytic oxidation of alkyl aromatic substrates with cobalt salts and dioxygen under corrosive conditions [4]. But a more environmentally benign and selective catalytic process is clearly desirable. Metal supported heterogeneous catalysts that can operate in conjunction with an amenable oxidant in the liquid phase are advantageous in that they are recoverable and have minimal environmental impacts [5]. Effective utilization of ethylbenzene, available in the xylene stream of the petrochemical industry to more value added products is an interesting proposition. Well known are the isomerization of ethylbenzene to xylenes and dehydrogenation to styrene monomer. Oxidation of ethylbenzene has not drawn much attention due to the complexity of the products [6].

The selective catalytic oxidation is the main route to obtain monomers and intermediates for organic synthesis. The catalysts used are solids, most often mixed oxides with elements of different oxidation states, with redox properties. The lattice oxygen is inserted in the hydrocarbon molecule while the so-reduced solid is oxidized by the gaseous oxygen. This mechanism is described by Mars and van Krevelen as a two steps mechanism: the first one involves the hydrocarbon oxidation by lattice oxygen and the second one, the catalyst re-oxidation by gaseous oxygen. In chemical processes where catalytic reactions are involved, several strategies can be taken in order to enhance efficiency, energy balance, environmental aspects and the economics of the process. In view of these issues, the improvement of the catalyst physico-chemical properties, in order to extend the scope of the applications of existing catalysts are of high interest. Oxidation of ethyl benzene to different products can take place in two ways. One is the aromatic ring hydroxylation under which the hydroxylation at the para position is preferred to some extent to ortho position. The other is the side chain oxidation at primary and secondary carbon atoms. The primary and secondary carbinols formed from the side chain oxidation undergo further oxidation to the respective aldehydes and ketones. The pathways of ethyl oxidation are shown in Fig. 6.1.

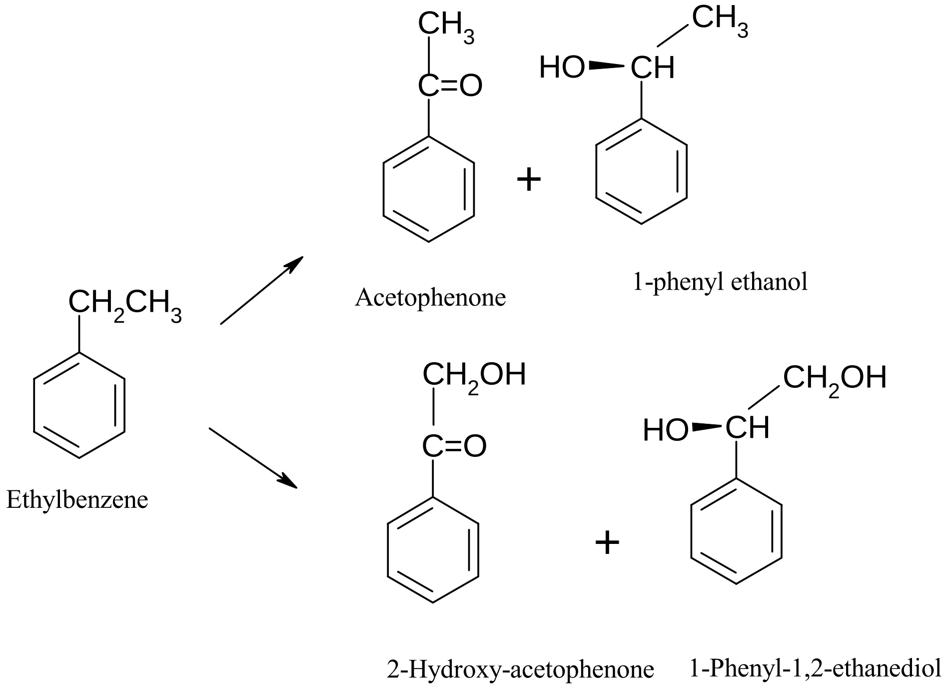

**Fig.6.1 Reaction Scheme for ethylbenzene oxidation**

Production of acetophenone, which is used as a component of perfumes and as an intermediate for the manufacture of pharmaceuticals, resins and alcohols is an important reaction in organic chemistry [7]. The presence of molecular oxygen or single oxygen donors such as tert-butyl hydroperoxide (TBHP) for the oxidation of alkanes to ketones are shown to be important [8]. Earlier, synthesis of acetophenone was performed using stoichiometric quantities of oxidizing agents like $KMnO_4$ or $K_2Cr_2O_7$, or via Friedel–Crafts acylation reaction of aromatics by acid halide/anhydride, using stoichiometric amounts of corrosive $AlCl_3$ catalyst. The current industrial production of benzylic ketones is based on the oxidation of alkyl benzenes with molecular oxygen using cobalt acetate as the catalyst in acetic acid [9]. Zeolite encapsulated Co(II), Ni(II) and Cu(II) complexes gave acetophenone as the only partial oxidation product during ethylbenzene oxidation with $H_2O_2$[10]. Titano silicates mainly catalyse ring hydroxylation of arenes with $H_2O_2$, whereas vanadium and chromium substituted zeolites and alumino phosphate molecular sieves have been known to favour side-chain oxidation selectively [11]. Chromium substituted aluminophosphates are found to favour the formation of ketones from alkyl arenes with TBHP as the oxidant [12]. Aromatic ketone acetophenone is an important intermediate for perfumes, drugs and pharmaceuticals [13]. Production of this aromatic ketone by Friedel Craft's acylation of aromatic compound by acid halide or acid anhydride using stoichiometric amount of anhydrous aluminium chloride or a homogeneous acid catalyst leads to the formation of a large volume of highly toxic and corrosive wastes [14, 15, 16]. In the past, efforts have been made to produce aromatic ketones by oxidizing the methylene group attached to an aromatic ring using stoichiometric quantities of oxidizing agent eg.the oxidation of ethyl benzene to acetophenone by $KMnO_4$ [17]. In this the waste produced is very large and the separation of reactants and the products from the reaction mixture is difficult. Acetophenone can also be produced by the liquid phase oxidation of ethyl benzene by oxygen in air using heterogeneous transition metals(viz. Co, Mn, Cu or Fe) compounds as catalysts [18, 19, 20, 21, 22]. In this reaction, the conditions are harsh, the product selectivity is poor, separation of the catalysts from the reaction mixture is difficult and catalyst cannot be reused. A lot of tarry waste products are also formed. It is therefore of great practical interest to develop a more efficient easily separable, reusable and environmental friendly catalyst for the production of aromatic ketone. In this study, we used transition metal modified mesoporous ceria as catalysts in the oxidation of ethylbenzene with TBHP as oxidant in the liquid phase reaction.

Ethyl benzene oxidation was conducted in a 50ml glass round bottom flask fitted with a water cooled condenser and a magnetic stirrer, placed in a thermostated oil bath. In a typical reaction, required amounts of ethyl benzene, solvent and catalyst were taken in the R.B. flask. It is stirred till a particular temperature is attained and then calculated amount of TBHP is added drop wise with stirring. The products are withdrawn at certain intervals and analysed using Chemito 8610 GC fitted with FID Detector and using SE-30 column. The products were identified by GC-MS.

## 6.2 Optimization of reaction parameters

For any reaction, conversion and product selectivity is influenced by catalyst composition, reaction conditions like temperature, time of reaction, substrate to reagent ratio and volume of solvent. So before carrying out the reaction using all the prepared catalysts, it is essential to optimize the reaction conditions. The results of the observations are given in the following section.

### 6.2.1 Effect of oxidant

Oxidation of ethyl benzene was conducted using *tert*- butyl hydroperoxide (TBHP) and hydrogen peroxide as oxidants. The data obtained is given in the Table 6.1

**Table 6.1 Effect of oxidant on oxidation of ethyl benzene**

| oxidant | Conversion (%) | Selectivity | |
|---|---|---|---|
| | | Acetophenone | 1-phenyl ethanol |
| $H_2O_2$ | 41 | 62.5 | 37.5 |
| TBHP | 88.7 | 93 | 7 |

*Reaction conditions: Ethyl benzene to oxidant mole ratio-1: 4, Acetonitrile-5mL, Time-6h, CeCr (10%)-0.05g, Temperature-70°C*

When $H_2O_2$ was used as the oxidant the conversion was 41% with 62.5 % acetophenone selectivity, while TBHP gave 88.7 % conversion with 93% selectivity of acetophenone. According to Sheldon et al. [23] metal ions which catalyse oxygen transfer reactions with $H_2O_2$ or $RO_2H$ are divided into two types based on the active intermediate: a peroxometal or oxometal complex. Transition metals, like Mo (VI), W (VI), Ti (IV), follow peroxometal pathways and first row transition metals like Cr(VI), V(V), Mn(V), Ru(VI), Ru(VIII), Os(VIII) use oxometal pathways. The prepared samples of mesoporous ceria modified with first row transition metals follow oxometal pathway with TBHP as oxidant. Since the oxidation with TBHP is more selective and efficient, TBHP is selected for further study.

### 6.2.2 Effect of reaction temperature

To study the effect of temperature on ethylbenzene oxidation, reactions were carried out at different temperatures: 60 to 90°C with 1:4 molar ratios of ethyl benzene and TBHP using 5ml of acetonitrile solvent and 0.05g of CeCr (10%) catalyst.

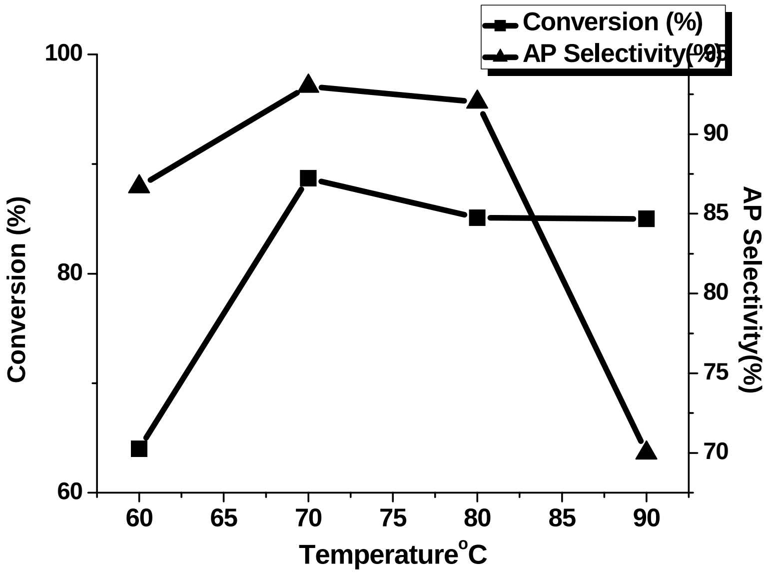

**Fig.6.2 Effect of temperature on oxidation of ethyl benzene**

*Reaction conditions: Ethyl benzene to oxidant mole ratio-1: 4, Acetonitrile-5mL, Time-6h, CeCr (10%)-0.05g*

From figures 6.2 it is clear that the conversion increases as the temperature rises from 60°C to 70°C for the catalyst and then decreases at 80°C. The increase in conversion as the temperature increased from 70 to 80°C may be due to the activation of t-butyl hydroperoxide at 70°C. The lower conversion at 90°C might be attributed to the decomposition of t-butyl hydroperoxide at higher temperature. Similar to conversion of ethyl benzene, the selectivity towards acetophenone also increases as the temperature increases from 60°C to 70°C. So 70°C is the optimized temperature for the reaction.

### 6.2.3 Effect of reaction time

To study the influence of reaction time on the efficiency of the catalyst the reaction was done at 70°C using 1:4 molar ratio of ethyl benzene to TBHP in the presence of 0.05 g CeCr (4%) catalyst and 5 ml of acetonitrile solvent. The result (Fig. 6.3) shows that the percentage conversion increased when the reaction was carried out for 6 hours. After that the increase in %conversion was very small for next 2 more hours of reaction, and the trend is continued. The selectivity also decreased after 6hours. At prolonged reaction for 24 hours, the conversion and selectivity are found to be increased, but the change is only 5% after 18 more hours of reaction. Hence further reactions were done for 6 hours.

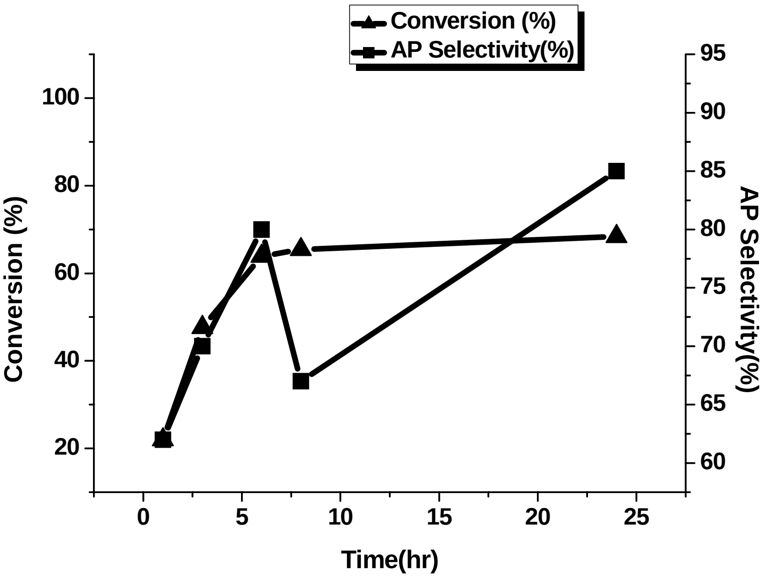

**Fig. 6.3 Effect of time on ethylbenzene oxidation**

*Reaction conditions: Ethyl benzene to TBHP mole ratio -1: 4, Temperature- 70°C, Acetonitrile-5mL, Catalyst -0.05g CeCr (4%)*

### 6.2.4 The effect of mole ratio of ethylbenzene to TBHP

To study the effect of mole ratio of ethylbenzene to TBHP, the reaction was carried out in previously optimized conditions of temperature and time, i.e., at 70°C for 6 hours at different molar ratios of ethyl benzene and TBHP, keeping the volume of ethyl benzene as 1ml.

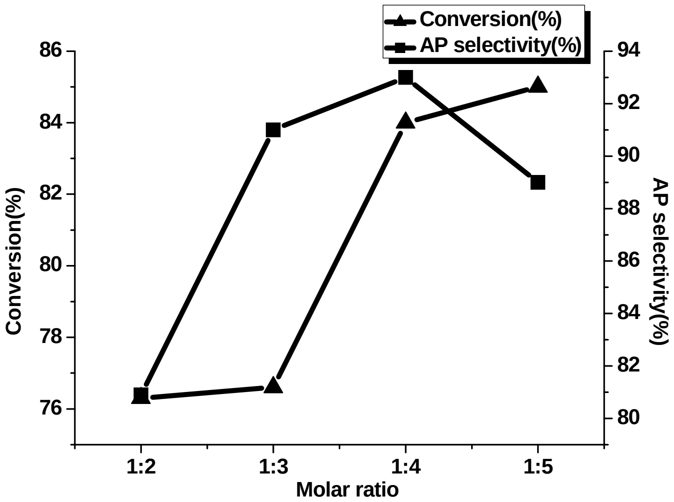

**Fig. 6.4 Effect of ethyl benzene to TBHP mole ratio on ethylbenzene oxidation**

*Reaction conditions: Temperature- 70°C, Acetonitrile-5mL, Catalyst-0.1g CeCr (10%)*

From the Fig. 6.4, it is found that the oxidation of ethyl benzene is sensitive to the molar ratio of the reactants. As the molar ratio increases, selectivity and the % conversion increases. When ratio is 1:5 the selectivity of acetophenone is found to be decreased. So the molar ratio of the reactants is optimized as 1:4 for conducting further reactions.

### 6.2.5 Effect of solvent

It has been reported in several articles that the liquid phase oxidation reactions are sensitive to the nature of the solvent used. The role of solvent on the reaction is very complex, especially on product distribution [24]. Among a series of solvents like acetonitrile, acetone, methanol, water, acetonitrile is found to give high conversion. Beliefa et al. observed that the presence of polar solvents makes vanadia- Titania catalyst more active for cyclohexane oxidation [25]. So we employed different solvents such as acetonitrile, acetone, methanol and water. The influence of the solvent on the oxidation of ethyl benzene is summarized in the Table 6.2.

**Table 6.2 Effect of solvent on reaction**

| Solvents | Conversion (wt. %) | Acetophenone selectivity (%) |
|---|---|---|
| Water | 24 | 84 |
| Acetone | 26.6 | 49 |
| Acetonitrile | 63 | 85 |
| Methanol | 30.4 | 81 |

*Reaction conditions: Ethyl benzene to TBHP mole ratio-1:4, Temperature- 70°C, Solvent- 5mL, Catalyst -0.05g CeCr (4%)*

The catalytic reaction shows much higher conversion when acetonitrile was used as the solvent. Maximum percentage conversion and selectivity was obtained when acetonitrile was used as the solvent.

With water, conversion was very low. So for the oxidation of ethyl benzene using TBHP, acetonitrile was found to be the suitable solvent. The oxidation of ethyl benzene was found to be influenced by the polarity of the solvent. The catalysts are persistently deactivated by strong interaction of the polar solvents thereby preventing diffusion of the reactants to the active sites. As a result the more polar solvents lead to lower conversion [26].

### 6.2.6 Effect of volume of the solvent

After optimizing acetonitrile as the suitable solvent for the oxidation of ethyl benzene using TBHP, the effect of volume of the solvent was studied. The reaction was carried out at a temperature of 70°C, for 6 hours using 1:4 molar ratios of ethyl benzene and TBHP. The relation between the volume of the solvent and percentage conversion and selectivity are shown in the Fig. 6.5

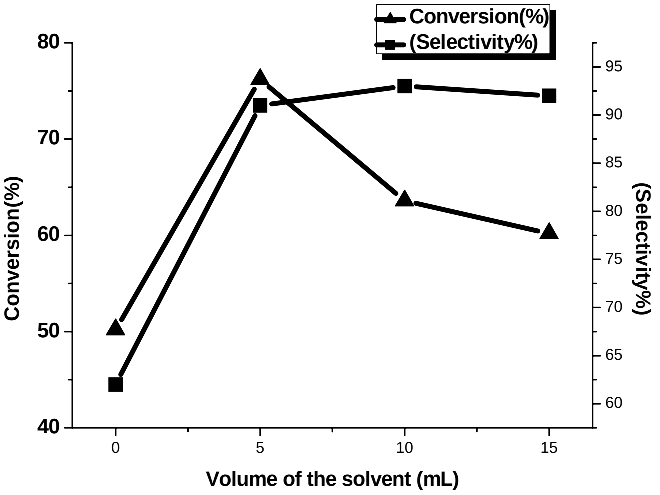

**Fig. 6.5 Effect of volume of the solvent on ethyl benzene oxidation**

*Reaction conditions: Temperature- 70°C, Time -6h, Catalyst - 0.1g CeCr(10%), Ethyl benzene to TBHP mole ratio-1: 4, Solvent -Acetonitrile*

The results show that a noticeable conversion and selectivity is obtained in the absence of solvent. But in the presence of catalyst, the % conversion and selectivity of acetophenone is increased to a considerable extent. When the volume of the solvent is increased from 0 to 5ml there was a two fold increase both in the percentage conversion of ethyl benzene and the selectivity of acetophenone. After that the conversion is decreased. Increase in the selectivity is not much pronounced by change in solvent amount after 5ml acetonitrile. This suggests that there is an optimum solvent concentration for maximum conversion. This may be due to the blocking of active sites of the catalyst by solvent molecules, and also may be due to the dilution of the reaction system. So 5ml acetonitrile was optimized for solvent in the reaction.

### 6.2.7 Effect of the weight of the catalyst

In heterogeneous catalysis the amount of catalyst plays a crucial role in determining the rate of the reaction. The oxidation was done using different weights of the catalyst (0.05, 0.1 and 0.15 g) for 6hours using CeCr (10%) catalyst and the results are represented in Fig. 6.6.

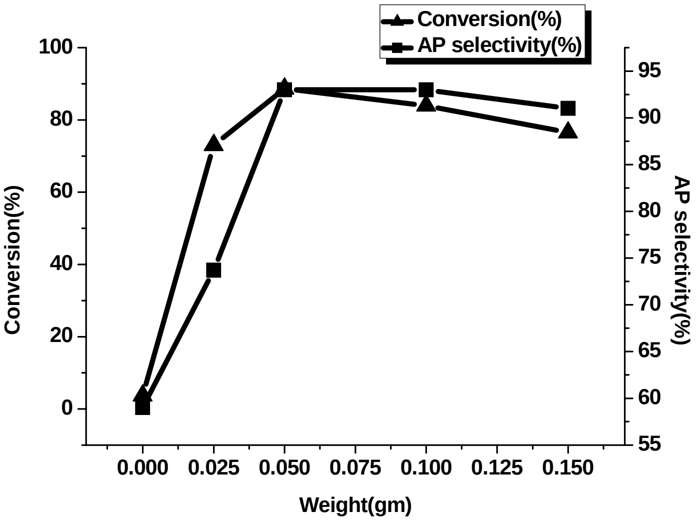

**Fig. 6.6 Effect of the weight of the catalyst**

*Reaction conditions: Temperature- 70°C, Time- 6h, Acetonitrile-5mL, Catalyst- CeCr (10%), Ethyl benzene to TBHP mole ratio -1: 3,*

From the data it can be seen that the amount of catalyst has an imperative function in the oxidation of ethyl benzene. It is found that when the weight of the catalyst is increased the conversion also increased establishing that the reaction proceeds through a pure heterogeneous mechanism. But when the catalyst weight was 0.05g, the selectivity and conversion were maximum. Then the conversion and selectivity decreases. So 0.05g of the catalyst is taken as the optimum catalyst amount for the effective performance for the reaction.

### 6.2.8 Optimized conditions

The optimization procedures reveal that the reaction parameters have strong influence on the oxidation activity and acetophenone selectivity of the catalyst systems. The optimized reaction conditions are summarized in Table 6.3.

**Table 6.3 Optimized conditions**

| **Time** | **6hours** |
|---|---|
| Reaction temperature | 70 °C |
| Molar ratio | 1:4 |
| Solvent | Acetonitrile |
| Volume of the solvent | 5 ml |
| Weight of the catalyst | 0.05g |

## 6.3 Leaching and reusability studies: Structural stability of the catalysts

An important requisite for a heterogeneous catalyst for the better catalytic performance is the stability of its active sites under the reaction conditions. Major causes that can lead to the deactivation of a catalyst include the disruption of the crystalline structure and changes in chemical composition during the reaction. The leached metal cation in solution can enhance the reaction rate whereby the pure heterogeneity of the reaction is lost. The regeneration of the catalyst after several repeated reaction runs also gives an idea about the stability of the system towards a particular reaction. Thus it becomes important to test the metal leaching on the catalytic activity and regeneration ability of the present systems. CeMn (10%) and CeCr (10%) are taken as the representative sample for these investigations.

### 6.3.1 Effect of metal leaching

A very important subject to be considered for the solid catalyst is the leaching phenomenon to find out the true nature of the catalytic reaction whether it is homogeneous or heterogeneous. Leaching can take place during a catalyzed reaction without an induction period and the nature of the reaction may gradually change from heterogeneous to homogeneous without any indication in the reaction profile. To prove the heterogeneous nature of the reactions, the solid catalyst was removed by filtration after 1hour from the reaction mixture at the reaction temperature. The mother liquor is again subjected for further reaction at the same conditions for five more hours. The results obtained using CeMn (10%) and CeCr (10%) are shown in Table 6.4

**Table 6.4 Effect of metal leaching in oxidation of ethyl benzene**

| Catalyst | Time(h) | Conversion (Wt %) |
|---|---|---|
| CeMn(10%) | 1hour | 25.3 |
| | 5hrs | 29 |
| CeCr (10%) | 1hour | 52.7 |
| | 5hrs | 76 |

From the results it is clear that in the case of CeMn (10%) the conversion remains more or less constant after the removal of the catalyst showing that metal ions are not leaching from the catalyst surface during the oxidation process. The investigation reveals the true heterogeneous nature of the reaction over modified ceria catalysts. But for CeCr (10%) there is increase in the conversion after the quenching by removal of the catalyst. It is clear that the Cr catalyst loses traces of Cr which catalysed the further reaction in a homogeneous manner. It is reported that no heterogeneous Cr catalyst have been prepared which have been stable under liquid phase oxidation conditions by performing tests for leaching [23].

### 6.3.2 Catalyst regeneration

One of the major objectives guiding the development of solid acid catalysts includes the easy separation of final products from the reaction mixture and efficient catalyst recovery. The recycling of the used catalyst for the same reaction is also a measure of catalyst structural stability. The reusability is tested for representative systems CeMn (10%) and CeCr (10%). The catalyst was removed by filtration from the reaction solution, washed thoroughly with acetone and then dried and calcined at 350 $^{o}$C for 4 hours. The same catalyst was again used for carrying out the subsequent run under similar reaction conditions.

**Table 6.5 Regeneration of the catalyst**

| catalyst | Number of cycles | Conversion (Wt %) |
|---|---|---|
| CeMn (10%) | 1 | 56.5 |
|  | 2 | 54 |
| CeCr (10%) | 1 | 88.7 |
|  | 2 | 77 |

*Reaction conditions: Ethyl benzene to TBHP mole ratio -1:4, Temperature- 70°C, time -6h, Acetonitrile-5mL, Catalyst weight- 0.05g*

From the Table 6.5., it is evident that the reuse of the catalyst gave %conversion without appreciable change. Thus the catalyst can be recycled without loss of activity.

## 6.4 Catalyst efficiency of different systems

We have prepared pure mesoporous ceria and three series of manganese, chromium, iron, cobalt, copper and nickel modified ceria systems. Under the optimized process parameters of temperature, time, molar ratio, catalyst weight and volume of the optimized solvent, all the prepared systems were tested for the oxidation of ethyl benzene using TBHP as the oxidizing agent. The activity of different catalytic systems in terms of percentage conversion and acetophenone selectivity are given in the Table 6.6.

**Table 6.6 Activity of the catalyst systems in the oxidation of ethyl benzene**

| Catalyst | Ethylbenzene Conversion (Weight %) | Selectivity (%) | | TON[a] | TOF[b] ($h^{-1}$) | Catalyst activity[c] ($mmol/m^2/h$) $x10^{-3}$ |
|---|---|---|---|---|---|---|
| | | Acetophenone | (*Others) | | | |
| Without catalyst | 3.7 | | | - | - | - |
| Ce | 4.7 | 74.1 | 25.9 | - | - | 0.4 |
| CeFe (2%) | 18.0 | 99.0 | 1.0 | 8700 | 1450 | 2.4 |
| CeFe (4%) | 12.1 | 99.0 | 1.0 | 2900 | 483 | 1.6 |
| CeFe (10%) | 18.9 | 59.7 | 40.3 | 1820 | 303 | 4.9 |
| CeCr(2%) | 26.2 | 78.6 | 21.4 | 11300 | 1883 | 2.9 |
| CeCr (4%) | 63.0 | 85.0 | 15.0 | 13600 | 2267 | 7.2 |
| CeCr (10%) | 88.7 | 93.0 | 7.0 | 7700 | 1283 | 12 |
| CeMn (2%) | 56.5 | 76.0 | 24.0 | 23700 | 3950 | 6.4 |
| CeMn (4%) | 51.7 | 89.5 | 10.5 | 11800 | 1967 | 5.9 |
| CeMn (10%) | 33.0 | 7.0 | 29.0 | 5200 | 867 | 4.1 |
| CeCo (2%) | 36.5 | 80.0 | 20.0 | 17600 | 2933 | 3.7 |
| CeCo (4%) | 28.4 | 86.6 | 13.4 | 6900 | 1150 | 3.1 |
| CeCo (10%) | 36.1 | 77.0 | 23.0 | 3500 | 583 | 4.5 |
| CeCu (2%) | 44.0 | 53.6 | 46.4 | 24100 | 4017 | 7.3 |
| CeCu (4%) | 51.2 | 76.5 | 23.5 | 14000 | 2333 | 8.7 |
| CeCu (10%) | 68.7 | 31.0 | 69.0 | 7500 | 1250 | 13 |
| CeNi (2%) | 15.0 | 72.0 | 28.0 | 7200 | 1200 | 2.1 |
| CeNi (4%) | 13.0 | 99.2 | 0.8 | 3100 | 517 | 1.99 |
| CeNi (10%) | 26.4 | 71.8 | 28.2 | 2600 | 433 | 4.2 |

*Reaction conditions: Ethyl benzene to TBHP mole ratio -1: 3, Temperature- 70°C, Time -6h, Acetonitrile-5mL*

*(* Others mainly include 2-phenyl ethanol traces of o/p-hydroxy acetophenone & Phenyl acetaldehyde etc)*

The Table 6.6. shows that compared to ceria, the modified systems are more active. In the absence of catalyst the conversion was only 3.7% with less acetophenone selectivity. In the case of the iron modified systems, though there is not much conversion, the acetophenone selectivity is very high. With the increase in the metal content, in the case of Fe, Co and Ni doped systems, conversion first decreases and then increases. For Cr and Cu modified systems there is a steady increase with increase in the metal content. In the case of Cr modified systems the metal content plays a crucial role in catalytic activity. On increasing the metal content from 2 to 4% a two-fold increase in activity is observed. For Mn doped systems the conversion decreases with % of metal doping. According to B. Viswanathan et al. [27], mesoporous Cr-$AlPO_4$ exhibits both acidic and redox properties by promoting dealkylation and oxidation in a concerted manner, whereas, under identical conditions, Cr-MCM-48 promotes only oxidation. Here among all the systems, Cr, Cu and Mn doped ones are giving % conversion more than 50%. CeCr (10%) is more active than the other two systems. Among the prepared catalyst systems 10% chromium doped ceria is found to be the most active catalyst with 88.7% conversion and 93% selectivity in the oxidation of ethyl benzene. Comparing the activities of Mn, Cu and Cr modified systems, Cr modified ones are most active and selective towards acetophenone. Next to chromium the better system is CeCu (10%). For ceria modified with Cr prepared by sol-gel method, the % conversion for ethyl benzene oxidation reaction was only 59% [28]. So Cr doped mesoporous ceria prepared by surfactant route is much more active than that prepared by sol-gel route.

From Table 6.6., it is evident that as the metal loading increases, the TON and TOF are getting decreased. This is because of the reason that with the increase in the metal loading, % conversion is not increased in a proportional manner.

It is reported that the oxidation of toluene with TBHP in the presence of chromium silicate catalyst proceeds through the reversible transformation of $Cr^{3+}$ and $Cr^{5+}$. Parentis et al. [29] suggested that in the presence of TBHP, $Cr^{3+}$ is oxidised to $Cr^{5+}$ in $Cr/SiO_2$ catalysts which oxidises the substrate via redox mechanism. The C-H bond activation at the benzylic position by transition metal complexes under mild conditions is an important transformation in the synthetic organic chemistry. Hexavalent chromium catalysts are extensively used for the transformation of alkyl aromatics to aromatic ketones and acids in homogeneous phase [30]. Sivasanker et al. [31, reported an efficient catalytic method for benzylic oxidation of alkyl arenes to the corresponding carbonyl compounds in good yields using Cr-MCM-41 catalyst and 70% tert-butyl hydroperoxide (TBHP) in MeOH as oxidant. Imamura et al. concluded that the effect of ceria was to produce Mn species with lower oxidation states ($Mn^{3+}$, $Mn^{2+}$) and combination of $Mn^{4+}$ with $Mn^{3+}$ or $Mn^{2+}$ was assumed to be the cause for the high activity of the catalyst [32].

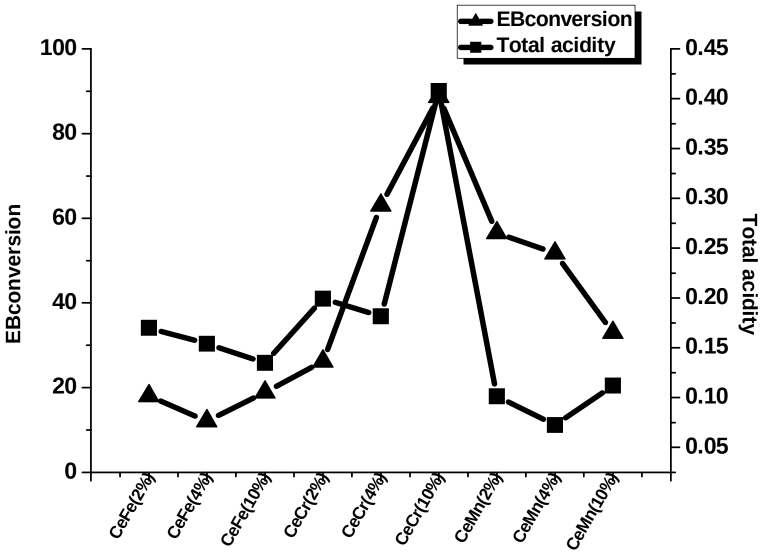

**Fig.6.5a** Correlation between the surface acidity and catalytic activity for Fe, Cr &Mn doped systems

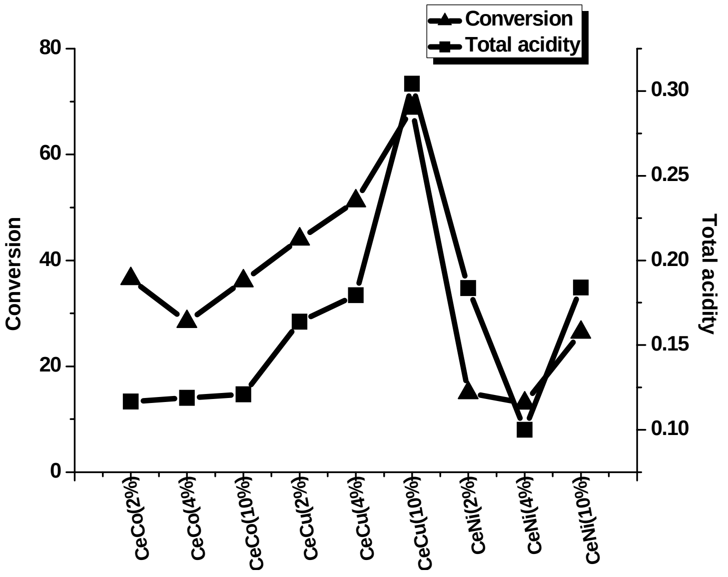

**Fig.6.5b** Correlation between the surface acidity and catalytic activity for Co, Cu & Ni doped systems

According to Sheldon et al. first row transition metals generally employ oxometal pathway which involves two-electron redox reactions of the metal ion. The highest activity for Cr, Mn, & Cu modified catalysts which can easily undergo redox reactions through oxometal path way. A correlation is also noticed between the surface acidity and catalytic activity. This is shown in the Fig. 6.5a & b.

## 6.5 Kinetic Parameters

### 6.5.1 Test of pseudo-first-order kinetic model for reaction at 70°C over CeCr (10%)

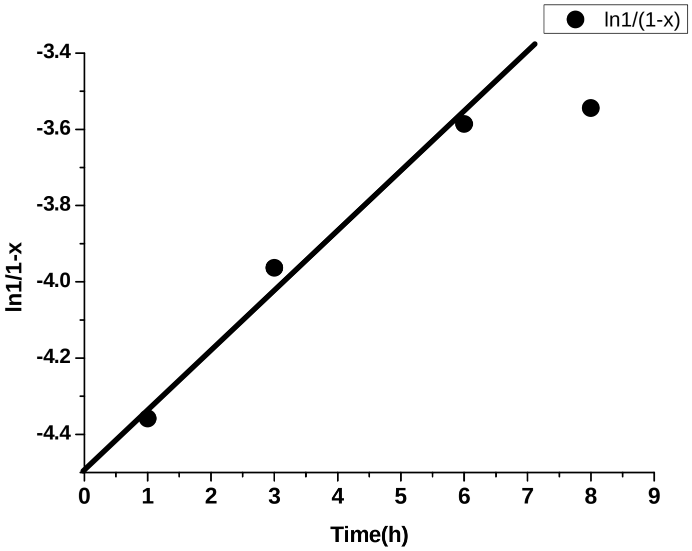

**Fig.6.6 First order kinetic plot of ethyl benzene oxidation**

Since the reaction is found to be pseudo unimolecular, the intrinsic rate constants in the units of ($min^{-1}m^{-2}$) was determined for each catalyst using the formula,

$$k(min^{-1}m^{-2}) = \frac{2.303}{twA}\log\frac{100}{100\text{-}\%yield}$$

The kinetic parameters ($E_a$ and the frequency factor A) were evaluated from the ethyl benzene conversion values in the temperature range 60-90°C, assuming the diffusion and mass transfer effects were insignificant. Rate constant k is calculated for the reaction at different temperatures using CeCr (10%) catalyst under the same reaction conditions. Based on the Arrhenius equation, $k = A \exp(-E_a/RT)$ using 'slope and intercept' of Arrhenius plot, the frequency factor A and the activation energy $E_a$ were evaluated as $15.3 \times 10^{8}$(kg of catalyst)$^{-1}$ h$^{-1}$ and 21.37 kJ/ mol, respectively.

$$\Delta H^{\dagger} = E_a - RT = 18.52 \text{kJ/ mol}$$

$$\Delta S^{\dagger} = R\,[\ln A - \ln (kT/h) - n] = -206.4 \text{J/mol /K}$$

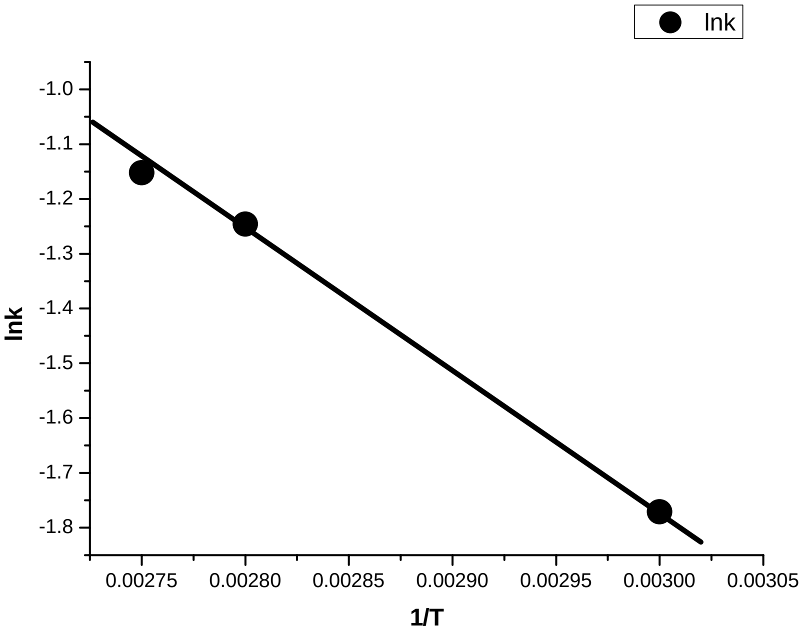

**Fig.6.7 Arrhenius plot with CeCr (10%) as the catalyst**

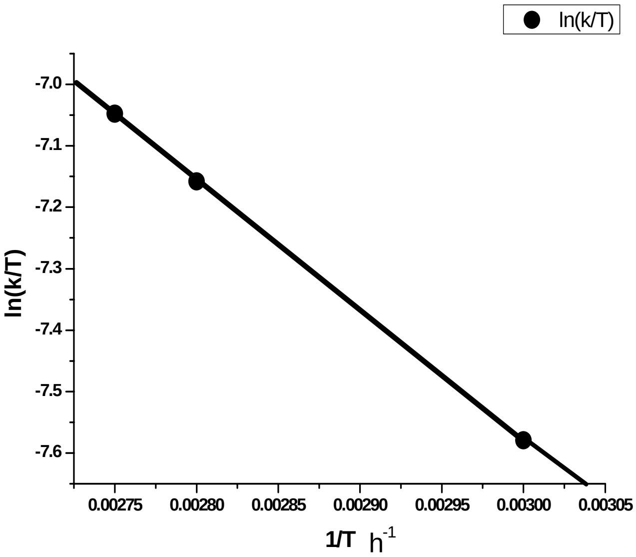

**Fig.6.8 Eyrings plot with CeCr (10%) as the catalyst**

**Table 6.5 Values of different kinetic parameters**

| Kinetic parameters | Values |
|---|---|
| Activation energy $E_a$ | 21.37 kJ/mol |
| Frequency factor A | $15.3 \times 10^8$ (kg of catalyst)$^{-1}$ h$^{-1}$ |
| Enthalpy of activation $\Delta H^\dagger$ | 18.52 kJ /mol |
| Entropy of activation $\Delta S^\dagger$ | - 206.4 J/Mol /K |

## 6.6 Conclusions

The present study on liquid phase oxidation of ethyl benzene can be summarized as given below.

1) Ethyl benzene can be oxidized effectively using mesoporous ceria modified catalyst using TBHP in liquid phase to get acetophenone selectively as the major product.

2) Reaction variables like temperature, weight of catalyst, time, solvent and volume of the solvent have predominant effect on the % conversion and selectivity to acetophenone.

3) Chromium, manganese and copper doped catalysts have more activity in the reaction and product selectivity. For the effective catalyst Cr doped ceria, the metal loading has pronounced influence on % conversion and selectivity.

4) These catalysts can replace the more hazardous, stoichiometric catalysts as these are regenerable and reusable.

5) Transition metal-incorporated mesoporous materials have proved to be potential catalysts in the oxidation of alkyl arenes to carbonyl compounds. The reactions were found to be extremely sensitive to the oxidant and solvents used. Mesoporous ceria materials appeared to be promising acid and redox catalysts and were also successfully applied as supports for active sites.

6) The reaction is proved to be following first order kinetics with ethyl benzene conversion with the frequency factor A and the activation energy $E_a$ evaluated as $15.3 \times 10^8$ (kg of catalyst)$^{-1}$ h$^{-1}$ and 21.37 kJ/ mol respectively for (CeCr10%). catalyst. The kinetic parameters like $\Delta H^\dagger$, $\Delta S^\dagger$ of activation for the reaction are calculated.

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Chapter 7

# ALKYLATION OF PHENOL

Contents

Selective C-methylation of phenol to o-cresol and 2, 6-xylenol in high yields have been carried out with methanol over mesoporous ceria modified by transition metals. The maximum conversion of 68% with 98% selectivity for corresponding ortho-alkylated products (o-cresol and 2, 6-xylenol) was obtained with 2% anisole as O-alkylated product. A series of catalysts with 2–10weight% metal loading were prepared and calcined at 350°C. The XRD results reveal the formation of single phase cubic fluorite structure after addition of metals. Metals and their compositions were found to influence the conversion and selectivity. The influence of various experimental parameters on phenol conversion and product selectivity has been investigated. The catalyst was active without any deactivation showing its longer life. The catalytic activity and selectivity is correlated with its acidity and structure.

## 7.1 Introduction

There is currently a significant world-wide interest in the use of solid acid and base catalysts to promote various organic reactions of industrial importance, since such systems often give value-added products with improved selectivity without creating major burdens to the environment. Alkylation of aromatic substrates catalysed by solid acids such as zeolites and metal oxides constitutes a class of reactions important both academically and industrially. Among alkylation reactions, methylation of phenol has attracted considerable attention due to industrial importance of methyl phenols as chemical intermediates in the manufacture of pharmaceuticals, agrochemicals, resins, various additives, polymerization inhibitors, antioxidants and various other chemicals [1]. In particular, ortho-alkylated phenols such as o-cresol, 2, 6-xylenol and trialkyl substituted phenols are more important alkyl phenols. For example, epoxy cresol novolac (ECN) and polyphenylene oxide (PPO) used in the electronic industries and automobile industries are derived from o-cresol and 2, 6-xylenol, respectively [2]. After suitable processing, o-cresol is used in the synthesis of herbicides as well as in sealing material for integrated circuits, whereas 2, 6-xylenol is used in manufacture of disinfectant and in high impact resistant resins [3]. Trimethyl phenols are precursors for the synthesis of Vitamin-E. Anisole and methyl aryl ethers (MAE) are considered as octane number booster for gasoline. It was found that a mixture of MAE can effectively substitute for the non-metallic additives such as methyl tertiary butyl ether (MTBE) [4]. C-alkylated phenols, in particular, tert-butyl-, iso-octyl-, and iso-decyl- phenols, are widely used in the chemical industry as drilling oil additives, antioxidants, and polymer stabilizers. The isomeric O-alkylated phenols also have numerous industrial applications, particularly in the production of dyes and agrochemicals. The selective synthesis of alkyl phenols especially o-cresol and 2, 6-xylenol is receiving increasing interest in recent years because of their importance as intermediates for the synthesis of a variety of resins, herbicides, insecticides and other chemicals[ 5]. o-Cresol is used in the manufacture of insecticides and herbicides and 2, 6-xylenol is a precursor for poly 2, 6 dimethyl phenoxide, a thermo resistant polymer used in special grade paints.

The catalytic alkylation of aromatic hydrocarbons is of significant fundamental and practical importance and has been intensively investigated in recent years. Although current homogeneous catalysts are efficient, their corrosive and toxic nature provide potential environmental hazards and their operational problems, including difficulty in separation, recovery, and reutilization result in higher capital costs. Friedel–Crafts catalysts such as $AlCl_3$, $BF_3$, $TiCl_4$, liquid HF, various types of zeolites, $\gamma$-alumina, silica-alumina, Nafion-H, phosphoric acid, ALPO, SAPO, metal phosphates, acidic and basic oxides; etc. producing a mixture of C- and O- alkylated products have been used for the alkylation of phenol [6]. Selective alkylation of phenol on the aromatic carbon atoms has not been very successful [7]. Furthermore, several problems are associated with these catalysts such as low selectivity, separation of the catalyst from reactants and products, and disposal of effluents. Alkylation of phenols is generally carried out using a liquid acid catalyst, giving wide product distribution. Typical strong acid catalysts promote a range of undesirable side reactions. A review covering the various aspects of the shape-selective catalysts in alkylation were published recently [8].

The formation of alkylated phenols is a major area of chemistry and clean processes are required. Alkyl phenols are valuable industrial chemicals. Both C- and O-alkylation of phenol is possible depending on reaction conditions such as temperature, source of reagent, and type of catalyst. The combination of some weakly acidic centres, along with basic sites, can lead to very good selectivity and a clean process. The use of highly corrosive and polluting liquid acids are major environmental problems and, therefore, heterogeneous solid acids like anion exchange resins, NaX and Y zeolites, hetero polyacids, acid-treated clays, and titania-supported $AlPO_4$ have replaced them.

Anisole is used as an additive in gasoline to boost octane number. The conversion of anisole to 2, 6- xylenol is an important target, and heterogeneous catalysts may provide the answer. The synthesis of 2, 6-xylenol by the alkylation of phenol with methanol has been attempted over different metal oxide catalysts [9, 10, 11, 12]. Alkylation of phenol, in general, leads to thermodynamically favourable m-isomer rather than the o- and/or p-isomers. However, the presence of a phenolic group in the reactant under consideration kinetically favours the latter. Although the o-isomer is kinetically more favourable than the p-isomer, the former isomerizes easily into stable p-isomer owing to steric hindrance at the ortho position.

The increasing demand for new and selective catalysts with larger molecular dimensions led to the discovery of mesoporous catalytic materials. Unlike in the case of microporous and macroporous solids, catalysts with a mesoporous structure can achieve an optimum compromise of high site density and good transport characteristics. Acidic and redox functionalities were generated in these materials by the incorporation of transition metals or by the encapsulation of well-defined homogeneous complexes inside the pores. Also, they opened up many new strategies for shape-selective, enantioselective, and regioselective conversions [8]. Further, the selectivity of the products depends mainly on the nature of the acidic sites present on the catalyst as well as the reaction temperature. Bautista and co-workers found that dealkylation to phenol is predominant over $AlPO_4$–$Al_2O_3$ catalysts in the alkylation of anisole with methanol [13]. Apart from the acid–base properties of the catalysts, the product selectivity is often influenced by the operating conditions and the nature of alkylating agent.

The process using solid catalysts and fixed bed reactors offer many advantages such as catalyst reusability, ease of product work up and continuity of operation. The vapour phase methylation of phenol with methanol using metal oxide or zeolite as catalysts has been done extensively. The products are usually mixtures of anisole (the product of O-methylation) and the products of ring methylation (cresols and xylenol), the selectivity being strongly depended on the catalyst. There can be two important pathways for the formation of 2, 6-xylenol and o-cresol. In the first pathway anisole formed first, react with methanol to form 2, 6-xylenol. In the second pathway direct C-alkylation takes place forming o-cresol which reacts further with another molecule of methanol to give 2, 6-xylenol. It is known that anisole can undergo intramolecular rearrangement reaction to o-cresol or intermolecular rearrangement between two molecules to methyl anisole and phenol [14].

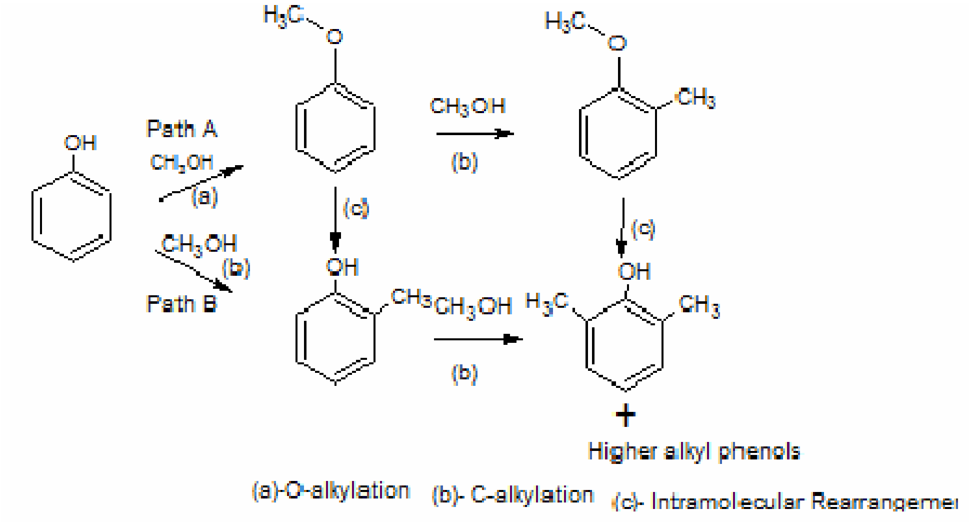

**Fig.7.1 Pathways for the formation of 2, 6-xylenol and o-cresol**

Oxide catalysts are found to be more selective for the synthesis of 2, 6-xylenol and o-cresol [12]. Reports on the selective O-methylation, however, have been very limited. Pierantozzi and Nordquist obtained 94% selectivity for anisole at a 12% yield over $La_2$ $(HPO_4)_3$ at 573K. Renaud et al. obtained 80% selectivity with an anisole yield in the range of 20-30%. It is generally accepted that the acid–base properties of the catalysts employed have a significant influence on the product distribution. Alkylation of phenol with methanol is catalysed by both Brönsted and Lewis acid sites as well as by basic sites. Phenol is adsorbed both on acidic and basic sites. For example, O-alkylation can easily occur on basic sites, while C-alkylation requires the presence of weak or stronger acid sites [15]. The formation of polyalkylated products requires more severe reaction conditions, i.e., higher reaction temperatures, longer contact times, an excess of methanol in the feed, and/or a sufficiently high acid strength of the catalyst. To prove that the secondary products stem to a large extent from anisole, Marczewski et al. [16] studied the reactions of anisole and of a mixture of anisole and methanol on H-USY (ultra stable zeolite Y). They proposed that the direct isomerization of anisole to cresols does not occur and that the alkylation of phenol by anisole leads to cresols and methyl anisoles as primary products. Anisole has been suggested to be an intermediate in the formation of cresols during phenol methylation [17]. Studying the methylation of phenol with methanol on zeolite H-Beta by conventional GC analysis, Xu et al. [18] came to the conclusion that anisole is an unstable primary product and an important reaction intermediate. The formation of the predominant product o-cresol was enhanced by lower temperature, less amount of alkylating agent in the feed and lower acidity of the catalyst. It is proposed that at lower temperature and lower residence time anisole is formed which undergoes rearrangement and further alkylation at higher temperature and high residence time to give o-cresol and 2, 6-xylenol at the expense of anisole. Methylating agents such as methyl carbonates favours O-alkylation and almost quantitative yields of anisole has been reported with dimethyl carbonate [19, 20]. Hence it can be concluded that basicity or very low acidity favours O-alkylation at lower temperature whereas moderate or high acidity favours C-alkylation.

The selective C-alkylation of phenol with methanol over basic MgO has also been explained on the basis of vertical orientation of phenoxide aromatic ring on the catalyst surface and O-alkylation due to its parallel orientation on acid catalyst surface [21]. Preferential C-alkylation can be attributed to large number of weak and medium acid sites whereas preferential ortho-alkylation is due to perpendicular orientation of phenol aromatic ring on catalyst surface. Selectivity in phenol alkylation (O- or C-alkylation) is reported to depend on the acid–base properties of the catalyst [22]. While basic catalyst favours C-alkylation, acidic catalyst does not favour this reaction (it gives O-alkylation) due to the orientation of phenol aromatic ring with respect to the catalyst surface as shown in Fig.7.1 a &b [23]. After adsorption on the catalyst surface, phenol dissociates in to phenoxide ion and proton. In case of basic catalyst the aromatic ring is shown to be perpendicular to the catalyst surface facilitating ortho-alkylation. However in case of acidic catalyst the aromatic ring is parallel to the catalyst surface and the electrons of the ring interact with the catalyst surface. It can be said that aromatic ring is perpendicular to the catalyst surface minimizing the interaction of Π electrons with the surface. This orientation facilitates the attack of adsorbed alkyl moiety at ortho position giving high yields of o-cresol and 2, 6-xylenol. In general, cresols can be formed both by direct C-alkylation of phenol with methanol and by conversion of the anisole formed by O-methylation of phenol [24]. Over the more acidic catalysts, phenol molecule may adsorb by interaction of its electron cloud, while on a more basic catalyst, it may adsorb by the –OH group [25].

Satoshi Sato et al. studied the vapour phase alkylation of phenol-methanol over $CeO_2$-MgO at temperature range between 450 -550°C and got excellent selectivity to the sum of o-cresole and 2, 6 –xylenol more than 98% [26]. Pure $CeO_2$ also showed excellent ortho cresol selectivity. The selectivity generally determined by Brönsted acidity of the molecular sieves, are also affected by other factors such as pore size and geometry. In the case of the AlPO-5 having initially high alkylation activity, a different mechanism is likely operative [27]. During alkylation of phenol with methanol using AlPO-5 exclusively C-alkylated (alkylation proceeds through ring) products were formed [28]. K.V.R. Chary et al. reported the alkylation of phenol with methanol over a series of pure zirconia and vanadium oxide catalyst supported on zirconia to produce selectively valuable o-cresol and 2, 6-xylenol (C-alkylated products).

The earlier reports indicate lot of discrepancies in correlation of acidic and basic nature of catalyst and its influence on C or O-alkylation of phenol. The presence of substantial amounts of anisole in the products with cresols to anisole ratio of 2 indicates that in the mechanism, both the schemes - scheme C and scheme D- are operating simultaneously with scheme C being the predominant one.

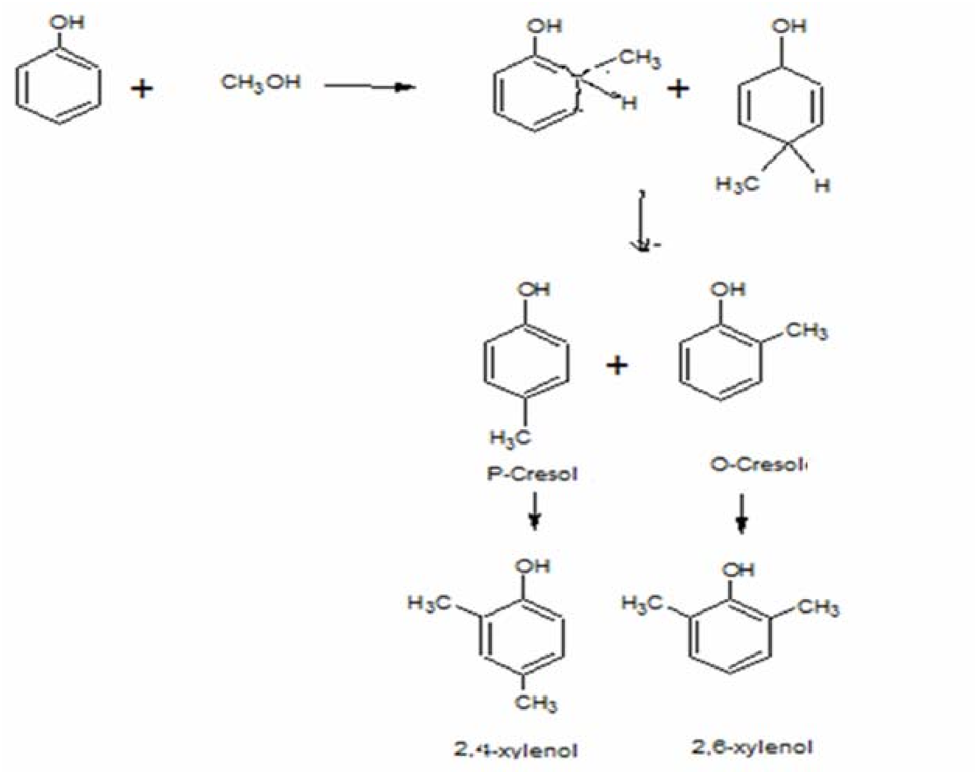

**Fig.7.2 Reaction scheme C -for methylation of phenol with methanol**

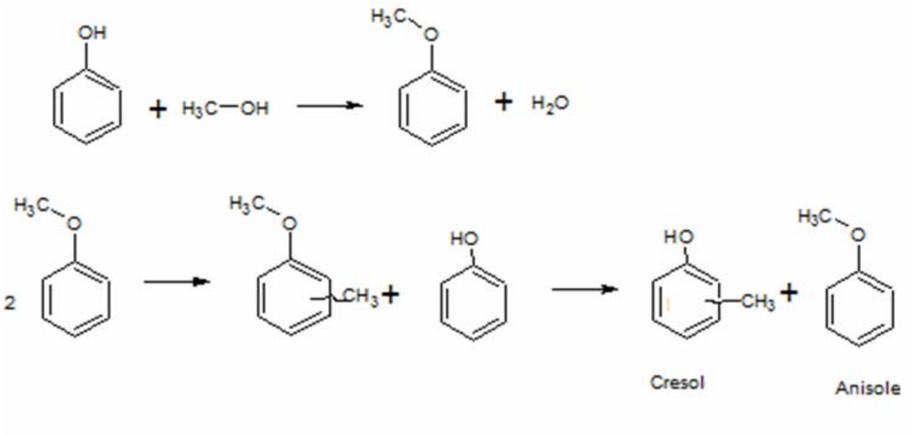

**Fig.7.3 Reaction scheme O- methylation of phenol with methanol**

## 7.2 Reaction Pathway

Phenol can adsorb on the surface perpendicularly as well as parallel. While perpendicular adsorption is expected to give ortho products, parallel adsorption will facilitate formation of para or oxygen substituted products. In the present study, major products were ortho substituted products. The formation of ortho substituted products rules out the parallel adsorption of phenol on catalyst surface. The ortho selectivity of the catalysts (formation of o-cresol, 2, 6-xylenol) can be attributed to perpendicular adsorption of phenol over catalyst surface. The shifting of electron cloud of the M-O bond towards oxygen makes it more basic and proton attracting. The phenol molecule is vertically absorbed on the surface with oxygen attached to $M^{n+}$ (Lewis acid site) as a phenoxide ion and hydrogen to the oxide ion (Lewis base site). Methanol absorbed on the Lewis base site through proton, abstracts the phenol proton, gets protonated and is converted to carbonium ion by releasing water molecule. An electrophilic attack by carbonium ion on the ortho position of phenoxide ion leads to formation of o-cresol and completing the catalytic cycle. Almost constant conversion to o-cresol and increased conversion to 2, 6-xylenol with increasing mole ratio of methanol to phenol, suggests the reaction to follow a consecutive mechanism. Due to presence of negative charge on the phenoxide ion, strength of the bond between this ion and Lewis site will increase with increasing acidity of the catalyst due to increasing $M^{n+}$ content. This will permit phenoxide ion to remain on the surface for longer time and help formation of 2, 6-xylenol.the mechanism is shown in scheme A of Fig. 7.4.

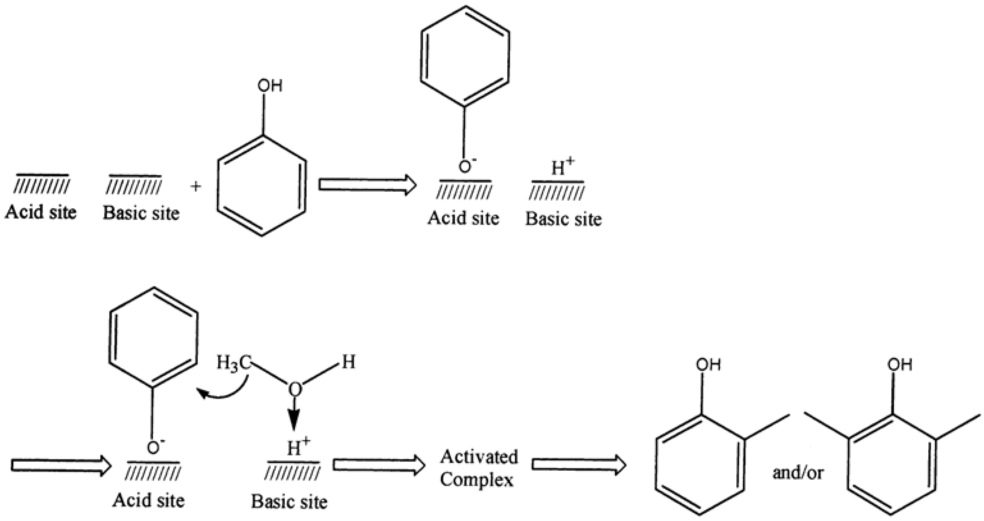

**Fig.7.4 Scheme A. Perpendicular orientation of aromatic ring on the catalyst surface-- Reaction mechanism of ortho methylation of phenol using methanol as the alkylating agent [29]**

Fig. 7.4. represents the reaction scheme for ortho methylation of phenol using methanol as the alkylating agent. According to this scheme, the phenolate ion is adsorbed on the Lewis acid site and the hydrogen ion is bound to the basic site. Such a protonated site accelerates methanol to produce carbonium ion, which then reacts with the aromatic ring of the adjacently adsorbed phenolate species at its ortho position.

## 7.3 Reaction procedure

Vapour phase methylation experiments were performed in a fixed-bed continuous down flow glass reactor at the atmospheric pressure. A tubular glass reactor of 10 mm diameter and 25 cm length was loaded with 0.25g of the modified mesoporous ceria catalyst in powder form. The upper part of the reactor was packed with inert ceramic beads as the preheating zone. The catalyst was preheated at 300$^{o}$C for 1 hour. The reactions were carried out by passing a mixture of phenol and methanol using syringe pump in the temperature range of 300–500$^{o}$C at the rate of 4 ml/h. The weight hourly space velocity (WHSV) was varied from 13 to 35 h$^{-1}$. The products were collected in an ice-cooled condenser and analysed by a gas chromatograph fitted with an OV-17 column and a flame ionization detector. The identity of the products was established by the comparison of retention times of authentic samples and also by GC-MS.

### 7.3.1 Process Optimization

For any reaction, % conversion and product selectivity are influenced by catalyst composition, reaction conditions like temperature, time of reaction, substrate to reagent ratio, time and flow rate. So before carrying out the reaction, it is essential to optimize the reaction conditions. The results of the observations are given in the following section**.**

### 7. 3.1.1 Effect of temperature

To study the effect of temperature on activity of the catalysts, the reaction was carried at different temperatures from 400 to 500$^{o}$C.The results of the phenol methylation carried out at various temperatures showed maximum conversion (50.5%) at 500$^{o}$C with 87% selectivity for ortho-alkylated products (Fig. 7.3.) for the catalyst CeFe(10%). But at temperature (450°C) the maximum selectivity of 92.7% was observed however with a slight low conversion (48.6%). As expected the rate of reaction and % conversion increases with temperature. The selectivity of 2, 6-DMP increases with the increase of reaction temperature, indicating that reaction

o- cresol + methanol → 2,6-DMP + $H_2O$ is more temperature sensitive than reaction

Phenol + methanol→ o-cresol + $H_2O$

The formation of poly-methylated products is the reason for decrease in selectivity at higher temperature. Also methanol undergoes decomposition in greater extent at very high temperature decreasing the reaction rate.

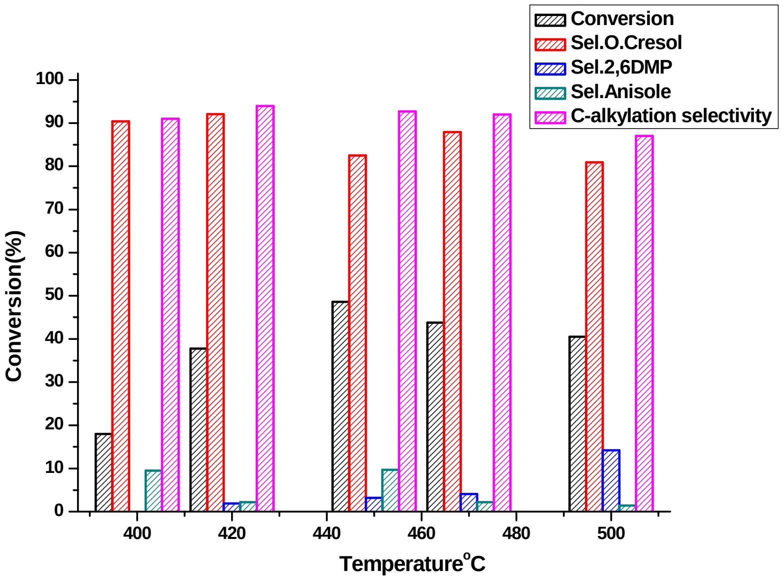

**Fig.7.5 Effect of temperature on methylation of phenol**

*Reaction conditions: Catalyst -0.25g CeFe (10%),*
*Phenol: methanol – 1:5,*
*Flow Rate: 4mL/h, Time of flow: 2 hrs*

According to literature basic catalysts favour O-alkylation at lower temperature and lower residence time, whereas C-alkylation is favoured by strong or medium acid sites. High temperature also favours C-alkylation. According to K. M. Malshe et al. basic Mg–Al–HT shows higher selectivity for anisole at low residence time whereas at higher residence time selectivity for C-alkylation increases at the expense of anisole [30]. Hence it is proposed that at lower temperature and lower residence time anisole is formed which undergoes rearrangement and further alkylation at higher temperature and high residence time to give o-cresol and 2, 6-xylenol at the expense of anisole. Our results are in good agreement with the literature. Mesoporous ceria catalyst which is moderately acidic, gives selective C-alkylation at high temperature (350–450$^{o}$C). Hence it can be concluded that basicity or very low acidity favours O-alkylation at lower temperature whereas moderate or high acidity favours C-alkylation.

### 7.3.1.2 Effect of methanol: phenol mole ratio on conversion and selectivity for C- Alkylated products

In order to choose an optimum feed mix ratio, the experiments were conducted at different molar ratio using different volumes of methanol keeping the volume of phenol constant. The reaction was done at optimised temperature of 450$^{o}$C using CeCr (10%) catalyst at a flow rate of 4ml /hr. The time of flow was selected as 2hr. The C-alkylated products such as o-cresol and 2, 6- xylenol were obtained as major reaction products. % Phenol conversion and product selectivity are plotted against phenol/ methanol molar ratio Effect of change in methanol: phenol mole ratio on conversion and selectivity is shown in Fig.7.4. Conversion % of phenol goes up as the mole ratio is increase from 3 to 5 due to the availability of additional methyl groups for the reaction, however with further increase in mole ratio there is a decrease in % conversion, and selectivity of o-cresole but selectivity for ortho-alkylated products increases as the yield of 2, 6-xylenol increased with more methanol concentration.

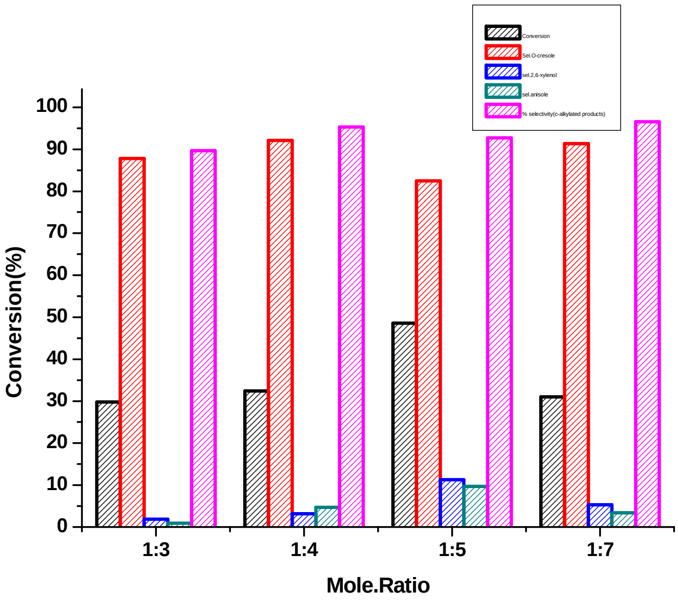

**Fig.7.6 Effect of mole ratio on methylation of phenol**

*Reaction conditions: Catalyst -0.25g CeFe (10%), Flow Rate: 4mL/h, Time of flow: 2 hrs, Temperature: 450$^{o}$C*

This is due to the consecutive methylation at higher mole ratio. This result indicates that o-cresol is the primary alkylated product, the one which on further alkylation produces 2, 6-xylenol. An increase in mole ratio retains the initially formed o-cresol on the catalyst surface and facilitates consecutive methylation to give 2, 6-xylenol [31]. The linear increase in the conversion of phenol at lower molar ratio suggests a Langmuir–Hinshelwood bimolecular reaction [32].

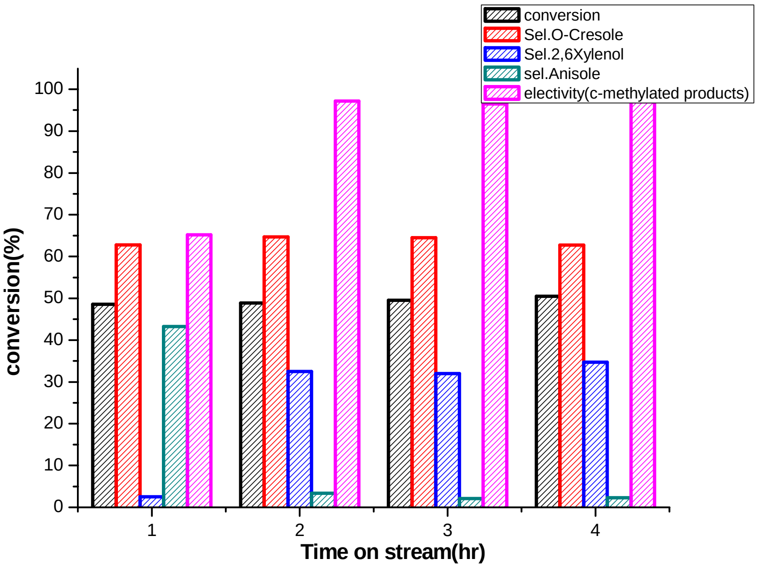

**Fig.7.7 Effect of time on methylation of phenol**

*Reaction conditions: Catalyst -0.25g CeFe (10%), Phenol: methanol – 1:5, Flow Rate: 4mL/h*

### 7.3.1.3. Effect of time on methylation of phenol

The time on stream studies using CeCr (10%) catalyst for methylation of phenol was done by carrying out the reaction for 4hrs. Results are shown in fig 7.5. Up to 4 hours of reaction there is steady rate in the conversion of phenol. The effect of contact time on product selectivity (Fig.7. 5) showed that, at low contact times, anisole was also a major product. As the contact time increased, the anisole selectivity decreased and o-cresol and 2, 6-xylenol increased. This shows that, anisole is to a large extent responsible for the formation of o-cresol and 2, 6-xylenol. It is proposed that at lower temperature and lower residence time anisole is formed which undergoes rearrangement and further alkylation at higher temperature and high residence time to give o-cresol and 2, 6-xylenol at the expense of anisole. The selectivity towards C-alkylated products varies with time on stream and maximum selectivity is obtained at 2 hours. The catalyst is found to be active up to this period which shows better stability, no obvious activity loss occurs within the running time. However the deactivation of catalyst after prolonged use may be due to the formation of a layer of carbon as coke on catalyst surface.

### 7.3.1.4 Effect of WHSV

Effect of contact time of the reactant molecules on catalyst surface is expressed in terms of weight hourly space velocity (WHSV).When (WHSV) is 7.5 $h^{-1}$, optimum result in terms of % conversion was observed (Fig. 7.6). At lower WHSV although conversion is high, selectivity for C-alkylated products is less. As WHSV increases there is a decrease in the conversion whereas the C- alkylation selectivity increases up to a WHSV of 11.25 $h^{-1}$. When it is above 13 both conversion and selectivity drastically decreased. At high WHSV the conversion is getting decreased, which suggests the attainment of high rate of diffusion of the reactants reducing the chemisorption on the catalyst surface. At higher flow rate the residence time of the reactant molecules on the catalyst surface is less compared to the lower flow rates which results in the lower conversion. Ortho-alkylated products are very low due to longer residence time at the catalyst surface leading to the formation of C-alkylated product by rearrangement reaction and polyalkylated products. The low conversion at very high contact time can be attributed to the increased rate of methanol decomposition as a side reaction. As contact time decreases, the rate of this side reaction also decreases, resulting in high phenol conversion. At higher WHSV, selectivity for o-cresol increased due to lower contact time resulting in lack of consecutive methylation of cresol [32].

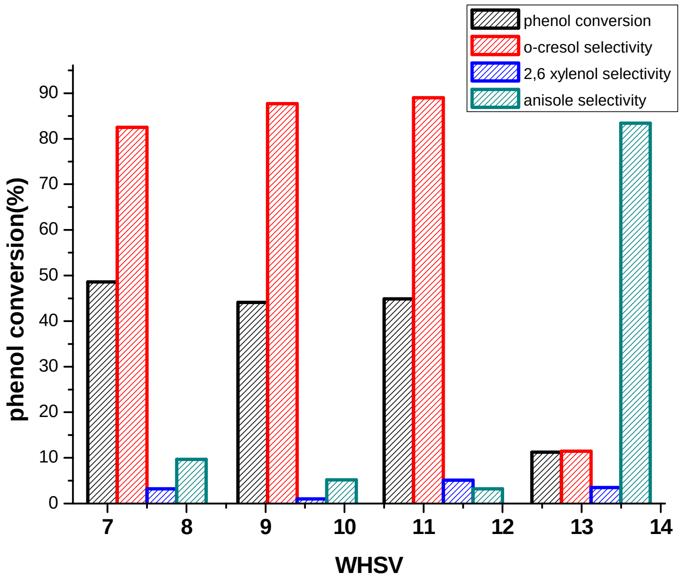

**Fig.7.8 Effect of WHSV on methylation of phenol**

*Reaction conditions: Catalyst -0.25g CeFe (10%), Phenol: methanol – 1:5,*
*Temperature-450$^o$C, Time-2hrs*

### 7.3.1.5 Effect of amount of catalyst

To study the effect of amount of catalyst on conversion and selectivity of methylation of phenol vapour phase reaction was done at 450$^o$C with phenol to methanol ratio of 1:5. The feed at a flow rate of 4ml/hr. is introduced at the top of a preheated reactor packed with different amounts of pre activated catalyst packed between silica beads. The products are collected after 2 hours of reaction and analysed by GC. The results are given in the Table7.1

When the catalyst amount is increased from 0.1 to 0.25g, the conversion increases from 45.4 to 48.6 wt%. Further when the amount doubled the increase in conversion is only by 1%. The change in the selectivity was also not appreciable. So the amount was optimised to be 0.25g.

Table 7.1 Effect of amount of catalyst on methylation of phenol

| Weight of catalyst(g) | Conversion (Weight %) | % selectivity (C-alkylated products) |
|---|---|---|
| 0.1 | 45.4 | 90.1 |
| 0.25 | 48.6 | 85.7 |
| 0.5 | 49.6 | 86.5 |
| 1 | 49 | 91 |

*Reaction conditions: Catalyst –CeFe (10%), Phenol: methanol – 1: 5,*
*Temperature-450$^{o}$C, Time-2hrs, Flow rate- 4mL/hr.*

## 7.4 Comparison of catalytic activities of prepared systems

Methylation of phenol was done under optimized reaction conditions using mesoporous ceria and all the prepared systems of ceria modified by transition metals. C-alkylated products mainly o-cresol and small amount of 2, 6–xylenol were obtained as the major products under optimized condition for most of the samples confirming perpendicular orientation of phenol on catalyst surface.

Table 7.2 Optimized parameters for the methylation of phenol.

| Parameters | Optimised conditions |
|---|---|
| Temperature | 450$^{o}$C |
| Molar ratio of phenol to methanol | 1:5 |
| WHSV | 7.5 h.$^{-1}$ |
| Weight of catalyst | 0.25g |
| Time on stream | 2hours |

A comparative evaluation of all the prepared systems is given in the Table7.3.

**Table 7.3 Methylation of phenol over mesoporous ceria and modified systems**

| sample | Phenol conversion | o- cresol selectivity | 2,6-xylenol selectivity | C-alkylated selectivity | Anisole selectivity |
|---|---|---|---|---|---|
| Ce | 52 | 83.2 | 6.9 | 90.1 | 9.9 |
| CeFe (2%) | 48.2 | 72.3 | 5.4 | 77.7 | 25.9 |
| CeFe (4%) | 53.2 | 74.8 | 3.2 | 78 | 13.1 |
| CeFe (10%) | 48.6 | 82.3 | 3.4 | 85.7 | 9.7 |
| CeCr (2%) | 56.7 | 62.8 | 2.6 | 65.4 | 31.1 |
| CeCr (4%) | 58.2 | 54 | 39.5 | 93.5 | 5.8 |
| CeCr (10%) | 73.7 | 91 | 6.2 | 97.2 | 2.1 |
| CeMn (2%) | 59.3 | 50.6 | 28 | 78.6 | 21.6 |
| CeMn (4%) | 57.7 | 34.9 | 0.6 | 35.5 | 56 |
| CeMn(10%) | 66.8 | 30.3 | 0.7 | 31 | 63.2 |
| CeCo (2%) | 58.1 | 52.3 | 40.9 | 93.2 | 3.8 |
| CeCo(4%) | 51.6 | 41.6 | 53.8 | 95.4 | 2.6 |
| CeCo(10%) | 45.3 | 56.7 | 41.4 | 98.1 | 1.9 |
| CeNi(2%) | 54.3 | 50.8 | 46.2 | 97 | 2 |
| CeNi (4%) | 53.2 | 55.8 | 41.9 | 97.7 | 1.9 |
| CeNi(10%) | 58.3 | 62.8 | 34.2 | 97 | 2.5 |
| CeCu (2%) | 60.5 | 48.4 | 47.6 | 96 | 3.5 |
| CeCu (4%) | 54.3 | 55.8 | 34.9 | 90.7 | 5.3 |
| CeCu(10%) | 61 | 61.4 | 36 | 97.4 | 2.3 |

*Reaction condition: - Catalyst wt-0.25g, Phenol: methanol – 1:5, Temperature-450$^{o}$C, Time-2hours, Flow rate- 4mL/h*

## 7.5 Acid-base property and catalytic activity

Among different transition metal modified samples, the catalytic activity and product selectivity strongly depend upon acid-basic properties of the catalyst, especially; the strength of the acidic sites plays a vital role in o-selective phenol alkylation. It was observed that the acidity increased with increasing content of the metal ion. This is due to decreased electron density on metal atom, which favours the adsorption of the phenoxide ion, leading to higher conversion of phenol. Phenol itself is highly polar, even very weak basic sites can easily bind with $H^+$ ion from the phenolic O–H bond. Moreover, the phenoxide ion is resonance-stabilized and a stronger acid site is required to interact with a phenoxide ion. Thus, in the case of phenol alkylation, it is the acidity rather than the basicity which controls the catalytic activity.

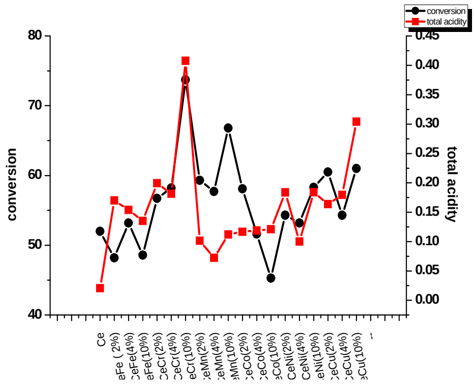

**Fig.7.9a** **Correlation of phenol conversion with total acidity**

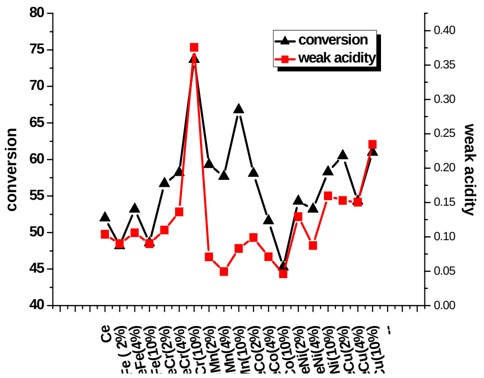

**Fig.7.9b** **Correlation of phenol conversion with weak acidity**

Here the conversion of phenol is correlated with total acidity (Fig.7.7a) and also with weak acidity (Fig.7.7b). A good correlation obtained between conversion and the acidity values shows agreement with reported literature. Among different samples prepared, CeCr (10%) got 73.7% phenol conversion with 97% selectivity of C- alkylated products.

This is highly correlated with the fact that this catalyst has the maximum acidity value among the different prepared samples.

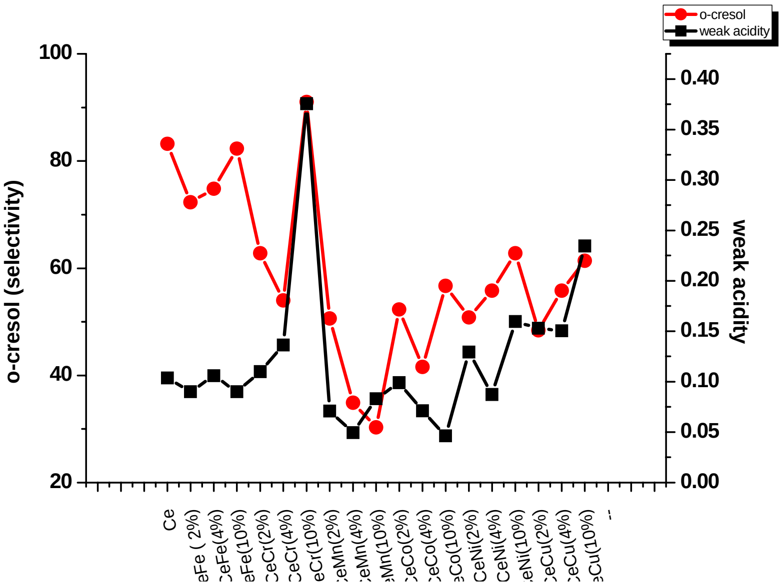

**Fig.7.10 Correlation of o-cresol selectivity with weak acidity**

But for all the other samples though a positive correlation is maintained between acidity and % conversion of phenol, the quantitative increase in % conversion is not found with the increase in acidity between different metals.

That is in the case of different samples of same the metal, there is linear change between acidity and % conversion. This is not maintained between different metals. This may be due to the fact that though acidity is a factor controlling the phenol methylation reaction, the catalyst activities also depend upon certain other factors like surface area, pore volume, structure of the catalyst etc.

In order to confirm the importance of acidity a regression equation was proposed by (32) Reddy et al. for the methylation of phenol over ferro spinel systems.

$$\ln(\text{activity}) = -0.18 \ln(\text{surface area}) + 0.27 (\text{acidity}) + 4.05$$

A large value of acidity coefficient suggests the reaction to be acidity directed. According to this equation surface area does not seem to contribute much to the activity.

The catalytic activity of metal promoted systems may be correlated with Lewis acidity. The increase in acidity was rather sharp when the metal loading varied. However such a change could not be observed in conversion. This indicates that the metal content or acidity is not the only the criteria favouring the reaction. The leveling off of the conversions at higher loading indicates that there exists a critical value for the acidity beyond which the reaction seems to be independent of acidity.

Preferential C-alkylation can be attributed to large number of weak and medium acid sites whereas preferential ortho-alkylation is due to perpendicular orientation of phenol aromatic ring on catalyst surface. Selectivity in phenol alkylation (O- or C-alkylation) is reported to depend on the acid–base properties of the catalyst [22]. The O & C-selectivity of the catalysts (formation of o-cresol, 2, 6-xylenol and 2- methyl anisole but not meta- or para-cresols or 4-methyl anisole) can be attributed to the nature of adsorption of phenol on these catalysts. As described by Tanabe [33] the phenolate ion is adsorbed on these catalysts such that the ortho-position is very near to the catalyst surface, hence only the ortho-position can be methylated. In our work the o-cresol selectivity of different samples are found to be in good correlation with weak acidity which support the reports [31]. The undesired side reactions such as the dealkylation to phenol and formation of poly methylated products are suppressed over these catalysts due to the unavailability of strong acid sites.

## 7.6 Rate of phenol methylation: Kinetic parameters

The heterogeneous model is based on the Langmuir–Hinshelwood–kinetics wherein the main reaction forming o-cresol & 2, 6–xylenol(C-alkylated products) is catalysed by the active sites on the catalyst. According to this, phenol and methyl alcohol are chemisorbed on dual adjacent active sites of the catalyst to form different carbonium ions. Both chemisorbed phenol and methanol react with each other to form C-alkylated products followed by desorption of products from the active sites. Here, the dual-site surface reaction is the rate controlling step [34].

For the synthesis of o-cresol and 2, 6-dimethylphenol (2, 6-DMP) from phenol, the reactions occur according to the following stoichiometry:

$$\text{Phenol} + \text{methanol} \rightarrow \text{o-cresol} + H_2O \text{------------------------} (1)$$

$$\text{o-cresol} + \text{methanol} \rightarrow 2,\ 6\text{-DMP} + H_2O \text{--------------------} (2)$$

Phenol methylation is highly exothermic with a standard heat of reaction of 146 kJ/mol for the formation of 2, 6-DMP. To determine the reaction rate parameters, the following differential equations were established to describe the reaction system by assuming a pseudo-first-order equation for phenol methylation:

$$-dC_{phenol} / d\,(1/WHSV) = k_1 C_{phenol} \text{----------------------------} (3)$$

$$dC_{o\text{-}cresol}/d\,(1/WHSV) = k_1\,C_{pheno\,l} - k_2 C_{o\text{-}cresol} \text{---------------} (4)$$

$$dC_{2,\,6\text{-}DMP}/d\,(1/WHSV) = k_2\,C_{o\text{-}cresol} \text{----------------------------} (5)$$

Integration of eqn. (3) yields

$$-\ln(1 - X) = k\,/WHSV \text{------------------------------------------} (6)$$

Experimental results were plotted according to equation(6), and a straight line passing through origin was obtained, indicating a good fit of the data to Equation (6), as illustrated in Fig. 7.9. Therefore, the rate of phenol disappearance (reaction 1) is first-order with respect to phenol concentration and zero order with respect to methanol. The rate equation can be written as'

$$r = kC_{phenol} \text{ --------------------------------------------------------- } (7)$$

### 7.6.1 Test of pseudo-first-order kinetic model for reaction at 450$^{O}$C over CeFe (10%)

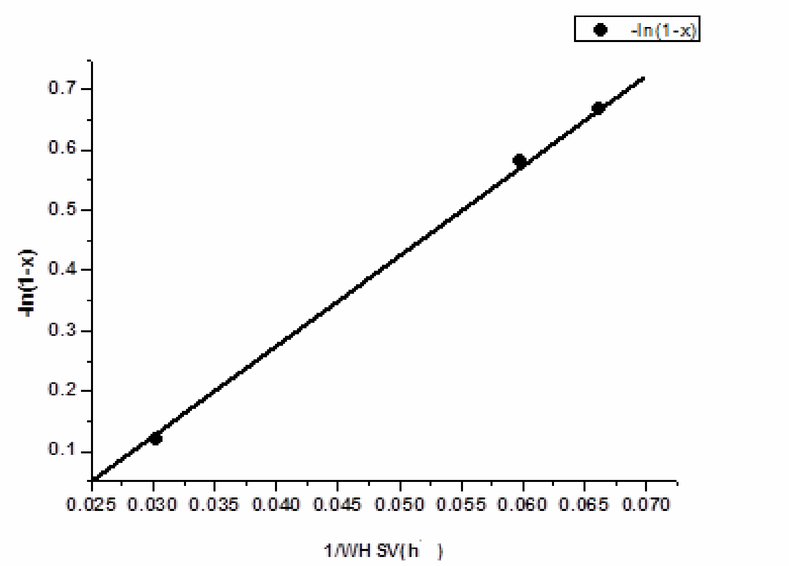

**Fig.7.11 First order kinetic plot of phenol methylation**

Considering the reaction as pseudo unimolecular, the intrinsic rate constants in the units of ($min^{-1}m^{-2}$) was determined for each catalyst using the formula

$$k(min^{-1}m^{-2}) = \frac{2.303}{twA} \log \frac{100}{100\text{-}\%yield}$$

Where, t= time of the reaction in minutes, w= weight of the catalyst (g) and A= BET surface area of the catalyst ($m^2$/g)

The kinetic parameters ($E_a$ and In A) were evaluated from the phenol conversion values in the temperature range 400-500°C, assuming the diffusion and mass transfer effects were insignificant. Rate constant k is calculated for the reaction at different temperatures using CeFe (10%) catalyst under the same reaction conditions. Based on the Arrhenius equation,

$$k = A \exp(-E_a/RT)$$

using 'least square method', the frequency factor A and the activation energy $E_a$ were evaluated as $9.6 \times 10^6$(kg of catalyst)$^{-1}$ h$^{-1}$ and 51 kJ/mol, respectively. The values of $E_a$ vary in the same range (30-130 kJ mo1$^{-1}$) as reported recently by several authors for phenol conversion over different catalyst. Recently Li et al. [35] have reported the $E_a$ value of 115.0 kJ mol$^{-1}$ for the conversion of phenol over manganese oxide catalyst, while Bautista et al. [36] has found it to be 20-60 kJ mol$^{-1}$ over various anions loaded $A1PO_4$-$A1_2O_3$. Santacesaria et al. [37] have estimated the same to be 50-70 kJ/mol over the H-ZSM-5 zeolite. The $E_a$ calculated in the present study also varies in the same range (30-130 kJ mol$^{-1}$) indicating the validity of the model assumed for the evaluation of kinetic parameters.

Employing the power law equation from Power law kinetics the rate of reaction for the present system would be [38].

$$-r = A \exp(-E_a / RT)\, C_{phenol}, \quad \text{--------------------------------}(3)$$

Where, $E_a$- the apparent activation energy and A- is the Arrhenius frequency factor.

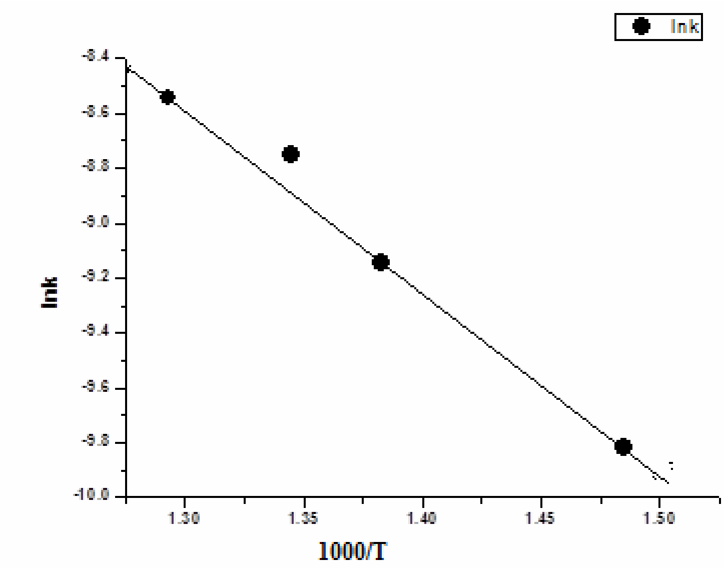

**Fig.7.12 Arrhenius plot with CeFe (10%) as the catalyst**

$E_a$- the apparent activation energy is calculated from the above plot is 57.2 kJ/mol which is approximately same as that calculated by 'least square method'. The rate constant for the catalyst CeFe (10%) at the reaction temperature of 723K is found to be 6.85 x$10^{-3}$ min$^{-1}$.

From the Arrhenius plot,

$E_a$= 57.2kJ/mol,
So $\Delta H^{\dagger}= E_a - RT = 51.2$ kJ/mol
$\Delta S^{\dagger} = R\ [\ln A- \ln(kT/h) - n] = -230$ J/mol /K

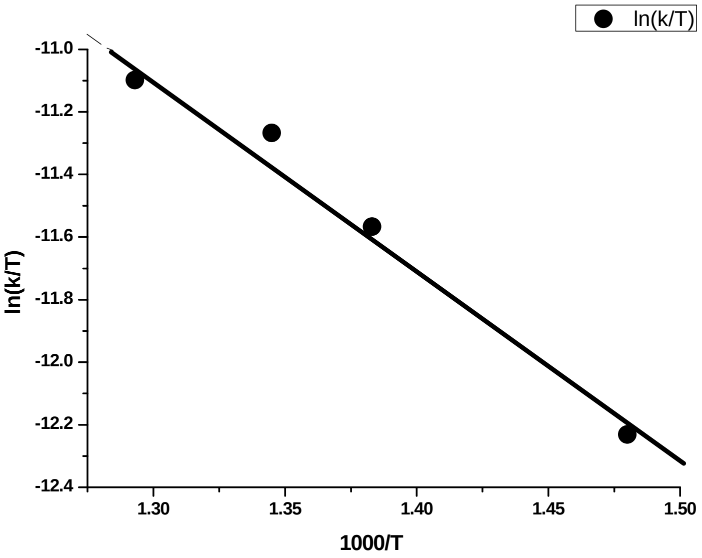

**Fig.7.13 Eyrings plot with CeFe (10%) as the catalyst**

The values of different kinetic parameters calculated according to Arrhenius equation and Eyrings equation are given in the Table7.4

**Table7.4 Values of different kinetic parameters**

| **Kinetic parameters** | **Values** |
|---|---|
| Activation energy $E_a$ | 57.2 kJ/mol |
| Frequency factor A | 9.6 x $10^6$ (kg of catalyst)$^{-1}$ h$^{-1}$ |
| Enthalpy of activation $\Delta H^{\dagger}$ | 51.2 kJ /mol |
| Entropy of activation $\Delta S^{\dagger}$ | -230J/Mol /K |

**Table7.5 Effect of metal loading on phenol methylation reaction**

| sample | Rate constant ($m^{-2}$ $min^{-1}$)x$10^{-4}$ | TON | TOF($h^{-1}$) | Catalyst activity (mmol $m^{-2}h^{-1}$) |
|---|---|---|---|---|
| Ce | 1.26 | - | - | - |
| CeFe (2%) | 1.55 | 5944 | 2972 | 0.0265 |
| CeFe (4%) | 1.78 | 3284 | 1642 | 0.0296 |
| CeFe (10%) | 3.36 | 1199 | 599 | 0.051 |
| CeCr (2%) | 1.24 | 6496 | 3248 | 0.025 |
| CeCr (4%) | 2.15 | 3350 | 1675 | 0.027 |
| CeCr (10%) | 4.37 | 1692 | 846 | 0.043 |
| CeMn (2%) | 1.72 | 7200 | 3600 | 0.027 |
| CeMn (4%) | 0.63 | 3503 | 1752 | 0.0268 |
| CeMn (10%) | 0.705 | 1622 | 811 | 0.034 |
| CeCo (2%) | 2.08 | 7570 | 3785 | 0.024 |
| CeCo (4%) | 1.8 | 3362 | 1681 | 0.023 |
| CeCo (10%) | 1.78 | 1181 | 590 | 0.023 |
| CeNi (2%) | 2.59 | 7059 | 3530 | 0.031 |
| CeNi (4%) | 2.74 | 3450 | 1725 | 0.033 |
| CeNi (10%) | 3.25 | 1512 | 756 | 0.037 |
| CeCu (2%) | 3.5 | 8571 | 4286 | 0.041 |
| CeCu (4%) | 2.8 | 3846 | 1923 | 0.038 |
| CeCu (10%) | 2.4 | 1728 | 864 | 0.046 |

*Reaction condition: - Catalyst weight-0.25g, Phenol: methanol – 1:5, Temperature-450$^{o}$C, Time-2hours, Flow rate- 4mL/hr*

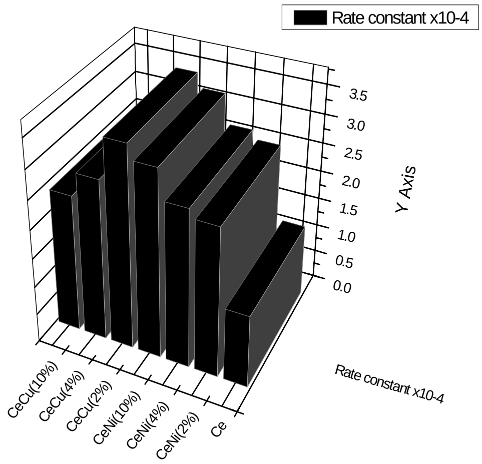

**Fig.7.14a** **Effect of loading of Cu & Ni on phenol conversion**

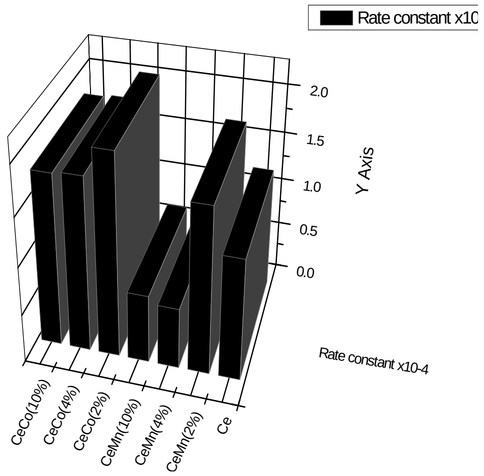

**Fig.7.14.b** **Effect of loading of Co & Mn on phenol conversion**

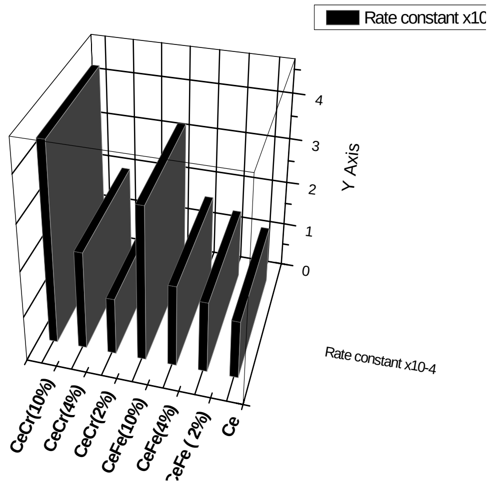

**Fig.7.14.c Effect of loading of Cr &Fe on phenol conversion**

For Cr, Fe & Ni modified samples, the rate constants increases as the metal content increases. For Co & Mn loaded samples the rate constant initially decreases with metal loading then it increases. However with Cu loading, the rate constant decreases steadily. Effect of metal loading on phenol conversion may be due to the higher uniform dispersion of metal ions on ceria support as well as moderate acidity.

At higher metal loading, the decrease in the conversion could be due to the non-uniform distribution of metal ions on ceria support as well as higher acidity. These results suggest that the moderate acidity is more favourable for this reaction than strong acidity.

The catalyst activity of Cr, Fe, Mn & Ni modified samples increase with metal concentration. As metal concentration increases, the acidity of the system increases with a corresponding reduction in the basicity. In other words, acid–base properties are mutually dependent and creation of new acidic centres occurs through the removal of existing basic centers [29]. In the case of phenol alkylation, for the Cr, Fe & Ni modified mesoporous ceria catalysts the catalytic activity progressively increased as metal content increased (Fig.7.13a). For Co samples the activities are almost same with negligible change with increase in metal loading (Fig.7.13b). The TON & TOF are inversely related to the metal concentration. This is because the change in conversion with metal loading is not that much pronounced with increase in the metal content.

The catalytic activity of metal promoted systems may be correlated with Lewis acidity. The increase in acidity was rather sharp when the metal loading varied. However such a change could not be observed in conversion. This indicates that the metal content or acidity is not the only the criteria favouring the reaction. The leveling off of the conversions at higher loading indicates that there exists a critical value for the acidity beyond which the reaction seems to be independent of acidity.

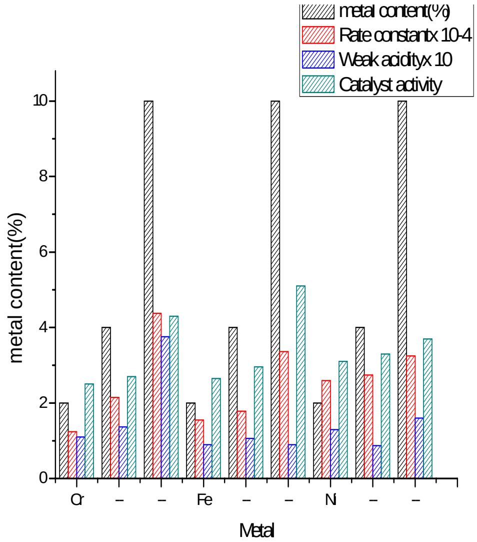

**Fig.7.15a** **Effect of Cr, Fe& Ni loading on phenol methylation reaction**

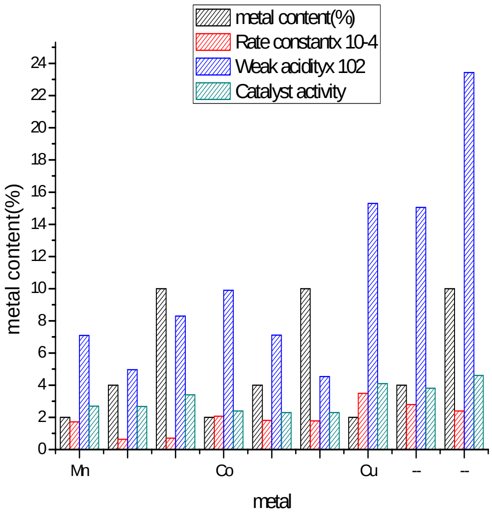

**Fig.7.15.b** **Effect of Co, Cu& Mn loading on phenol methylation reaction**

## 7.7 Summary and conclusions

Mesoporous ceria permit the alkylation of bulk molecules for which micro porosity of zeolite imposes limitations to the reaction. It is important to control both porosity and acidity to get the desired product. It is a challenge to develop a satisfactory solid alkylation catalyst that makes the chemical transformation economically feasible and environmentally friendly, which has a high yield of alkylate, selectivity to the desired product, a long life cycle, regenerability, and greatly reduced environmental and safety risks. We report herein the development of an environmentally friendly process for C-methylation of phenol derivatives with methanol using mesoporous ceria modified solid acid catalysts. In summarizing the results, the following conclusions can be deduced:

- These systems are highly efficient for alkylating phenol in the ortho position, leading to o-cresol as the major product. Under optimized conditions, for the best catalyst among the prepared samples (CeCr10%) the total ortho selectivity was higher than 97% with a phenol conversion of 74%.
- Preferential C-alkylation can be attributed to large number of weak and medium acid sites whereas preferential ortho-alkylation is due to perpendicular orientation of phenol aromatic ring on catalyst surface. The undesired side reactions such as the dealkylation to phenol and formation of poly methylated products are suppressed over these catalysts due to the unavailability of strong acid sites.
- Formation of poly methylated products is suppressed over these catalysts due to the unavailability of strong acid sites. Direct C-alkylation over the prepared catalysts is due to the higher acidity of catalysts. The catalyst is highly stable and does not deactivate even after a number of cycles.
- A tentative mechanism for the ortho selective methylation of phenol over the catalyst has been proposed. Phenol is adsorbed perpendicularly on Lewis acidic site by lone pair electrons of oxygen atom and is alkylated by methanol, which is possibly in the form of methyl carbonium ion.
- The reaction is proved to be following first order kinetics with phenol conversion with the frequency factor A and the activation energy $E_a$ evaluated as 9.6 x $10^6$ (kg of catalyst)$^{-1}$ h$^{-1}$ and 57.2 kJ/ mol, with (CeFe10%)catalyst. The values of $E_a$

vary in the same range (30-130 kJ $mo1^{-1}$) as reported recently by several authors for phenol conversion over different catalyst. The kinetic parameters like ΔH, ΔS of activation for the reaction are calculated.

- For Cr, Fe & Ni modified samples, the rate constants increases as the metal content increases. For Co & Mn loaded samples the rate constant initially decreases with metal loading up to a higher concentration then it increases. However with Cu loading, the rate constant decreases steadily. Effect of metal loading on phenol conversion may be due to the higher uniform dispersion metal ions on ceria support as well as moderate acidity.
- The activity of Cr, Fe, Mn & Ni modified samples increase with metal concentration. For Co samples the activities are almost same with negligible change with increase in metal loading.
- The TON & TOF are inversely related to the metal concentration. This is because the change in conversion with metal loading is not that much pronounced with increase in the metal content.

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Chapter 8

# SUMMARY AND CONCLUSIONS

Contents

My Ph.D. research work is concerned mainly on developing new mesoporous materials. A wide range of important organic reactions can be efficiently catalyzed by these materials, which can be designed to provide different types of acidity as well as high degrees of reaction selectivity. Industrial catalysis was developed from an art to science. A typical industrial catalyst should be regenerable, reproducible, mechanically and thermally stable and economical and should possess suitable morphological characteristics apart from its activity, selectivity, and stability.

A variety of methodologies for synthesizing mesoporous metal oxides have been investigated. Here in this work mesoporous ceria was prepared by soft templating method using the neutral surfactant hexadecyl amine. The mesoporous ceria thus prepared is modified with transition metals Cr, Fe, Mn, Cu, Co and Ni. The applications of these catalysts in industrially important reactions like ethyl benzene oxidation, alkylation of aromatics, protection and de-protection of acetone like cyclohexanone are also investigated. This chapter reviews the summary of the work detailed in the previous chapters. The important conclusions arrived from different studies are also presented in this chapter.

## 8.1 Summary

Chapter I deal with the literature survey in which the introduction about the heterogeneous catalysis, detailed informations about the solid catalysts, their importance in heterogeneous catalysis and in industrial processes and the use of metal oxides as solid acids are dealt with. The new generation mesoporous solids can be obtained from various metal precursors employing different methods of preparation are discussed here.

In the field of catalysis, much effort has been spent in the preparation, characterization and application of ceria and ceria based mixed oxide materials for automotive exhaust catalysis and oxidation of environmental pollutants. The influence of the redox properties of ceria on several reactions has also been investigated systematically. Doping can improve the sintering properties of ceria, by stabilizing the ceria surface area and crystal size. The effect of modification of mesoporous ceria by transition metals in the study is discussed in this section.

Surface acidity and basicity investigations have received great attention due to its application in determining catalytic behaviour which is used to describe the effectiveness of a catalyst. The acidity of the solids plays a significant role when these are used as supports. The necessity for the determination of surface acidity and the test reaction of acidity are also discussed in this chapter. Finally the activities of prepared catalysts studied using different industrially important reactions and the importance of these reactions are discussed.

Chapter II deals with the materials and the experimental procedures used for catalyst preparation, surface acidity and catalytic activity measurements. The structural and morphological characteristics of the prepared samples were investigated by the techniques like wide and low angle XRD, BET surface area and pore volume measurements, BJH sorption studies, TEM, FT- IR, TG-DTA, SEM, EDX, ICP –AES, TPR in $H_2$ and UV-Vis DRS. Ammonia TPD, and cumene cracking as the test reaction for acidity are adopted for the surface acidity determination. For the activity study of the prepared systems, liquid phase reactions like oxidation of ethyl benzene using TBHP to get acetophenone as the main product, Friedel Crafts benzylation of toluene, o-xylene, anisole and benzene using benzyl chloride as the benzylating agent, acetalization and deacetalization of cyclohexanone for the protection of ketone functional group and vapour phase reaction of methylation of phenol are done.

Chapter III describes the results of physico–chemical characterization of prepared catalysts. A detailed investigation of physico-chemical characterization of the catalytic systems was performed by techniques such as wide and low angle XRD, BET surface area, pore volume and pore distribution by sorption studies of nitrogen gas, EDX, ICP-AES, SEM, TEM, thermogravimetry, UV-Vis DRS, FT-IR and TPR in $H_2$. Surface acidic properties of the systems were obtained from TPD of Ammonia and the results were tested by the test reaction of vapour phase cumene cracking. The results of these techniques are discussed.

Chapter IV deals with the liquid phase benzylation of toluene, o-xylene and anisole using benzyl chloride as benzylating agent. Here in this chapter, conversion of the reaction in terms of benzyl chloride is correlated with the acidities of the prepared catalysts. The various reaction parameters like temperature, molar ratio of substrate to benzyl chloride, weight of catalyst and time of the reaction were optimized using iron loaded catalyst for toluene benzylation. Then o-xylene and anisole were also benzylated in this optimized condition.

In chapter V the synthesis of dimethyl acetals of carbonyl compound such as cyclohexanone, is successfully carried out by the reaction between cyclohexanone and methanol using different prepared catalysts are described. The strong influence of the textural properties of the catalysts such as acid amount and adsorption properties (surface area and pore volume) on the catalytic activity is interrelated in this chapter.

Chapter VI presents the investigation, about the oxidation of ethyl benzene carried out in liquid phase using the mesoporous ceria and transition metal modified ceria systems using tert.butylhydroperoxide (TBHP) as the oxidizing agent. The reaction was studied in different temperatures and using different solvents. Based on this report in the present study, we utilized mesoporous ceria modified with different transition metals as catalysts for the oxidation of ethyl benzene using TBHP as oxidant in liquid phase. The stability and reusability of the catalyst is studied using representive samples. The kinetic parameters of the reaction with Cr modified catalyst are calculated considering the reaction to be pseudo unimolecular.

In chapter VII discussions about selective C-methylation of phenol to o-cresol in high yield carried out with methanol over mesoporous ceria modified by transition metals are done. The influence of various experimental parameters on phenol conversion and product selectivity has been investigated. The catalyst was active without any deactivation showing its longer life. The catalytic activity and selectivity is correlated with its acidity and structure. A tentative mechanism for the ortho selective methylation of phenol over the catalyst has been proposed. Phenol is adsorbed perpendicularly on Lewis acidic site by lone pair electrons of oxygen atom and is alkylated by methanol, which is possibly in the form of methyl carbonium ion. The kinetic parameters of the reaction with Fe modified catalyst are calculated considering the reaction to be pseudo unimolecular.

## 8.2 Conclusions

Mesoporous ceria modified with various transition metals can be successfully synthesized by template method using Hexadecyl amine as surfactant. All the samples prepared have ordered pores. Major conclusions that can be drawn from the present research work are the following.

Mesoporous ceria can be successfully prepared by surfactant route using neutral surfactant hexadecyl amine that has more surface area.

- The surface area and pore volume of the support decrease with the introduction of transition metals. Adsorption isotherms of ceria calcined at different temperatures resemble Type IV of IUPAC classification which is characteristic of mesoporous materials. The narrow pore size distribution shows uniformity of the pore.
- The XRD data of the prepared systems agree well with the standard values for the cubic fluorite structure of ceria. No additional peaks corresponding to the doped metal oxide is found for Cr, Fe, Mn, Ni & Co. This shows that metals are highly dispersed within the frame work structure. For Cu when the concentration exceeds a limit the metal peaks are found in the XRD pattern.

- From FT-IR studies it can be seen that the neutral surfactant is successfully removed at a lower calcination temperature attaining maximum surface area. It also shows large amount of surface hydroxyl groups present which are responsible for Brönsted acidity.
- From the interpretation of the total acidities of samples measured by temperature programmed desorption of ammonia gave good correlation with the cumene cracking conversion. It confirms the enhancement of surface acidity upon modification with transition metals.
    - The study on liquid phase Friedel Crafts benzylation reaction of toluene shows that they are suitable solid acid catalysts for reaction. The most efficient catalysts for Friedel Crafts benzylation among the prepared samples are iron modified ones. Exceptionally high activity in the case of iron systems proposed a free radical mechanism, which was confirmed by the effect temperature as well as the presence of an induction period for the reaction.
    - The catalysts are regenerable and can be used again. This reusability regenerability, high selectivity, 100% conversion, moderate reaction temperature, and absence of solvent, etc. make these catalyst to be used in a truly heterogeneous manner and makes the benzylation reaction an environment friendly one. Hence this solid acid catalyst can be used in efficient green chemical process for the manufacture of industrially important compounds.

  - From the study on acetalization and deacetalization of cyclohexanone it can be concluded that the prepared catalysts are successful in the protection of ketone group and afterwards the same catalysts can be used to regenerate the ketone group in the substrate by de protection in a simple manner. We introduced a mild and selective reagent for the oxidative cleavage of acetals under aqueous and heterogeneous conditions. The stability, simple work-up and high yields of the products are among the advantages of this procedure which make it an attractive supplement to the present reported methods.

The present study on liquid phase oxidation of ethyl benzene can be summarized as given below.

- Ethyl benzene can be oxidized effectively using mesoporous ceria modified catalyst using TBHP in liquid phase to get acetophenone selectively as the major product.
- Reaction variables like temperature, weight of catalyst, time, solvent and volume of the solvent have predominant effect on the % conversion and selectivity to acetophenone.
- Chromium, manganese and copper doped catalysts have more activity in the reaction and product selectivity. For the effective catalyst Cr doped ceria, the metal loading has pronounced influence on % conversion and selectivity.
- Transition metal-incorporated mesoporous materials have proved to be potential catalysts in the oxidation of alkyl arenes to

carbonyl compounds. The reactions were found to be extremely sensitive to the oxidant and solvents used. Mesoporous ceria materials appeared to be promising acid and redox catalysts and were also successfully applied as supports for active sites.

- We report herein the development of an environmentally friendly process for C-methylation of phenol derivatives with methanol using mesoporous ceria modified solid acid catalysts In summarizing the results, the following conclusions can be deduced:.
- These systems are highly efficient for alkylating phenol in the ortho position, leading to o-cresol as the major product. Under optimized conditions, for the best catalyst among the prepared samples (CeCr10%) the total ortho selectivity was higher than 97% with a phenol conversion of 74%.

Preferential C- alkylation can be attributed to large number of weak and medium acid sites whereas preferential ortho-alkylation is due to perpendicular orientation of phenol aromatic ring on catalyst surface. The undesired side reactions such as the dealkylation to phenol and formation of poly methylated products are suppressed over these catalysts due to the unavailability of strong acid sites.

- Formation of poly methylated products is suppressed over these catalysts due to the unavailability of strong acid sites. Direct C-alkylation over the prepared catalysts is due to the higher acidity of catalysts. The catalyst is highly stable and does not deactivate even after a number of cycles.

- A tentative mechanism for the ortho selective methylation of phenol over the catalyst has been proposed. Phenol is adsorbed perpendicularly on Lewis acidic site by lone pair electrons of oxygen atom and is alkylated by methanol, which is possibly in the form of methyl carbonium ion.
- The reaction is proved to be following first order kinetics with phenol conversion with the frequency factor A and the activation energy $E_a$ evaluated as $9.6 \times 10^6$ (kg of catalyst)$^{-1}$ h$^{-1}$ and 57.2 kJ/ mol, with (CeCr10%) catalyst. The values of $E_a$ vary in the same range (30-130 kJ mo1$^{-1}$) as reported recently by several authors for phenol conversion over different catalyst. The kinetic parameters like $\Delta H^\dagger$, $\Delta S^\dagger$ of activation for the reaction are calculated.
- For Cr, Fe & Ni modified samples, the rate constants increases as the metal content increases. For Co & Mn loaded samples the rate constant initially decreases with metal loading up to a higher concentration then it increases. However with Cu loading, the rate constant decreases steadily. Effect of metal loading on phenol conversion may be due to the higher uniform dispersion of metal ions on ceria support as well as moderate acidity.

## 8.3 Future Outlook

The present study on the mesoporous ceria shows that the textural and catalytic activity of the support can be modified by the loading with various transition metals. Among the prepared systems Cr and Fe modified systems are found to be efficient for oxidation, acetalization of cyclohexanone and Friedel Crafts benzylation and alkylation reactions. These systems can be used for further studies for acetalization of various carbonyl compounds, oxidation and Friedel Crafts alkylation various organic compounds. The improved acidities and redox properties can be utilized for the application in environmental pollution control. Cerium oxide has been identified as a potentially important catalytic support for the hydrogen production from syngas due to its ability to undergo rapid reduction/oxidation cycles. The possibility of using these prepared catalysts with improved OSC and reducibility can be studied for WGS activity.

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# PAPERS PRESENTED/ATTENDED IN INTERNATIONAL/NATIONAL CONFERENCES

- ***Characterisation and Catalytic Activity of Mesoporous Ceria Modified by Cr in Ethyl Benzene Oxidation*** - ROSE PHILO K.J. and S.SUGUNAN* (International Congress on Analytical Science 2008 ISAS)
- ***Characterisation and Catalytic Activity of Ceria Modified by Cr, Prepared via Sol- gel Route*** - ROSE PHILO K.J, and S.SUGUNAN*( 20th National Symposium On Catalysis –IIT Madras ,Chennai 2010)
- ***Characterisation and Catalytic Activity of Transition Metal Modified Mesoporous Ceria****- ROSE PHILO K.J. and S.SUGUNAN* (International Congress on Analytical Science 2010 ISAS )
- ***Characterisation and Catalytic Activity of Ceria Modified by Mn, Prepared via Sol- gel Route***-ROSE PHILO K.J. and S.SUGUNAN* ( National Seminar on Current Trends in Chemistry CTric 2011-CUSAT)
- ***Characterisation and Catalytic Activity of Mesoporous Ceria Modified by Cr-A Solid Acid for Green Chemistry****-ROSE PHILO K.J. and S.SUGUNAN*(*National Seminar Govt.College, Pattambi 2011 )
- ***Characterisation and Catalytic Activity of Mesoporous Ceriamodified by Cr in Benzylation of Toluene****-ROSE PHILO K.J. and S.SUGUNAN* (*National Seminar on Current Trends in Chemistry CTric 2012-CUSAT)
- U.G.C. Sponsored *National Symposium in Chemistry* organised by St.Paul’s College, Kalamassery2008.
- Workshop on *Applications of Mass spectrometry and related Hyphenated Technologies in AnalyticalScience*, held by ISAS 2009

- Workshop on *Molecular Probes –Technology and Application* organized by ISAS 2010.
- National Seminar on *Modern Trends in Chemistry* organized by Sacred Heart College, Thevara, 2010.
- National seminar on *Chemistry and Environment* organized by St.Paul's college, Kalamassery.

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