

INTRODUCTION AND LITERATURE SURVEY

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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.

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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 homogeneously 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 Brønsted 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 Brønsted acids (proton donors) and Lewis acids (electron acceptors) are known, with the action of Brønsted sites in zeolites being particularly well understood. Solid acids can be described in terms of their Brønsted / Lewis acidity, the strength and number of these sites, and

the morphology of the support (typically in terms of surface area and porosity). Typically, Brønsted 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 Brønsted 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 Brønsted 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 Brønsted acids [10]. Pure Lewis acids are more difficult to achieve, because Brønsted 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 Brønsted 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 $>1000\text{m}^2\text{ g}^{-1}$, 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 ($> 1000 \text{ m}^2 \text{ g}^{-1}$) 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.

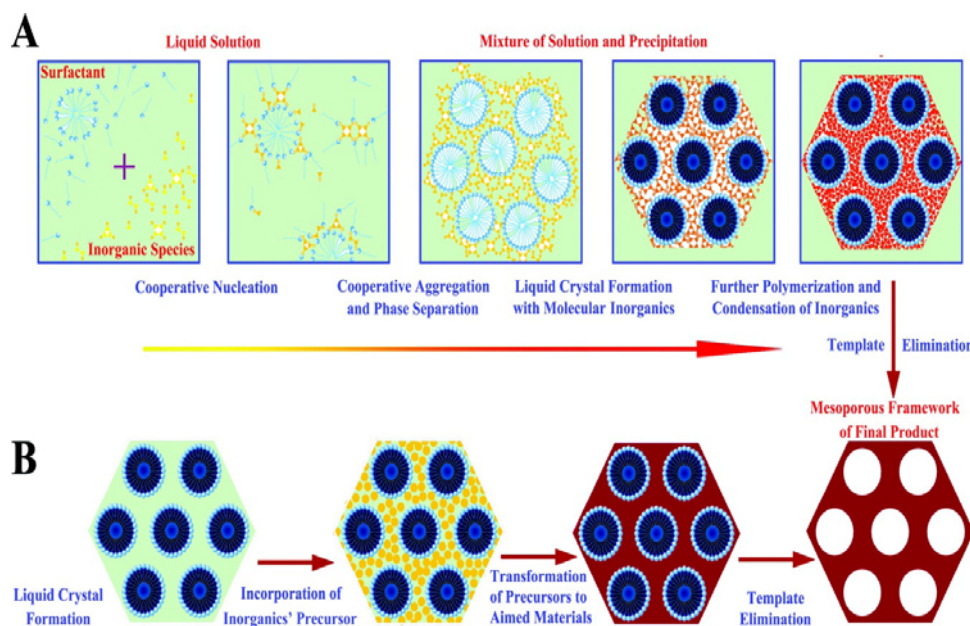


Fig.1.1 Two synthetic strategies of mesoporous materials: (A) co-operative self-assembly; (B) “true” liquid-crystal templating process [39].

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].

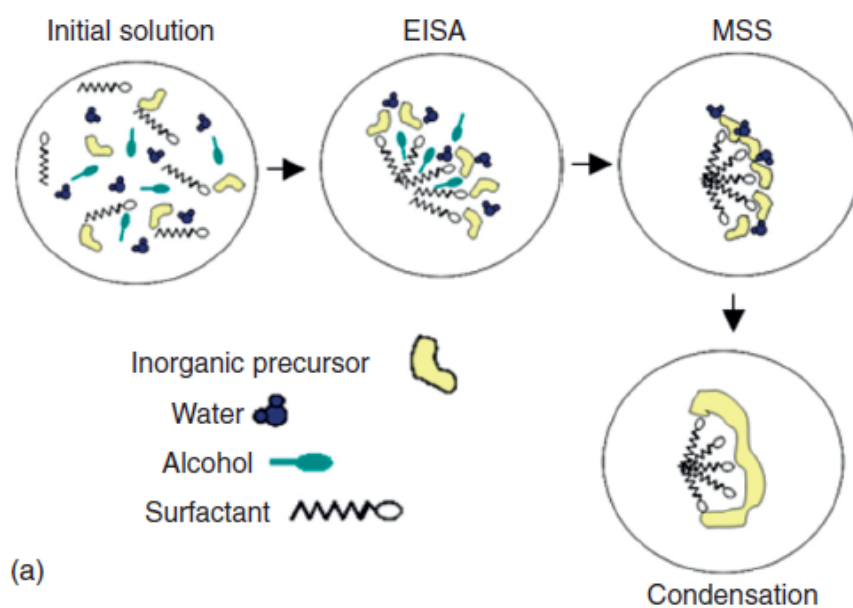


Fig.1.2 Schematic representation of evaporation-induced-self-assembly for the preparation of long-range ordered meso structures [40]

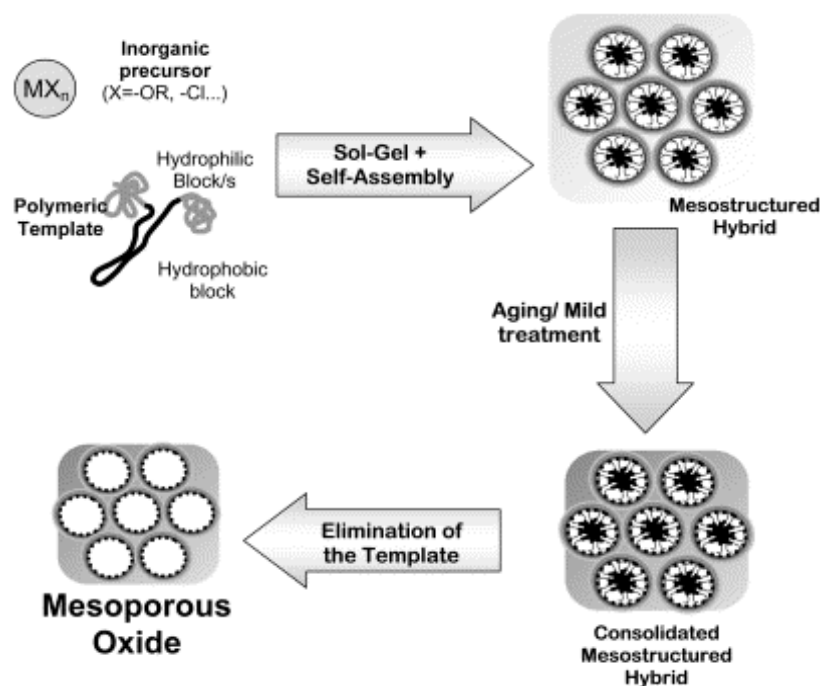


Fig.1.3 Schematic views of the steps leading from composite solution to mesoporous oxide [42]

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.

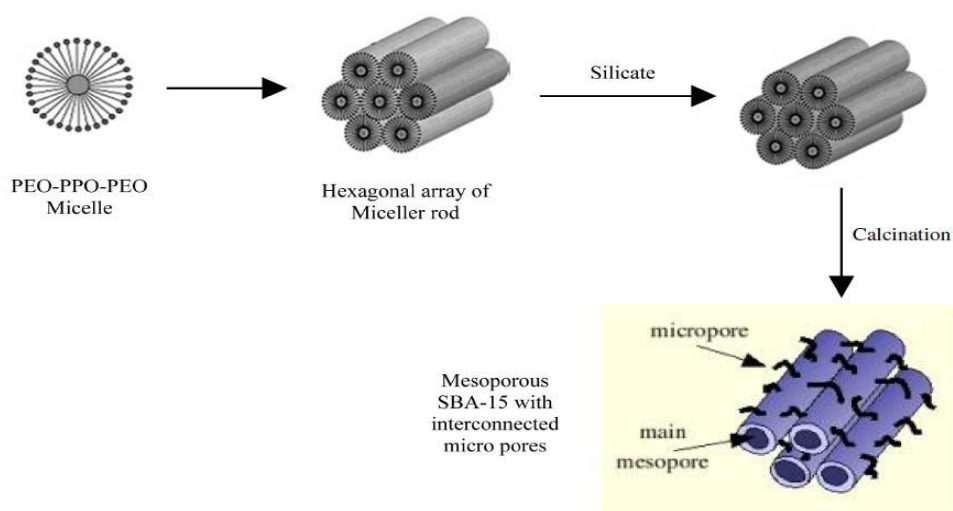


Fig.1.4 Mechanistic pathway for the formation of SBA-15

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].

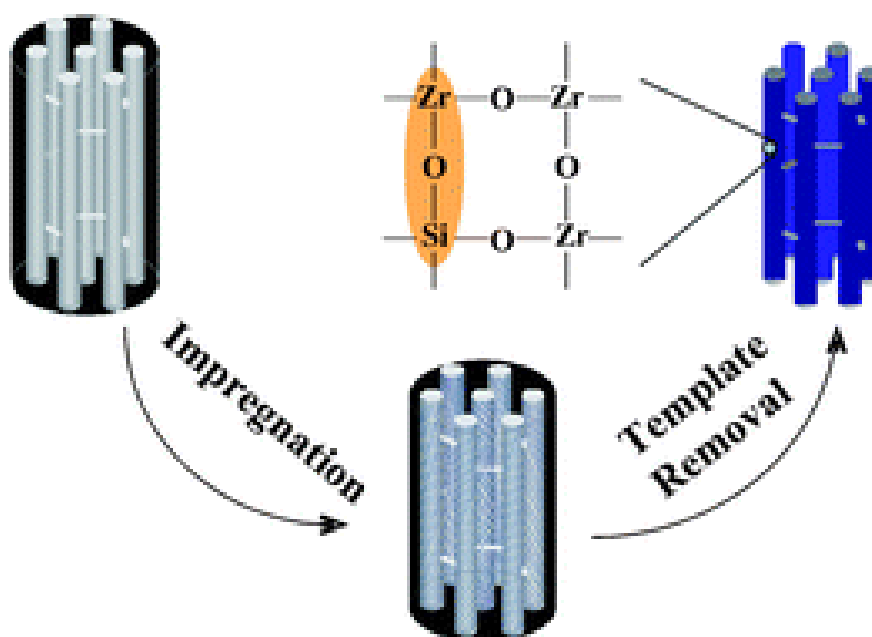


Fig.1.5 Schematic representation of the replica process (64)

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^0) and neutral inorganic precursors (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 ($\text{pH} = 6.75\text{--}8$). 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.

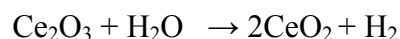
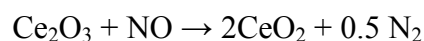
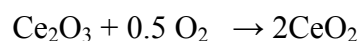
1.8 Mesoporous ceria

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

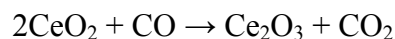
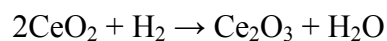
metals. The interest in cerium oxide (CeO_2) has increased in the past decade because it plays a vital role in emerging technologies for environmental and energy-related applications [48]. Among a variety of oxides, cerium oxide (CeO_2) is particularly interesting to several catalytic processes. For 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 $\text{CeO}_{(2-x)}$ [$0 \leq x \leq 0.5$]. 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,



Under rich conditions,



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 $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$ charge transfer and is known to crystallize in fluorite structure (CaF_2) with a space group of $\text{Fm}\bar{3}\text{m}$. 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.

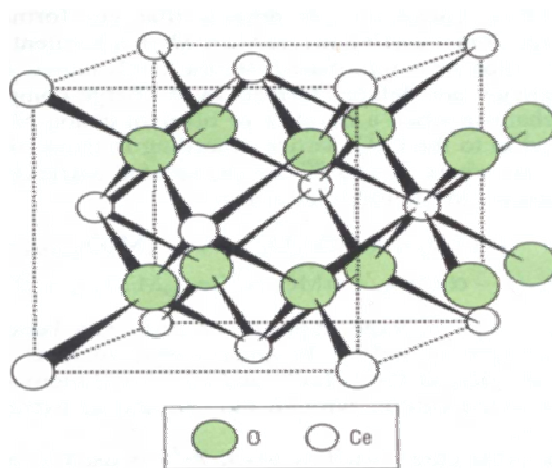


Fig.1.6 Fluorite crystal structure of CeO_2 . [68]

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 nonstoichiometric 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 Ce₂O₃ phase. This phase is stable at room temperature and possesses identical structure as that of La₂O₃. The ability of the cerium ion to switch between the Ce⁴⁺ and Ce³⁺ oxidation states depending on the ambient oxygen partial pressure is represented as:



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 CeO₂. 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 Ce⁴⁺ to Ce³⁺. 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 CeO₂. The performance of CeO₂ in catalysis could be optimized by increasing the surface area and decreasing particle size distribution simultaneously.

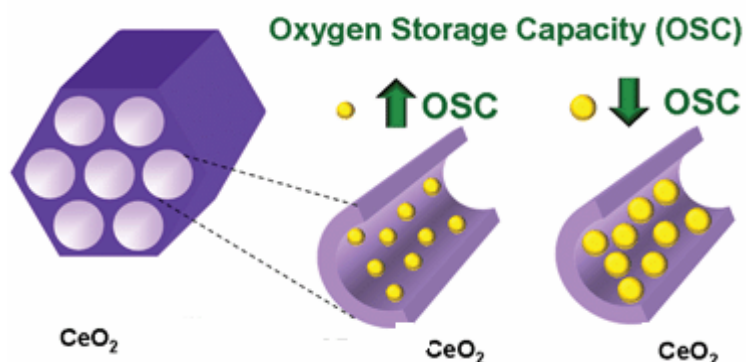


Fig. 1.7 OSC of Ceria

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 Ce³⁺ ion (1.14 Å) is larger than that of Ce⁴⁺ (0.97 Å), and hence the lattice expansion is a consequence of the reduction of Ce⁴⁺ ions to Ce³⁺. 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 Ce⁴⁺ to Ce³⁺ 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 SiO₂, Al₂O₃, MgO and ZrO₂ [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 ≤ x ≤ 0.5). The Ce³⁺ ions form the main defect centres and the charge imbalance is neutralized by the formation of oxygen ion (O²⁻) vacancies [54]. Ceria retains its fluorite structure when reduced at

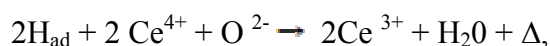
temperatures below 900 K. The reduced form of ceria can be completely oxidized when exposed to air at room temperature. This easy availability of lattice oxygen and retention of the structural feature has been exploited in several cases for catalytic reactions involving oxidative process. Temperature 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-CeO₂ 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, ZrO₂ 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 CeO₂ 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 ZrO₂, HfO₂ 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 CeO₂ and CexZr_{1-x}O₂ occurs due to the direct dissociative chemisorption of H₂ on surface site leading to the formation of water via hydroxyl groups followed by the creation of surface oxygen vacancies and reduction of Ce⁴⁺ ions to Ce³⁺ ions. This can be written as,



where Δ 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 CeO₂ surfaces even at very low temperatures. Ceria reduction occurs in two steps: (i) first one is the extraction of surface capping O²⁻ 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/CeO₂ materials along with the resistance of the metal particles from thermal sintering. The M/CeO₂ 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, Ce⁴⁺/Ce³⁺ 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 Ce⁴⁺ cations to Ce³⁺ 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}/Al₂O₃ system the synergistic effect between the supported Pd metal and CeO₂ 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 Zr⁴⁺ 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 CeO₂ 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 SiO₂, Al₂O₃, TiO₂, Nb₂O₅, CeO₂ and ZrO₂. 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 TiO₂ and Nb₂O₅ 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 H₂ 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 m²/g for ceria prepared by the reverse microemulsion method [70], 200 m²/g for ceria prepared using surfactants [71] or 240 m²/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 Brønsted 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 CeO₂ 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 H β zeolite is found to have better catalytic performance than H β 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/SiO₂ 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, benzylolation 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 SiO₂ [89], SiO₂-Al₂O₃ [90], NiSO₄ [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 Cu₂O are semiconductors and effective for redox-type reactions such as oxidation or dehydrogenation. Many copper based catalysts such as CuO-ZnO [93], Cu-ZnO-Al₂O₃ [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 CeO₂ prepared by sol-gel method [96]. The results showed that CeO₂ could enhance the surface dispersion of copper and prevent it from sintering. It is suggested that the high activity, selectivity and stability of CeO₂ 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-CeO₂ 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-CeO₂ mixed oxides have much higher catalytic activity than those of pure MnO_x and CeO₂. 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-CeO₂ 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 Brønsted/ 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 Brønsted 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 Brønsted and Lewis sites are widely used to get total acid amount of the systems. Brønsted 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 Brønsted 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 Brønsted acid ratio of a catalyst. Cumene is cracked to benzene, ethyl benzene, styrene and propene over Brønsted 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-H₂ 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.

1.13 References

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