Abstract

Catalysis research is central to the science of modern chemical processing, fuel technologies and environmental control. It controls more than 90% of the world's chemical manufacturing process and is one of the most important technologies in national economies. Modern society as we know it would be impossible without catalysis. Catalysis is a multidisciplinary science. It is a combination of fundamental and applied science with major contribution from chemistry, physics and material science. Its technological importance lies in the tremendous achievements of this science to give humanity some cheap, highly convenient and outstanding material. The most significant of the oxides of rare-earth elements in industrial catalysis is certainly CeO₂. Its use in catalysis has attracted considerable attention in recent years. This chapter deals with the general introduction and literature review of different components of the newly developed system and the various reactions undertaken for the present investigation.
1.1 Catalysis

A catalyst was defined by J. J. Berzelius in 1836 as a compound, which increases the rate of a chemical reaction, but which is not consumed by the reaction. This definition allows for the possibility that small amounts of the catalyst are lost in the reaction or that the catalytic activity is slowly lost. However, the catalyst affects only the rate of the reaction, it changes neither the thermodynamics of the reaction nor the equilibrium composition. The principal theme in catalysis is the desire to control the rate of chemical reactions and the secondary theme is to understand the mechanism of the control. Catalysis is of crucial importance for the chemical industry, the number of catalysts applied in industry is very large and catalysts come in many different forms, from heterogeneous catalysts in the form of porous solids over homogeneous catalysts dissolved in the liquid reaction mixture to biological catalysts in the form of enzymes.

Catalysis plays a prominent role in our society. The majority of all chemicals and fuels produced in chemical industry have been in contact with one or more catalysts. Catalysis becomes also progressively more important in environmental pollution control. Stoichiometric processes which generate waste problems are more and more replaced by selective catalytic routes. The three-way catalyst effectively reduces pollution from car engines. Catalytic processes to clean industrial exhaust gases are currently developed and installed. In short, catalysis is vitally important for our economies now and it will be even more important in future.

1.1.1 Heterogeneous Catalysis

Catalysts which operate on reactions taking place on surfaces, heterogeneous catalysts, are of great importance in chemical industry and in living organisms. In heterogeneous catalysis, the reacting species are held on the surface of the catalyst by a physical attraction called adsorption while the reaction takes place. Adsorption may
be relatively weak (physical adsorption) or may have a strength comparable to the strengths of chemical bonds (chemisorption). In either case adsorption is generally not uniform across a solid surface. Adsorption, and therefore catalysis, occurs primarily at certain favorable locations called active sites. The function of the catalyst is to provide an energetically favorable pathway for the desired reaction, in which the activation barriers of all intermediate steps are low compared to the activation energy of the uncatalyzed reaction.

1.2 Oxide Catalysts

Historically, oxide catalysts have been used primarily for vapor phase reaction in the petroleum and petrochemical industries. Recent work, however, has shown that these catalysts can also be effective in promoting a number of synthetically useful reactions. While simple oxides show activity for some oxidations they are more commonly used as solid acids or bases. Complex oxides can act as acids or bases as well as oxidation catalysts. Complex oxide can range in composition from the simple, amorphous, binary oxides to the more complex ternary and quaternary systems. The use of zeolites and clays can impart shape selectivity to a number of reactions, a feature that makes these systems particularly appealing for use in synthesis.

Oxide catalysts fall into two general categories. They are either electrical insulators or they can act as semiconductors. Insulator oxides are those in which the cationic material has a single valence so they have stoichiometric M:O ratios. The simple oxides, MgO, Al₂O₃ and SiO₂ and the more complex zeolites, which are aluminosilicates, fall into this category. These materials are not effective as oxidation catalysts and find more use as solid acids or bases.

Semiconductor oxides are most commonly used in oxidations. They are materials in which the metallic species is relatively easily cycled between two valence states. This can be two different positive oxidation states as in Fe₂O₃, V₂O₅, TiO₂,
CuO or NiO, or the interconversion between the positive ion and neutral metal as with the more easily reduced oxides such as ZnO and CdO\textsuperscript{5,6}.

Basically, some oxides are semiconductors because they can have either a slight excess or deficiency of electrons. In the former case there is a net negative charge so the material is referred to as an n-type semiconductor. A net positive charge gives a p-type semiconductor. These two types are appreciably different in their adsorption and reaction characteristics.

1.2.1 Simple Oxides

A simple oxide catalyst can be used in either the bulk state or supported on an inert oxide support material. In general, the simple semiconductor oxides are not very good catalysts for synthetic reactions. The insulator oxides like Al\textsubscript{2}O\textsubscript{3} can be used as acid catalysts\textsuperscript{7,8} and MgO and BaO for base catalyzed reactions\textsuperscript{3,4}.

1.2.2 Supported Oxides

Supported oxides have several advantages over unsupported materials\textsuperscript{9}. Supports can be used to improve the mechanical strength, the thermal stability and the lifetime of the catalyst. They can also provide the means for increasing the surface area of the active species. In addition, data have shown that supported oxides frequently have structural features and chemical compositions different from those on the surface of the support material. There are several general ways in which the active oxide can be found on the surface of the support material\textsuperscript{10}.

The active component and the support can be intimately mixed throughout the catalyst particle. This arrangement provides the maximum interaction between the support and the catalyst so it maximizes the catalyst support interaction. Unfortunately, it also leaves a large portion of the active material buried in the bulk of the particle. The active component can be molecularly dispersed on the support with
respect to maximizing the catalyst support interaction. Here individual molecules of the catalytically active species are bound to the support surface as a localized binary oxide. The nature of the support can then have a significant influence on the reaction characteristics of the catalyst.

The catalyst component can form an active molecular monolayer on the support. Here, too, catalyst support interactions can be strong because of the large contact area between the support and oxide relative to the surface area of the support. It is this monolayer coverage that is considered the best for a number of supported oxides but, realistically, it is recognized that it is improbable that the entire surface of a high surface area porous support material will be uniformly covered by the catalytic species. Instead, there will be areas of monolayer coverage accompanied by some larger supported oxide particles and some uncovered support surface.

1.3 Ceria, Zirconia and Ceria-Zirconia

1.3.1 Ceria

Cerium is the most abundant member of the series of elements known as lanthanides or rare earths, the elements in the periodic table in which the inner 4f electron shell is being filled. Cerium is characterized chemically by having two stable valence states, Ce⁴⁺, ceric and Ce³⁺, cerous and this property underlies several technological uses. The ceric ion is a powerful oxidizing agent but when associated with the strongly coordinating ligand, oxygen, is completely stabilized and indeed cerium oxide, Ce⁴⁺O₂, (also called ceria) is the form of cerium most widely used. Ceria has the fluorite, CaF₂, structure, space group Fm3m, with 8-coordinate cations with oxygens filling all the tetrahedral holes; the structure-determining OCe₄ coordination tetrahedral thereby share all edges in three dimensions."
Ceria is now the focus of constant and varied research due to its industrial applications in areas such as high temperature ceramics, catalysis and solid oxide fuel cell applications\textsuperscript{12}. This is because of its oxygen storage capacity which is based on a unique ability to undergo reversible redox transitions to form a series of non-stoichiometric phases of composition CeO\textsubscript{2}→CeO\textsubscript{2-x} and this underpins the current interest\textsuperscript{13}. As a vital component in the so-called three-way catalysts (TWC) for automotive exhaust emission control, ceria has proven useful in several ways; it aids the stabilization the alumina washcoat, prevents the inward diffusion of noble metals such as rhodium into the washcoat and prevents those metals being deactivated by being held in high oxidation states. However, it is its oxygen storage capacity (OSC) that gives ceria-based catalysts the unique ability to oxidize unburnt hydrocarbons or reduce nitrous oxides under fuel rich and lean conditions respectively\textsuperscript{14}.

1.3.2 Zirconia

Zirconium oxide (ZrO\textsubscript{2}) known as zirconia is also a relevant material in adsorption and catalysis. Zirconium dioxide is found in nature in small quantities as the mineral baddeleyite (monoclinic zirconia). It can also exist in tetragonal and cubic forms, both stable at higher temperature but stabilized by doping down to room temperature\textsuperscript{15}. The most significant difference between monoclinic, tetragonal and cubic structures is the change in the coordination of Zr atoms which is seven in the monoclinic phase and eight in the other two. The presence of seven fold coordination in the m-ZrO\textsubscript{2} is consistent with the strong covalent character of Zr-O bonding.

Zirconia is a special transition metal oxide that possesses bifunctional characteristics of weak acid and base properties\textsuperscript{16,17}. The p-type semiconductivity exhibits abundant oxygen vacancies on its surface. The high ion-exchange capacity and redox activities make it possible to be used in many catalytic processes as the catalyst, the supporter, and the promoter. In addition, the superior chemical stability,
mechanical strength, and ion-exchange capacity are favorable for applications in ceramic toughening, thermal-barrier coating, electronics, and oxygen sensors \(^{18-22}\).

### 1.3.3 Ceria-Zirconia

In recent studies it has been shown that the redox behavior of cerium oxide can be severely modified by incorporation of zirconium and the formation of mixed Ce-Zr oxides. Among the possible compositions and phases forming Zr-Ce mixed oxides, it has been shown that the greatest promoting effect on cerium reduction is produced for compositions with Ce/ Zr (atomic ratio) close to one and in the presence of pseudo cubic phase \(t'\) (with Zr and Ce cations occupying the corresponding positions in the cubic fluorite-type lattice, but with overall tetragonal symmetry due to oxygen displacement from the ideal fluorite sites \(^{23}\)). CeO\(_2\)-ZrO\(_2\) mixed oxides are extensively used as promoters for three way catalysts. Due to their high thermal stability and enhanced redox properties compared to traditionally employed ceria, these systems are now employed as a so-called oxygen storage device. Oxygen storage and release capacity is the ability of a TWC to store oxygen under net oxidizing conditions and release it under net reducing conditions, thereby maintaining the air to fuel ratio at close to stoichiometric conditions, where the highest conversions are attained. For highly sintered CeO\(_2\)-ZrO\(_2\) mixed oxides, a remarkable property is that insertion of ZrO\(_2\) into the CeO\(_2\) lattice distorts the oxygen sublattice, making mobile lattice oxygen available for redox processes \(^{24}\).

### 1.4 Methods of Preparation of Metal Oxides

A heterogeneous catalyst is a composite material, recognized by: (a) the relative amounts of different components (active species, physical and/or chemical promoters, and supports); (b) shape; (c) size; (d) pore volume and distribution; (e) surface area. The optimum catalyst is the one that provides the necessary combination
of properties (activity, selectivity, lifetime, ease of regeneration and toxicity) at an acceptable cost. These requirements are in many cases in conflict and catalyst design mainly consists of the achievement of a suitable compromise.

1.4.1 Precipitation and Co-precipitation

Precipitation is one of the most widely employed preparation methods and may be used to prepare either single component catalyst and supports or mixed catalysts. In the latter case intimate mixing of the catalyst components can be achieved by either the formation of very small crystallites or the formation of mixed crystallites containing the constituents. During coprecipitation the pH has to be adjusted and kept constant. Hydroxides and carbonates are the preferred precipitates because of their low solubility, easy decomposition and minimal toxicity and environmental problems.

1.4.2 Impregnation

Impregnation is the procedure whereby a certain volume of solution containing the precursor of the active phase is contacted with the solid support, which, in a subsequent step, is dried to remove the imbibed solvent. Two methods of contacting may be distinguished, depending on the volume of solution: wet impregnation and incipient wetness impregnation. In wet impregnation an excess of solution is used. After a certain time the solid is separated and the excess solvent is removed by drying. The composition of the batch solution will change and the release of debris can form a mud which makes it difficult to completely use the solution. The heat of adsorption is released in a short time. In incipient wetness impregnation the volume of the solution of appropriate concentration is equal or slightly less than the pore volume of the support. Control of the operation must be rather precise and repeated applications of the solution may be necessary.
1.4.3 Adsorption

Adsorption allows the controlled anchorage of a precursor (in an aqueous solution) on the support. The term adsorption is used to describe all processes where ionic species from aqueous solutions are attracted electrostatically by charged sites on a solid surface. Often consideration is not given to the difference between true ion exchange processes and electrostatic adsorption at the charged surface of oxides. Catalyst systems, which need charge compensating ions, are ideal materials for ion exchange (zeolites, cationic clays or layered double hydroxides). Instead most oxide supports, when placed in an aqueous solution, develop a pH-dependent surface charge. These oxides may show a tendency for adsorption of cations ($\text{SiO}_2-\text{Al}_2\text{O}_3$, $\text{SiO}_2$), or anions ($\text{ZnO}$, $\text{MgO}$) or both, cations in basic solutions and anions in acid solutions ($\text{TiO}_2$, $\text{Al}_2\text{O}_3$). The surface charge of an oxide depends on its isoelectric point as well as on the pH and ionic strength of the solution.

1.4.4 Deposition-Precipitation

In deposition–precipitation two processes are involved: (1) precipitation from bulk solutions or from pore fluids; (2) interaction with the support surface. Slurries are formed using powders or particles of the required salt in amounts sufficient to give the desired loading, and then enough alkali solution is added to cause precipitation. However, precipitation in the bulk solution must be avoided, since it gives rise to deposition outside the pores of the support. A well-dispersed and homogeneous active phase is reached when the OH- groups of the support (for example, the silanols of silica) interact directly with the ions present in the solution, thereby also determining the nature of the phase formed. The nucleation rate must be higher at the surface than in the bulk solution and the homogeneity of the solution must be preserved. A method to obtain uniform precipitation is to use the hydrolysis of urea as a source of OH- instead of conventional alkali. Urea dissolves in water and
decomposes slowly at 90°C, giving a uniform concentration of OH- in both the bulk and pore solutions.

1.4.5 Sol-gel Method

The sol-gel method is a homogeneous process which results in a continuous transformation of a solution into a hydrated solid precursor (hydrogel). Sol-gel methods have several promising advantages over precipitation. In general, sol-gel syntheses have been recognized for their versatility which allows better control of the texture, composition, homogeneity and structural properties of the final solids. The nanoscale chemistry involved in sol-gel method is a more direct way to prepare highly divided materials. Four main steps may be identified in taking a precursor to a particular product via sol-gel preparation: formation of a hydrogel, its ageing, removal of solvent and heat treatment. The versatility of this preparation method lies in the number of parameters that can be manipulated in each of these steps36.

In the sol preparation, the precursors (either organic or inorganic) undergo two chemical reactions: hydrolysis and condensation or polymerization, typically with acid or base as catalysts, to form small solid particles or clusters in a liquid (either organic or aqueous solvent). The solid particles or clusters are so small (1~1,000 nm) that gravitational forces are negligible and interactions are dominated by van der Waals, coulombic and steric forces. Sols are stabilized by an electric double layer, or steric repulsion, or their combination. Sol-gel processing is a simple technology in principle but has required considerable effort to become of practical use. Sol-gel enables materials to be mixed on an atomic level and thus crystallization and densification to be accomplished at a much low temperature. However, a true atomic level homogeneity in a multiple component system is an endeavor; the difficulty arises from the fact that the chemical reactivity varies greatly from precursor to
precursor. Precursor modification and step-wise partial hydrolysis are the common approaches to homogeneity in multiple component systems.

The advantages of the sol-gel process in general are high purity, homogeneity, and low temperature. For a lower temperature process, there is a reduced loss of volatile components and thus the process is more environmental friendly. In addition, some materials that cannot be made by conventional means because of thermal and thermodynamical instability can be made by this process. The sol-gel process has many applications in synthesis of novel materials. Examples include aerogels used in space crafts to capture stellar dust, xerogels as matrix in biosensors, and high power laser materials. It is well known that the properties of materials show a huge change when particle size is reduced to submicrometric or nanometric scale.

1.5 Preparation of Ceria, Zirconia and Ceria-Zirconia

Ceria based catalysts were prepared by a large variety of techniques such as mechanochemical processing, hydrothermal hydrolysis, atomic layer deposition, ultrasonic aerosol decomposition, homogeneous precipitation route, hybrid organic/inorganic route, inert gas condensation, solid state decomposition technique, homogeneous precipitation with microemulsion etc. Thermally stable ordered Mesoporous ceria has been synthesized with the use of neutral surfactants by Lyons et.al.

A few research groups prepared ceria sols by using the commercial 20 wt.% CeO₂ aqueous colloidal dispersions or peptizing CeO₂ precipitation by addition of an equimolar quantity of HNO₃. Zou et al. synthesized high surface area cerium oxide and high concentration ceria sols by a new method based on homogeneous precipitation method in an acidic environment using cerium (IV) nitrate as the precursor. Li et al. reported synthesis of ceria nano particles by solid phase
mechanochemical reaction of hydrate cerium chloride with hydrate sodium carbonate. Khalil et al.\textsuperscript{52} carried out a two step sol-gel process for the preparation of cerium oxide in which Cerium (IV) isopropoxide was dispersed in isopropanol by the aid of ultrasonic radiation to overcome the solubility problem. Zhou et al.\textsuperscript{53} were successful to synthesize ceria nanorods with well-defined reactive planes as a result of the recent development of controlled synthesis of nanostructured materials. Rane et al.\textsuperscript{54} used three ceria sols prepared from different precursors (commercial sol, cerous sol and ceric sol) to prepare unsupported ceria membranes. They confirmed fluorite type phase for ceria derived from all these sols. Ozer\textsuperscript{55} showed that crystalline ceria films can be prepared by the sol-gel process using cerium ammonium nitrate as precursor. Orel et al.\textsuperscript{56, 57} and his coworkers used aqueous based sol-gel process for the preparation of ceria. Transparent colloidal solution containing 2 nm ceria particles were synthesized by Inoue et al.\textsuperscript{58}. Atkinson et al.\textsuperscript{59} prepared ceria sol by peptizing a slurry of cerium hydroxide with nitric acid. They could obtain de-aggregated primary particles about 8 nm in size.

Extensive methods have been explored to synthesize zirconia, including precipitation\textsuperscript{60}, sol-gel\textsuperscript{61}, thermal decomposition\textsuperscript{62} and hydrothermal treatment\textsuperscript{63}. Among these, the sol-gel process is considered to be a promising way to produce homogeneous sols with modified physico-chemical properties. Zhao et al.\textsuperscript{64} found out that highly stable, homogeneous zirconia sols could be prepared from zirconium n-propoxide modified by diglycol. Zirconium n-propoxide was used as the precursor because of its high reactivity with water and it being typically representative of metallic alkoxides. Ferino et al.\textsuperscript{65} prepared zirconia catalysts from xero- and aerogels obtained using zirconium n-propoxide.

Many preparation methods have been applied for the preparation of CeO\textsubscript{2}-ZrO\textsubscript{2} solid solutions for catalytic applications. These include microemulsion method\textsuperscript{66, 67}, hydrothermal synthesis\textsuperscript{68}, sol-gel route\textsuperscript{69-72}, Co-precipitation route\textsuperscript{73-75},
high energy ball milling\textsuperscript{76}, glycine-nitrate process\textsuperscript{77,78}, sonochemical processing\textsuperscript{79}, flame spray synthesis\textsuperscript{80}, spray drying technique\textsuperscript{81}, pechini process\textsuperscript{82}, solution combustion synthesis\textsuperscript{83} etc.

1.6 Transition Metal Modified Ceria and Ceria-Zirconia as Catalyst

Among the rare earth metal oxides that have been widely investigated in ceramics and industrial catalysis, cerium dioxide ($\text{CeO}_2$) certainly stands apart\textsuperscript{14,84}. The redox property of ceria plays a prominent role in catalyzed reactions. 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\textsuperscript{68,85,86}. Replacing cerium ions by cations of different size or charge modifies ion mobility inside the modified lattice, resulting in the formation of a defective fluorite-structured solid solution. Such modifications in the defect structure of ceria confer new properties to the catalyst such as better resistance to sintering at high temperatures and high catalytic activity for various reactions\textsuperscript{87}. The mixing of two different oxides could result in the formation of new stable compounds that may lead to totally different physico-chemical properties and catalytic behaviour\textsuperscript{88}.

Supported chromium oxide catalysts have been of significant industrial importance for many decades and are now vital for the polymerization of ethylene (in the manufacture of high-density polymers) as well as the generation of valuable alkenes via the dehydrogenation of low-cost alkane feedstocks\textsuperscript{89-91}. More recently cerium oxide supported chromia catalysts have been used for the oxidative dehydrogenation of isobutane where the activity of these materials was attributed to dispersed $\text{Cr}^{6+}\text{O}_x$ species\textsuperscript{92,93}. Harisson et al.\textsuperscript{94} studied chromium promoted cerium catalysts towards oxidation of CO and propane. The thermal decomposition behavior
of ceria supported chromia phase and the effect of support in various chemical and molecular states of chromia with the temperature was reported by Viswanath et al.\textsuperscript{95}.

Rossi et al.\textsuperscript{96} has examined structural and catalytic properties of numerous chromia/zirconia, chromia/alumina and chromia/silica catalysts, covering a wide range of Cr concentration. Dehydrogenation activity per total Cr atom is substantially higher for zirconia-based catalysts. This higher activity was related to the higher concentration on zirconia of mononuclear Cr\textsuperscript{V} species, which reduce to the active mononuclear Cr\textsuperscript{III} species under reaction conditions. Effect of preparation route and thermal treatment on the nature of copper and chromium doubly promoted ceria catalysts was reported\textsuperscript{97}.

Interestingly, MnO\textsubscript{x}-CeO\textsubscript{2} mixed oxides have been developed as environmental friendly catalysts for the abatement of contaminants in both liquid phase and gas phase, such as oxidation of ammonia\textsuperscript{98}, pyridine\textsuperscript{99}, phenol\textsuperscript{100} and acrylic acid\textsuperscript{101}. It was further showed that the MnO\textsubscript{x}-CeO\textsubscript{2} mixed oxides had much higher catalytic activity than those of pure MnO\textsubscript{x} and CeO\textsubscript{2} owing to the formation of the solid solution between manganese and cerium oxides. Incorporation of manganese ions into ceria lattice greatly improved the oxygen storage capacity of cerium oxides as well as the oxygen mobility on the surface of the mixed oxides. Qi et al.\textsuperscript{102} reported that MnO\textsubscript{x}-CeO\textsubscript{2} is a superior catalyst for NO reduction by NH\textsubscript{3}. The high activity is attributed to the highly dispersed Mn species and the more active oxygen species that is formed. Mn/Ce composite catalysts are found to be effective for the wet oxidation of phenol\textsuperscript{103,104}, ammonia\textsuperscript{105} and poly (ethylene glycol)\textsuperscript{106}.

The vapor-phase synthesis of 3-pentanone from 1-propanol was investigated over CeO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3} catalysts by Kamimura et al.\textsuperscript{107}. The addition of Fe\textsubscript{2}O\textsubscript{3} to CeO\textsubscript{2} enhances the ability of CeO\textsubscript{2} for the catalytic dehydrogenation of 1-propanol to propanone without losing the ability for the dimerization of propanol, whereas the
stability of catalyst is related to the catalyst composition. Nagashima et al.\textsuperscript{108} investigated ketonization of different carboxylic acids over CeO\textsubscript{2} based catalysts. CeO\textsubscript{2} catalysts modified with Mg, Al, Fe, Ni, Cu and Zr are effective for the ketonization of propnaoic acid form 3-propanone. CeO\textsubscript{2}-Mn\textsubscript{2}O\textsubscript{3} is the most efficient catalyst. The degree of mixing in a solid solution affects the catalytic activity for the ketonization. Nascente et al.\textsuperscript{109} found out using X-ray photoelectron spectroscopy that the addition of iron oxide to CeO\textsubscript{2}-ZrO\textsubscript{2} mixed oxide helped the stabilization of tetragonal phase. Mitchell et al.\textsuperscript{110} examined the decomposition of dimethyl methylphosphonate (DMMP) on supported cerium and iron co-impregnated oxides at room temperature. They suggested that the active component for DMMP decomposition is a two dimensional ceria network on the alumina support and the effect of iron is to increase the number of ceria defect sites in the crystallites that do form by disrupting the crystal structure and/of facilitating the formation of smaller particles.

Cobalt based catalysts are currently the best systems for obtaining paraffins of high molecular weight with little CO\textsubscript{2} or alcohol formation. Ernst et al. reported the effects of highly dispersed ceria addition on reducibility, activity and hydrocarbon chain growth of a Co/SiO\textsubscript{2} Fischer-Tropsch catalyst\textsuperscript{111}. CoO/\textit{Co}_{3}O_{4}/CeO\textsubscript{2} composite catalysts of various cobalt loading have been prepared and tested for carbon monoxide oxidation by Kang et al.\textsuperscript{112}. These catalysts showed good resistance to water vapor poisoning, due to the strong interaction of the two materials. The study of the cinnamaldehyde hydrogenation over supported cobalt catalysts showed that the addition of cerium to cobalt increases selectivity to unsaturated alcohol without decrease of the activity\textsuperscript{113}.

Nickel has been explored as a possible substitute for precious metals since nickel-based catalysts are relatively inexpensive and have been known to possess high
activities for the synthesis gas-forming reaction\textsuperscript{114-117}. Upadhya et al.\textsuperscript{118} reported that Ni-stabilized zirconia can be used for the chemoselective transfer hydrogenation of nitroarenes, aldehydes and ketones with propan-2-ol. Incorporation of Ni into the bulk structure of ZrO\textsubscript{2}, not only stabilized ZrO\textsubscript{2} in its cubic form but also moderated the reactivity of Ni in the stabilized zirconia enabling chemoselective functional group reduction. CeNi\textsubscript{x}O\textsubscript{y} mixed oxides were used in oxidative dehydrogenation of propane\textsuperscript{119}.

CuO-CeO\textsubscript{2} mixed-metal oxides have important applications as electrolytes in fuel cells\textsuperscript{120}, gas sensors\textsuperscript{121} and efficient catalysts for various reactions such as the combustion of CO and methane\textsuperscript{122,123}, the water-gas shift reaction\textsuperscript{85} the reduction of SO\textsubscript{2} by CO\textsuperscript{124}, methanol synthesis\textsuperscript{125} and wet oxidation of phenol\textsuperscript{126}. Cu-Ceria-Yttria stabilized zirconia anodes for solid oxide fuel cells were used by Krishnan et al.\textsuperscript{127}. Rao et al.\textsuperscript{128} investigated the surface and catalytic properties of Cu-Ce-O composite materials prepared by solution combustion method. CO oxidation using copper oxide supported on cerium-zirconium mixed oxide has been studied by Martinez-Arias et al.\textsuperscript{129}. They concluded that the two main factors governing the catalytic activity of this kind of system are the facility for the partial prereduction of the copper oxide component at the interface zone and the redox properties of the interface between that partially reduced copper oxide component and the underlying ceria based support. Catalytic production for hydrogen by steam reforming of methanol reaction over Cu/Al\textsubscript{2}O\textsubscript{3} promoted with CeO\textsubscript{2} was reported. The results showed that CeO\textsubscript{2} could enhance the surface dispersion of copper on catalysts, and prevent copper crystallites from sintering. It is suggested that high activity, selectivity and stability of CeO\textsubscript{2} promoted catalysts have been resulted from higher copper dispersion and smaller copper crystallites and the synergetic effect of ceria\textsuperscript{130}. CO oxidation of nonstoichiometric nanostructured CuO\textsubscript{x}/CeO\textsubscript{2} composite particles prepared by inert gas condensation was studied by Skarman et al.\textsuperscript{131}. The interaction between a metal
oxide catalyst such as copper oxide and the ceria support is complicated since a variety of metal-support interaction can lead to synergetic effects and enhanced catalytic properties. Further more of chemical factors, such as crystal structure, oxidation state, crystallinity, morphology and dispersion effect influence the activity of Cuₓ/CeO₂ during catalysis for CO oxidation^{132,133}. 

Ceria based catalysts are very effective for the synthesis of cyclic carbonate such as ethylene carbonate and propylene carbonate by the reaction of CO₂ with ethylene glycol and propylene glycol. The addition of Zr to CeO₂ was very effective at maintaining the high surface area of the catalysts calcined at high temperature and this is related to the calcination temperature dependence. On the basis of the catalyst characterization it is suggested that the active sites could be weak acid-base sites which are present on the plain surface of the catalyst calcined at high temperature^{134}. The redox cycle of Ce⁴⁺→Ce³⁺ on the surface of ceria is found to play a role for the dehydration of diols^{135,59}. Sugunan et al.^{136} investigated structural and catalytic investigation of vanadia supported on ceria promoted with high surface area rice husk silica.

Banwenda et al.^{137} demonstrated that cerium dioxide is a potential photocatalyst that can be used to decompose water to produce oxygen in aqueous suspension containing an electron acceptor. Ceria is abundant, nontoxic and inexpensive. Furthermore, ceria is an n-type semiconductor with a band gap of 2.9 eV and consequently it can be phptoactivated by irradiation with light in the near UV-vis range^{138}. These characteristics suggest that CeO₂ could be potentially used as a photocatalyst for the oxidation of pollutants. Coronado et al.^{139} carried out EPR study of radicals formed upon irradiation of ceria-based photocatalysts (CeO₂, TiO₂, CeO₂/TiO₂). The photocatalytic activity was tested for toluene oxidation. They concluded that the main effect of ceria incorporation to the titania sample is the partial
blockage of the surface sites available for photodegradation. It is proposed that the main effect of UV photoactivation of CeO\(_2\) could be to favor the formation of surface oxygen vacancies.

1.7 Surface Acidity Measurements

Supported metal oxides often show acidic properties and form an important "class" of solid acids. Thus, many such systems have been thoroughly investigated. However, the origin of the acidity, the development of the acid sites, and their relations with the surface species are not, to date, fully understood. Ceria-based composite oxides have been increasingly studied for their role as acid-base catalyst/promoter for various reactions. The promoting/catalyzing effect of ceria in pure or in the form of composite oxide is attributed to the combination of acid-base and redox properties of ceria. Incorporation of zirconia into ceria lattice modifies the surface acid-base properties. The Zr\(^{4+}\) radius (0.84 Å) is smaller than that of the Ce\(^{4+}\) (0.97 Å) and is likely to exhibit acidic nature in solid solution. Generation of acid sites is due to the exposed Ce\(^{4+}\) and Zr\(^{4+}\) ions which are accompanied by exposed O\(^2-\) ions which are the basic sites. Sato et al.\(^{140,141,142}\) examined CeO\(_2\)-MgO catalysts towards alkylation of phenol and concluded that the generation of weak basic sites at low ceria content is effective for the reaction.

The acidic and basic properties of solid catalysts are usually measured by a method utilizing the temperature-programmed desorption spectra of ammonia (NH\(_3\)-TPD)\(^{143-147}\) and carbon dioxide (CO\(_2\)-TPD)\(^{148-149}\), respectively. Tago et al.\(^{150}\) proposed a new TPD method for simultaneously characterizing the acidic and basic properties of solid catalysts by utilizing the co-adsorption of NH\(_3\) and CO\(_2\) on catalysts.

Dealing with catalytic systems that involve at least one acid/base catalytic step, it is quite important to be able to evaluate nature and amount of surface acidic centers. This need becomes particularly important in the case of systems in which
both protonic Brønsted acidity (B acid sites) and aprotic Lewis acidity (L acid sites) are simultaneously present in variable proportion\textsuperscript{151}. It is long time now that the identification of the type of acidity present at the surface of oxidic systems of catalytic interest is carried out routinely by the IR spectroscopic study of the adsorption/desorption of pyridine (py) at temperatures ranging between ambient temperature (RT) and some 423 K. This is so because it has been long recognized that, in the complex mid-IR spectrum of adsorbed pyridine, there are two bands, centered at ~1540 cm\textsuperscript{-1} (broad, and of m-intensity) and at ~1445 cm\textsuperscript{-1} (sharp, and of s-intensity) that are analytical of B-bound py species ([py-B]) and of L-bound py species ([py-L]), respectively\textsuperscript{152}. Zaki et al.\textsuperscript{153} reported in situ FTIR spectra of pyridine adsorbed on SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, ZrO\textsubscript{2} and CeO\textsubscript{2}. Granados et al.\textsuperscript{154} used infrared spectrum of chemisorbed pyridine to characterize phosphated ceria samples. They could observe only one band due to molecularly adsorbed pyridine and no infrared bands of pyridine chemisorbed on Bronsted acid sites were visible. They concluded that Ce(IV) ions show similar acid strength on the surfaces or pure ceria and of phosphated samples. The integrated molar absorption coefficients of the infrared bands characteristic of adsorbed lutidine (2,6-dimethylpyridine) were determined for the purpose of quantifying the acid sites of solid catalysts by Onfroy et al.\textsuperscript{155}.

1.8 Test Reactions for Acidity

The conversion of cumene is a model reaction for identifying the Lewis/Bronsted acid site ratio of a catalyst: cumene is cracked to benzene and propene over Bronsted acid sites, whereas dehydrogenation to \(\alpha\)-methylstyrene occurs over Lewis acid sites. The relative amounts of benzene and \(\alpha\)-methylstyrene in the product mixture can therefore be a good indication of the types of acidities possessed by catalyst\textsuperscript{156}. 
Kooli et al.\textsuperscript{157} used cumene cracking to compare titania pillared clays using montmorillonite, saponite and rectorite hosts. High cumene conversion and significant activity of saponite sample reflected the higher Bronsted acidity seen for these materials. Various rare earth phosphates were characterized by catalytic activities on cracking/dehydrogenation reaction of cumene\textsuperscript{158}. Lanthanum and samarium polyphosphates gave low selectivity of cumene to benzene and propene which showed that these catalysts had poor Bronsted acid sites. High selectivity of cumene cracking products, benzene and propene over Ce, Pr, Nd, Yb and Y polyphosphates showed that there are rich Bronsted acid sites over these catalysts. Nanosized sulfated TiO\textsubscript{2} obtained by sol-gel hydrothermal route showed high activity for cumene cracking indicating the presence of medium and strong Lewis acid sites\textsuperscript{159}. Gedeon et al.\textsuperscript{160} reported that AISBA materials showed a high and durable activity in cumene cracking. The cracking products were only benzene and propene, indicating that the active sites are of Bronsted type.

Alcohol decomposition reaction has been widely studied because it is a simple model reaction to determine the functionality of an oxide catalyst. Dehydration activity is linked to the acidic property and dehydrogenation activity to the combined effect of both acidic and basic properties of the catalyst. Cyclohexanol decomposition reaction is considered as universal test reaction for acid-base properties of solid catalysts. Besides, in the dehydration reaction, cyclohexene is produced, a liquid compound easier to handle, instead of gaseous alkene obtained in the reaction of several aliphatic alcohols alternatively used in this respect\textsuperscript{161}. Furthermore stronger acid sites may also be detected in this probe reaction, by the formation of methyl cyclopentenes through the consecutive (or secondary) reaction of cyclohexene\textsuperscript{162}.

Jothiramalingam et al.\textsuperscript{163} found that cerium incorporated OMS-2 catalysts favor the dehydrogenation of cyclohexanol due to the presence of basic sites in the
cerium incorporated OMS-2 catalysts. Bautista et al.\textsuperscript{164} studied the influence of acid-base properties of catalysts in the gas-phase dehydration-dehydrogenation of cyclohexanol on amorphous AlPO\textsubscript{4} and several inorganic solids. They concluded that this reaction can be used as a reaction model for the characterization of solid acid-base catalysts, but taking into account that dehydration reaction is carried out not only in acid sites but also in basic ones, and that cyclohexanone obtained throughout dehydrogenation reaction requires an additional redox ability not necessarily associated to basic sites. Sugunan et al.\textsuperscript{165} correlated cyclohexanol conversion to total acidity for vanadia supported ceria promoted with rice husk silica. Mishra et al.\textsuperscript{166} reported that addition of ceria into ZnO matrix generates new acidic sites along with increased number of basic sites which correlates with the catalytic activity obtained for cyclohexanol dehydrogenation.

1.9 Reactions Selected for the Present Study

1.9.1 Ethylbenzene Oxidation

Oxidation is a fundamental transformation in organic synthesis. The selective oxidation of hydrocarbons is one of the main processes since the reaction products are either vital themselves or intermediates in numerous industrial organic chemicals. The oxidation products of ethylbenzene are widely employed as intermediates in organic, steroid, and resin synthesis. However selective oxidation of hydrocarbons is still a challenge to scientific community as they are currently oxidized by environmentally detrimental chromates and permanganates in stoichiometric amounts\textsuperscript{167-169}. These processes also lead several problems like difficulty separation, recovery and recycling of catalysts after reaction as well as the disposal of wastes, deactivation complications etc., which makes them highly unattractive. Owing to the limitations of stoichiometric reagents/homogeneous catalysts, and in the wake of increasingly stringent environmental legislation, attention is being focused towards
the design and development of greener processes such as heterogeneous catalytic oxidation.\textsuperscript{170}

Silicate xerogels containing cobalt is found to be especially active for the oxidation of alkyl aromatic compounds.\textsuperscript{171} Sivasanker et al.\textsuperscript{172} reported oxidation of ethylbenzene over zeolite Y-encapsulated copper tri- and tetraaza macrocyclic complexes. Al\textsubscript{2}O\textsubscript{3} supported V\textsubscript{2}O\textsubscript{5} catalysts have been effectively used for acetophenone synthesis from ethylbenzene.\textsuperscript{173} Using H\textsubscript{2}O\textsubscript{2} oxidant Ti, V- and Sn-containing silicalites with MFI structure found to catalyze ethylbenzene oxidation.\textsuperscript{174} The major products were 1-phenyl ethanol and acetophenone arising from the oxidation of side chain. Aromatic ring hydroxylation leads to the formation of ortho- and para-hydroxy ethylbenzene as a minor side reaction. The differences in the product selectivities could be explained on the basis of the reaction intermediates. Vetrivel et al.\textsuperscript{175} examined the catalytic activity of manganese containing MCM-41 molecular sieves for the liquid phase oxidation of ethylbenzene using t-butyl hydroperoxide as oxidant. Both primary and secondary carbons of the side chain of ethylbenzene are observed to be acted upon by activated t-butyl hydroperoxide giving \(\alpha\)-phenylethanol as the major product and acetophenone, benzaldehyde and phenylacetaldehyde other products.

1.9.2 Benzylation of Toluene and \(o\)-xylene

Alkylation of aromatic compounds is an important area of industrial research. Benzylated aromatics, a class of alkyl aromatics are very useful intermediates in petrochemicals, cosmetics, dyes, pharmaceuticals and may other chemical industries.\textsuperscript{176} Liquid phase alkylation of aromatic compounds, using homogeneous acid catalysts such as AlCl\textsubscript{3}, BF\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4} pose several problems, such as difficulty in separation and recovery, disposal of spent catalysts, corrosion, high toxicity, etc. Development of reusable solid acid catalysts is, therefore, of great practical
importance. Choudhary et al.\textsuperscript{177} reported highly active, reusable and moisture sensitive catalyst obtained from basic Ga-Mg-hydrotalcite anionic clay for Friedel-Crafts type benzylation and acylation reactions. Sugunan et al.\textsuperscript{178,179} investigated liquid phase benzylation of toluene and \(\alpha\)-xylene over different catalysts.

Bhaskaran et al.\textsuperscript{180,181} reported that rare earth oxides like \(\text{CeO}_2\) and \(\text{Pr}_2\text{O}_3\) are effective for benzylation and benzylation of \(\alpha\)-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. Sugunan et al.\textsuperscript{182} studied benzylation of toluene over tungsten incorporated pure and sulfated ceria systems producing monoalkylated products.

\subsection*{1.9.3 Methylation of Phenol and \(\alpha\)-cresol}

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\textsuperscript{183}. In particular, ortho-alkylated phenols such as \(\alpha\)-cresol, 2,6-xylenol and trialkyl substituted phenol are more important alkyl phenols. The alkylation of phenol with methanol being an acid-base catalyzed reaction the product selectivity depends upon the acidity as well as the basicity of the catalyst\textsuperscript{184}.

Sato et al.\textsuperscript{185} investigated the alkylation of phenol over various oxides of rare earth metals and they found that only \(\text{CeO}_2\) had sufficient activity and selectivity for the reaction. They have also reported the ortho-selective methylation and propylation of phenol catalyzed by \(\text{CeO}_2-\text{MgO}\)\textsuperscript{141,142}. They proposed that the ortho-position of phenol adsorbed perpendicularly on the weak basic site on \(\text{CeO}_2\) species is selectively alkylated by the alkylating agent which is possibly activated in the form of hydroxyl
alkyl radical. A new ternary system based on SnO₂ with the addition of cerium
dioxide and rhodium oxide (Sn-Ce-Rh-O) was applied for the ortho-selective
methylation of phenol with methanol by Klimkiewicz et al. ¹⁸⁶ and they concluded that
the presence of weak acid sites and comparatively strong basic sites facilitates the
reaction.

2.0 Main Objectives of the Present Work

Looking into the future, one can see many exciting challenges and
opportunities for developing totally new catalytic technologies. Knowledge of the
local structure of the catalyst surface and of factors that determine the surface
structure has played an important role in developing and optimizing supported metal
oxide systems in heterogeneous catalysis. Characterization of the surface structure of
supported metal oxides however is complicated since several different structures as
well as chemical states might coexist in the supported metal oxide systems.

From the literature sited, it is clear that the surface properties and catalytic
activity of ceria can be improved by synthesizing appropriate ceria-based composite
oxides. The thesis is based on the sol-gel preparation, characterization and catalytic
activity studies of transition metal incorporated (Cr, Mn, Fe, Co, Ni, Cu) ceria and
ceria-zirconia mixed oxides. The main objectives of the present work are,

- To prepare transition metal (Cr, Mn, Fe, Co, Ni and Cu) incorporated ceria
  and ceria-zirconia mixed oxide catalysts through sol-gel route.
- To investigate the surface properties of the prepared systems by techniques
  such as XRD, EDX, SEM, BET surface area-Pore volume measurements, FT-
  IR, FT-Raman, DRS UV-vis, TGADTA and EPR.
- To examine the surface acidic properties of the catalytic systems using
  various independent techniques such as TPD of ammonia, TGA of adsorbed
2,6-DMP and test reaction like cumene cracking and cyclohexanol decomposition.

➢ To explore the catalytic activity of the systems towards oxidation of ethylbenzene.

➢ To test the catalytic activity of the system towards liquid phase benzylation of \( \sigma \)-xylene and toluene.

➢ To evaluate catalytic performance of the prepared systems in methylation of phenol and \( \sigma \)-cresol.

References


Chapter 1


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General Introduction and Literature Survey


