Chapter I

INTRODUCTION
Introduction

1. General Introduction:

1.1 What is Catalysis?

In chemistry and biology, catalysis is the acceleration of the reaction rate of a chemical reaction by means of a substance, called catalyst that is itself not consumed by the overall reaction. Catalysts participate in reactions but are neither reactants nor products of the reaction they catalyzed. A good catalyst must possess both high activity and long term stability. But the most important quality is its selectivity, which reflects its ability to direct conversion of reactants in a specific way. The specificity of a catalyst enables a chemical process to proceed more efficiently with less waste. Modern industries are learning more and more about the applications and benefits of catalysts and different ways to bring down the cost of production. Catalytic process technologies generally involve less capital investment, lower operating costs, higher purity products and reduce environmental hazards. Hence, catalysis is of crucial importance to the chemical industry. The better defined areas of industrial catalyst are petroleum, pharmaceutical and environmental catalysis. Catalysis is important in many aspects of environmental science, from the catalytic converter in automobiles to the causes of the ozone hole. Various techniques and concepts of solid state are applied for synthesizing and modifying catalysts with required structure and chemical properties. Thus it goes without saying that the modern chemical industries cannot operate without proper study of catalysts and their specific action. Catalysts can be either heterogeneous or homogeneous. Biocatalysts are often seen as a separate group. Heterogeneous catalysts are present in different phases from the reactants (e.g. a solid catalyst in a liquid reaction mixture), whereas homogeneous catalysts are in the same phase (e.g. a dissolved catalyst in a liquid reaction mixture). Each of the catalytic processes possesses its own advantages and disadvantages. In homogeneous catalysis the catalyst is a molecule which facilitates the reaction. The reactant(s) coordinate to the catalyst (or vice versa), are transformed to product(s), which
are then released from the catalyst. The synthesis of fine chemicals and pharmaceuticals generates large amount of waste, which is in particular due to the fact that most of the reactions are stoichiometry or use environmentally non-friendly homogeneous catalysts. The substitution of these polluting and corrosive homogeneous catalysts by solid catalysts, which do not possess such disadvantages, is one of the main industrial challenges. Besides the environmental improvement, heterogeneous catalysis has many technical advantages, in particular easy separation of products, easy development of continuous processes and possibility of catalyst regeneration. In recent years, considerable advances have been achieved in the study of surface structure and mechanism of the catalytic reaction. A simple model for heterogeneous catalysis involves the catalyst providing a surface on which the reactants (or substrates) temporarily become adsorbed. Catalysis is the chemical reaction brought about by a catalyst. A catalyst is the chemical version of a "matchmaker" because it physically brings together two chemicals in such a way that their chance to react is maximized. However, catalysts can't make a match between chemicals if there's no "chemistry." Instead, they make it possible for reactions to happen faster; fast enough to be used in environmental cleanup or to produce a chemical product. No matter what the catalyst's structure, is, it speeds up reactions without being changed itself.

The overall catalytic reaction rate depends on these physical or chemical processes or steps. Each of these steps contributes to a greater or lesser extent to the overall reaction rate.

The general steps involved in the heterogeneous catalysis are:

1. External diffusion: Transfer of the reactants from the bulk fluid phase to the fluid-solid interface and external surface of the catalyst particle.
2. Internal diffusion (if particle is porous): Intraparticle transfer into the catalyst particle.
3. Adsorption: Physiosorption and chemisorptions of reactants at the surface (sites) of the catalyst particle.
4. Surface reaction: Chemical reaction of adsorbed species to produce adsorbed products; this is the intrinsic or true chemical reaction step.
5. Desorption: Release of adsorbed products by the catalyst.

6. Internal diffusion: Transfer of products to outer surface of the catalyst particle.

7. External diffusion: Transfer of products from fluid-solid interface into the reaction stream.

1.2 How Catalysts Work?
Catalysts permit an alternate mechanism for the reactants to become products, with a lower activation energy and different transition state. A catalyst may allow a reaction to proceed at a lower temperature or increase the reaction rate or selectivity. Catalysts often react with reactants to form intermediates that eventually yield the same reaction products and regenerate the catalyst. Note that the catalyst may be consumed during one of the intermediate steps, but it will be created again before the reaction is completed.

1.3 Mechanism of catalysis
Catalysts work by changing the activation energy for a reaction, i.e., the minimum energy needed for the reaction to occur. This is accomplished by providing a new mechanism or reaction path through which the reaction can proceed. When the new reaction path has more energy than the activation energy, the reaction rate is increased and the reaction is said to be catalyzed. If the activation energy for the new path is higher, the reaction rate is decreased and the reaction is said to be inhibited. Inhibitors can provide an interesting challenge to the chemist. For example, because oxygen is an inhibitor of free-radical reactions, many of which are important in the synthesis of polymers, such reactions must be performed in an oxygen-free environment, e.g., under a blanket of nitrogen gas. In some reactions one of the reaction products is a catalyst for the reaction; this phenomenon is called self-catalysis or autocatalysis. Some substances that are not themselves catalysts increase the activity of a catalyst when added with it to some reaction: such substances are called promoters [1].
1.4 What are ferrites?
Ferrites are chemical compounds with the formula $\text{AB}_2\text{O}_4$, where A and B represent various metal cations; usually including iron [2]. Ferrites are a class of spinels i.e. materials that adopt a crystal consisting of cubic closed pack oxides with A cations occupying $1/8$th of the octahedral voids and B cations occupying half of the octahedral voids. For inverse spinel structure, half the B cations occupy tetrahedral sites and both the A and B cations occupy the octahedral sites. Divalent, trivalent and tetravalent cations can occupy the A and B sites and they include Mg, Zn, Fe, Mn, Al, Cr, Ti and Si.

1.5 Types of ferrites
Spinel ferrites have received much attention in technologically anchored modern society due to their promising magnetic properties [3, 4]. They find an extensive application in microwave devices, radar, digital recording, ferro fluids, catalysis and magnetic refrigeration systems [5]. Spinel ferrites are classified into various types as

1.5.1 Hard Ferrites
The permanent ferrite magnets are made of hard ferrites, which have a high coercivity and high remanence magnetization. These are composed of iron and barium or strontium oxides. In a magnetically saturated state they conduct magnetic flux well and have a high magnetic permeability [6]. This enables these so-called ceramic magnets to store stronger...
magnetic fields than iron itself. They are cheap and are widely used in household products such as refrigerator magnets [7].

1.5.2 Soft ferrite

Ferrites having low coercivity are called as soft ferrites. Soft ferrites are used in transformer or electromagnetic cores containing nickel, zinc, and/or manganese. The low coercivity means the material's magnetization can easily reverse direction without dissipating much energy (hysteresis losses); while the material's high resistivity prevents eddy currents in the core, another source of energy loss. Because of their comparatively low losses at high frequencies, they are extensively used in the cores of radio frequency (RF) transformers and inductors in applications such as switched-mode power supplies (SMPS). The most common soft ferrites are manganese-zinc (MnZn, with the formula Mn$_a$Zn$_{1-a}$Fe$_2$O$_4$) and nickel-zinc (NiZn, with the formula Ni$_b$Zn$_{1-b}$Fe$_2$O$_4$). NiZn ferrites exhibit higher resistivity than MnZn, and are therefore more suitable for frequencies above 1 MHz. MnZn have in comparison higher permeability and saturation induction. In soft ferrites the divalent metal ions (M$^{2+}$) and trivalent metal ions (M$^{3+}$) can migrate between tetrahedral and octahedral sites and can alter the catalytic properties of the material. On the basis of relative proportion of M$^{2+}$ and M$^{3+}$ on the either site of catalyst the soft ferrites are classified as follows.

Spinel ferrites are an important group of magnetic as well as catalytic material with the general formula MFe$_2$O$_4$ in which M represents a divalent metal ion, such as Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Mg$^{2+}$, Cu$^{2+}$ etc. the combination of these cations are also possible and in this case we refer to them as a solid solution of two ferrites, mixed crystal or in general terms, as a mixed ferrites. They exhibit unique chemical, electrical, mechanical structural and magnetic properties and have a variety of promising technological applications in high density recording devices, color imaging, ferrofluids, high frequency devices and magnetic refrigerators [8].
a) Normal spinel structure

In the spinel structures unit cell there are 8 MO$_2$O$_3$ molecules. In this structure the eight M$^{2+}$ ions occupy eight tetrahedral sites and the 16 Fe$^{3+}$ ions occupy 16 octahedral sites [9]. In other words, in this structure, the non-magnetic ions occupy the A sites and consequently there is no AB interaction. The negative BB interaction now makes itself felt and the trivalent iron ions align themselves in an anti-parallel fashion, producing zero net magnetization [10]. The general formula of normal spinel structure is (A)$_{8c}$[B$_2$]$_{16o}$O$_4$. e.g. (Mg)[Al$_2$]O$_4$, (Zn)[Fe$_2$]O$_4$.

b) Inverse spinel structure

In this structure, half of the Fe$^{3+}$ ions are tetrahedrally coordinated while the other half of the Fe$^{3+}$ ions and all of the M$^{2+}$ ions are octahedrally coordinated. Each octahedral site has six nearest neighbor O$^{2-}$ ions arranged on the corners of an octahedron; meanwhile, each tetrahedral site has four nearest neighbor O$^{2-}$ ions arranged on the corners of a tetrahedron [11]. In the inverse spinel structure there are 8M$^{2+}$ ions which occupy 8 octahedral sites and the 16 Fe$^{3+}$ ions are divided, the 8 occupy octahedral sites and 8 tetrahedral sites as shown in Table 1. The general formula of inverse spinel structure is (B)$_{8o}$[A. B]$_{16o}$O$_4$. e.g. (Fe)[Fe$_2$]O$_4$, (Fe)[NiFe]O$_4$.
### Table 1: Ionic distribution of tetrahedral and octahedral sites in spinel oxides

<table>
<thead>
<tr>
<th>Types of Interstitial Site</th>
<th>Number available</th>
<th>Number occupied</th>
<th>Normal spinel</th>
<th>Inverse spinel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedral</td>
<td>64</td>
<td>8</td>
<td>8M$^{2+}$</td>
<td>8Fe$^{3+}$</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>32</td>
<td>16</td>
<td>16Fe$^{3+}$</td>
<td>8Fe$^{3+}$ 8M$^{12}$</td>
</tr>
</tbody>
</table>

#### c) Mixed spinel structure

In the mixed spinel structure there is a random population of M$^{2+}$ and Fe$^{3+}$ ions on the tetrahedral and octahedral sites. The general formula of mixed spinel structure is e.g. ($B_{0.67}A_{0.33}$)$_{tet}$($A_{0.67}B_{1.33}$)$_{oct}$O$_4$

Ferrites having general formula $MFe_2O_4$ (M = divalent metal ion, e.g. Ni, Co, Cu, etc.) are one of the most attracting class of materials due to their fascinating applications like transformer core, antenna rod, recording head, loading coil, memory and microwave devices. Practical applications of ferrites include household, electronics and computers. Apart from their technological importance in the electronic and magnetic industries, ferrites have been used as a sensor material for highly reproducible gas [12, 13] and humidity [14]. Also, as ferrites are metal iron oxides, which exhibit properties such as various redox states, electrochemical stability, pseudo capacitive behavior, etc. and due to that now a days they can be used in super capacitors and in Li-batteries [15], such devices require the methods to be found to deposit ferrite in thin film form. Ferrite is chemically stable because of the lattice bonding between heavy metal ions and Fe ion. The structure
of ferrite is very similar to that of natural mineral, which has limited ions exchangeability, thermal stability and chemical stability. Concerning the spinels prepared at low temperature, we have developed a quantitative analysis by derivative thermogravimetry (DTG) for estimating directly the cation distribution, that is both valence and location on A or B sites of each cation. This method is based on the fact that each cation oxidizes at a specific temperature characteristic of its location in the spinel lattice and of its degree of oxidation. For example, the B-site Fe$^{3+}$ ions are more mobile than the A-site Fe$^{2+}$ ions, so that B-site ions are oxidized near 200°C whereas the A-sites are oxidized above 400°C. Such a difference in the reactivity evidences a more covalent character of the tetrahedral Fe-O bond when compared to the octahedral one [16, 17].

Spinel ferrites with the general formula $\text{AB}_2\text{O}_4$ are a class of chemically and thermally stable materials suitable for a wide variety of applications including catalysis [18], magnetic recording media and magnetic fluids for the storage and/or retrieval of information [19], magnetic resonance imaging (MRI) enhancement [20], magnetically guided drug delivery [21], sensors [22], pigments [23], etc. It is established that various binary and ternary spinel ferrites are effective catalysts for a number of industrial processes such as oxidative dehydrogenation of hydrocarbons [24], decomposition of alcohols and hydrogen peroxide [25], treatment of automobile-exhaust gases [26], oxidation of various compounds such as CO [27], H$_2$, CH$_4$ and chlorobenzene [28], phenol hydroxylation [29], alkylation reaction [30], hydrodesulphurization of crude petroleum [31], catalytic combustion of methane [32], etc.

1.6 Alkaline earth metal ferrite as a catalyst

Alkaline earth metal (AEM) ferrites have attracted a considerable attention due to their potential application as magnetic materials in the various electronic, magnetic and microwave devices [33, 34]. The wide application of these materials is mainly due to its excellent chemical stability, high mechanical durability, resistant to corrosion [35]. They have also been employed as heterogeneous catalysts and electrode materials [36, 37]. In order to get high-powered alkaline earth metal ferrite, different synthesis techniques have been developed, such as micro emulsion [38], hydrothermal reaction [39], salt-melt
technique [40], etc. All these methods have many drawbacks such as small area of deposition, requirement of sophisticated instruments, high working cost of system, prolonged calcination time for crystallization etc. When sol–gel technique [18] is used, we get high-powered ferrite material. The atomic-level blending of the constituent elements in the required stoichiometry ratio is attained in the citrate precursor complex, which enables the decomposition of the precursor directly into the final binary oxide at lower temperature, without the formation of intermediate oxide phases that delay the formation of the final oxide [41].

1.7 Literature review of ferrite in catalysis

Ferrites are very hard, brittle and chemically inert magnetic ceramic materials. They have been used for various applications including recording media, pigments, microwave absorbents and sensors [42]. The general composition of such ferrites is MFe$_2$O$_4$ where M represents one or several of the divalent transition metals [42, 43]. Recently most of the researchers are focused on the catalytic application of transition metal ferrites towards the various organic transformations. In order to resolve the environmental problems, a lot of methods have been used to mitigate CO$_2$ emissions, such as chemical, photochemical, and biological methods [44]. In 1990, Tamaura and Tabata [45] reported that oxygen-deficient Fe$_3$O$_4$ can decompose CO$_2$ to C with an efficiency of nearly 100% at 290 °C. It provided a new way to deal with the reduction and utilization of CO$_2$. Subsequently, the binary spinel structure of MFe$_2$O$_4$ (M= transition metals) has been systematically investigated [46] since it can also decompose CO$_2$ to C at about 300 °C. Also there are many papers exhibiting CO$_2$ decomposition over completely reduced ferrite [47, 48]. Cota et al. [49] has used the CoFe$_2$O$_4$ with inverse spinel for the decomposition of H$_2$O$_2$. Researchers have done lot of research over the applications of transition metal mixed oxides and have shown a high catalytic activity of zinc–iron oxide. The zinc ferrite can be successfully used in hydrocarbon combustion [50] and reduction of nitrogen oxides in propane–butane mixture [51]. The zinc ferrite’s ability to absorb visible light and excellent photochemical stability allowed Zhihao and Lide [52] to find out, that this oxide can be used as a photocatalyst. Valenzuela et al. [53] used zinc spinel as a photocatalyst
for phenol degradation under ultraviolet radiation. However, Lee et al has reported the catalytic activity of ZnFe₂O₄ for oxidative dehydrogenation of n-butene [54, 55] and the photocatalytic behavior of the simple and TiO₂ added ZnFe₂O₄ [56]. Selective oxidation of olefins has been considered to be an important subject for the production of a number of chemical intermediates in the petrochemical industries [57, 58]. Various metal ferrite catalysts such as magnesium ferrite [59], zinc ferrite [60], cobalt ferrite and copper ferrite [61] have been employed in the oxidative dehydrogenation of n-butene. Among these catalysts, zinc ferrite has been widely investigated as an efficient catalyst only.

Spinels of the type M²⁺M³⁺O₄ attract the research interest because of their versatile practical applications [62, 63]. In the case of M³⁺ = Fe, the resulting spinel ferrites having a general chemical composition of MFe₂O₄ (M = Mn, Mg, Zn, Ni, Co, Cd, etc.). Current years have seen increased interests in studying the gas sensing properties of ferrites [64–66]. Reddy et al. reported the response of copper ferrite (CuFe₂O₄) and zinc ferrite (ZnFe₂O₄) for hydrogen sulfide (H₂S) and that of nickel ferrite (NiFe₂O₄) for chlorine gas (Cl₂) [64]. Liu et al. confirmed that ZnFe₂O₄ possessed gas sensing property for H₂S [65]. Magnesium ferrite (MgFe₂O₄) is one of the important ferrites with spinel structure [67]. apart from its magnetic applications [68]. it is used as a catalyst [69] and humidity sensor [70]. Among various oxides, transition metal oxides based on iron oxide in combination with other metal oxides are found to be the most active and selective for ortho alkylation reactions [71, 72]. Spinel ferrites are found to be highly active towards many aromatic alkylation reactions such as methylation of phenol, aniline, pyridine, phenol tert-butylolation etc. [73–75]. It is established that various binary and ternary spinel ferrites are effective catalysts for a number of industrial processes such as oxidative dehydrogenation of hydrocarbons [76], decomposition of alcohols and hydrogen peroxide [77], treatment of automobile-exhaust gases [78], oxidation of various compounds such as CO [27], H₂, CH₄ and chlorobenzene [79], phenol hydroxylation [80], alkylation reaction [81], hydrodesulphurization of crude petroleum [82], catalytic combustion of methane [83], etc.

To enhance the catalytic efficiency of metal ferrites few of the researchers have done the substitution of either divalent metal ion or trivalent metal ions to form substituted i.e.
ternary metal ferrites. Recently, several ternary ferrites, such as Ni–Zn ferrite [84], Ni–Cu ferrite [85], Mn–Zn ferrite, and Mn–Ni ferrite [86] have been proposed and showed better decomposition performance than those of binary ferrites.

In above literature survey it is clear that the catalysis field is maximum covered by the oxides and ferrites of transition metals only. Due to their variable oxidation state most of the researchers have done work on them but apart from transition metals, alkali and alkaline earth metal oxides as well as hard ferrites are also applied in catalysis. The activity either oxides or mixed oxides of alkaline earth metal are not comparatively studied by scientific word.

Many of the research groups has studied the synthesis of MgFe₂O₄ by polymeric precursor method and chemical method also [87, 88]. Berbenni et al has studied the role of mechanical activation on the ferrite formation where the solid state formation of calcium ferrite (mixture of CaFe₂O₄ and Ca₃Fe₂O₅) from thermal decomposition of mixtures Ca₂(C₆H₅O₇)₂·4H₂O·Fe₂(C₂O₄)₃·6H₂O. The calcination temperature of CaFe₂O₄ and Ca₃Fe₂O₅ is 1100 °C and 1180 °C respectively [89]. Some of the research groups have observed the changes of the magnetic and catalytic properties of calcium oxide and ferric oxide into calcium ferrite [90]. Tsipis et al have studied the oxygen ionic conductivity, Mössbauer spectra and thermal expansion of CaFe₂O₄ [91]. Jagadish et al have done studies on synthesis of calcium ferrite-based bio glass ceramics [92]. The synthesized p-type CaFe₂O₄ is used for the photo catalytic reduction of carbon dioxide [93], perovskite type calcium ferrite is also prepared by mechanochemical method for low temperature conversion of CO [94]. Randhawa et al has synthesized the magnesium and calcium ferrite from the thermolysis of M₃[Fe(cit)₂]₂·xH₂O precursors. Candeia et al have synthesized and characterized the spinel type CaFe₂O₄ [23] and BaFe₂O₄ [95] by using polymeric precursor method along with haxaferrites as impurities and applied as ceramic pigments. Strontium hexaferrite (hard ferrite) are prepared by different research groups by different method. Yongfei et al [96] have prepared nano-SrFe₁₂O₁₉ particles by sol–gel method and studied the magnetic properties. Hernández [97] studied the influence of sintering atmosphere on the strontium ferrites. Wang et al [98] have examine the effect of Sm substitution on the hydrothermally synthesized strontium hexaferrite.
Veeverka et al reported the strontium ferrite nanoparticles synthesized in presence of polyvinyl alcohol: Phase composition, microstructural and magnetic properties [99]. Rakshit et al have done the thermodynamic studies on SrFe$_2$O$_3$(s), SrFe$_3$O$_4$(s), Sr$_2$Fe$_2$O$_5$(s) and Sr$_3$Fe$_2$O$_6$(s) prepared by citrate gel combustion method [100]. Muhammad Iqbal has reported the effect of annealing temperature and substitution of Zr-Cu on magnetic properties of strontium hexaferrite nanoparticles [101]. Barium ferrite nanoparticles with a hexagonal phase were successfully synthesized by a sodium citrate-aided process in the presence of sodium hydroxide and studied the various physical properties [95]. Choi et al. [102]. Pillai et al. [103] and Xu et al. [104] has synthesized and studied the mechanism and magnetic properties Ba-Mg ferrite powders prepared by self-propagating high-temperature synthesis, micro emulsion method and reverse micro emulsion technique respectively. BaFe$_{12}$O$_{19}$ synthesized by simple, conventional, and inexpensive one-step in situ polymerization method, without the aid of any surfactant, organic dopant, or template is also reported [105]. Jing-ping et al compare the barium hexaferrites prepared by using sol-gel method and co-precipitation method [106]. Mendoza-Suárez et al focused on the influence of stoichiometry and heat treatment conditions on the magnetic properties and phase constitution of Ba-ferrite powders prepared by sol–gel [107]. Influence of pH on characteristics of BaFe$_{12}$O$_{19}$ powder prepared by sol–gel auto-combustion, substrate temperature on the texture of barium ferrite [106]. heat treatment conditions on the structure and magnetic properties of BaFe$_{12}$O$_{19}$ and sintering atmosphere on the formation and photo catalytic property of BaFe$_2$O$_4$ studied by Yang et al [108]. Some physical properties of M-type barium ferrite doped by selected ions studied by Slama et al [109]. The fine M-type barium hexaferrite (M-Ba-ferrite) particles were synthesized from sugar and nitrates as chelating agent in forming solid precursors of BaFe$_{12}$O$_{19}$ [110]. Jacobo et al synthesize the ultrafine particles of barium ferrite by chemical co-precipitation [111]. Wenyu et al reported synthesis of M-type barium ferrite nanobelt by spark plasma sintering method [112]. Synthesis and characterization of hard magnetic composites hollow microsphere/titania/barium ferrites were prepared by wet-chemical method [113]. From the above review it is clear that most of the researchers have synthesized the hard or
hexaferrites of alkaline earth metal and studied the physicochemical properties only while few of them have got the soft ferrite as an impurity up to 2 to 5\% only. However Gao et al. has synthesized the spinel MgFe$_2$O$_4$ by citrate gel method and used it as catalyst for the selective oxidation of styrene to benzaldehyde. To improve their physico-chemical properties the divalent or trivalent metal ion of the hard ferrites are substituted by other metal ions and prepared substituted AEM ferrites. To enhance the physico-chemical properties of AEM ferrites are tailored by substituting either divalent or trivalent metal ion by suitable AEM ion or transition metal ions by various research groups.

Substituted alkaline earth metal ferrites are also synthesized by few of the research groups like Rewatkar et al the synthesis and magnetic study of Co–Al substituted BaFe$_{12}$O$_{19}$ are reported [114]. Microwave dielectric properties of M-Type barium, calcium and strontium hexaferrite substituted with Co and Ti are also studied by Narang et al [115]. Mg$_{1-x}$Ca$_x$Fe$_2$O$_4$ reported by Nomura, et al investigates the thermal characteristics of Mg$_{1-x}$Ca$_x$Fe$_2$O$_4$ ferrite powder by applying AC magnetic field and to predict the effect of thermal coagulation in vivo [116]. Synthesis, physical, magnetic and electrical properties of Al–Ga substituted co-precipitated nano crystalline strontium hexaferrites are also studied by Iqbal et al [117]. Strontium and barium cations form ferrites with perovskite structure due to their comparatively larger/suitable cationic sizes [118]. Pan et al has prepared and studied microwave absorption properties of electroless Co–Ni–P coated strontium ferrite powder [119]. Singh et al studied M-type hexagonal ferrite powders. Ba$_{0.5}$Sr$_{0.5}$Co$_x$Ru$_{12-2x}$Fe$_{2-2x}$O$_{19}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2$) have been synthesized by conventional ceramic method. Magnetic properties have been investigated as a function of substitution of Co and Ru ions [120]. (Ni, Zn, Sn) Ru and (Ni, Sn) Sn substituted barium ferrite prepared by mechanical alloying and the influence of substitution of ions in barium ferrite are examined by A. Gonzalez [121]. Nadeev et al studied the high temperature studies La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ solution using synchrotron radiation [122]. Vogt et al has prepared the B-site substituted lanthanum strontium ferrites as electrode materials for electrochemical applications [123]. Liu et al examine the influences of La$^{3+}$ substitution on the structure and magnetic properties of M-type strontium ferrites [124]. Structural and magnetic properties are studied of
Sr$_{1-x}$Fe$_{12-x}$O$_{19}$ ($x = 0-0.15$) prepared by using a sol-gel method [125]. Tabatabaie et al studied the microwave absorption properties of Mn- and Ti-doped strontium hexaferrites [126]. Favre and coworkers carried synthesis of barium hexaferrites and its catalytic behavior in the combustion of methane was observed [127]. Shirtcliffe et al synthesized aluminium doped barium and strontium ferrite nanoparticles by citrate auto-combustion method [128].

1.8 Need to develop a new catalyst

Some strong oxidants such as KMnO$_4$, CrO$_3$, and HNO$_3$ [129, 130] were applied traditionally to alcohol oxidation, which might result in much serious pollution and some potential risks in the process of operation. In terms of atom efficiency and environment friendly, after oxygen, aqueous hydrogen peroxide (H$_2$O$_2$) is a very attractive oxidant for industrial applications since water is the only by-product, and it is easy to be dealt with after reactions. The latest studies have therefore focused on the catalytic alcohol oxidations with H$_2$O$_2$ as the terminal oxidant [131-134]. Moreover, transition metal-catalyzed oxidation of alcohols is of current interest, and the various effective catalysts have been reported, such as molybdenum and tungsten [135], ruthenium [136], cobalt [137], manganese [138], iron [139] and rhenium [140] based catalysts. However, based on the fact that most of the metal containing catalysts are expensive and some of them may lead to the environmental pollution, some poisonous reagents are required as solvents with a time-consuming process [135] and so on, it becomes more and more urgent to focus on finding out a more efficient and environmental friendly catalytic system.

1.9 Oxidation of olefins

Heterogeneous catalysis has been employed as an important chemical technology because of its inherent operational advantages such as ease of handling, separation, and recovery for the reuse of catalysts [141]. The oxidative conversion of olefins to aldehydes and ketones is important in chemical industry. The current practices can be divided into three categories: (i) the cleavage of C=C bond over materials such as osmium tetraoxide and
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ruthenium tetraoxide in stoichiometric amount [142]. (ii) the ozonolysis of olefins to ozonides and the subsequent conversion to aldehydes or ketones in reductive workup conditions [143], and (iii) the oxidation of olefins by hydrogen peroxide [144]. Due to waste problem and chemical cost, the practice of using metal oxides and metal salts as oxidants is not desirable [145]. From the viewpoint of environmental protection, oxidation by means of hydrogen peroxide appears to be a better alternative [144] in which methyltrioxorhenium [146], nanosized spinel-type MgFe$_3$O$_4$ [18], peroxovanadium [147], and TS-1 [148] have been reported to be active catalysts.

Environmental concerns have force the chemical industry to reevaluate many of its processes to reduce or eliminate the formation of waste produced in the synthesis of organic product [149]. This need is specially required in oxidation technology and can be addressed by the development of clean and safe oxidation procedures. This is possible by establishment of green catalytic process by environment friendly oxidants and green catalysts. H$_2$O$_2$ is an attractive oxidant from economic and environmental perspective. In addition, H$_2$O is the only theoretical byproduct when H$_2$O$_2$ is used as an oxidant. Catalytic oxidation is widely used in bulk chemical manufacturing and is becoming increasingly important in synthesis of fine chemicals. The oxidation of alkenes to carbonyl compounds has many synthetic applications. Since simple hydrocarbons are not miscible with aqueous H$_2$O$_2$, reaction is carried out in either polar solvent like acetonitrile, water, acetone etc. or in two phase system using chlorinated hydrocarbon and quaternary ammonium catalyst ion pair to maximize the surface contact and reactivity [150].

Therefore an important goal in the hydrocarbon oxidation is to carry out reaction without addition of organic solvent with safe, clean, economical and environmentally benign oxidant. This reaction is known as one of the most challenging oxidation reactions because of high stability of benzene ring. Using heterogeneous systems, both gas and liquid phase operations were intensively studied. Various oxidants such as nitrous oxide [151-153], molecular oxygen or air [154-157], the mixture of oxygen/hydrogen [158-164], the mixture of oxygen/ammonium [162, 163] and hydrogen peroxide [164-171] were investigated. Using nitrous oxide as oxidant has economic advantage only when
nitrous oxide comes as by-product from the adipic acid production and is clean. In contrast, the use of molecular oxygen or air as oxidant, oxygen/hydrogen system and oxygen/ammonium system result in low conversion and quite often in low selectivity. Hydrogen peroxide seems to be an attractive oxidant, which can be applied in a green process under mild conditions.

1.9.1 Epoxidation of styrene/cyclohexene

Catalytic oxidation of alkenes into more valuable epoxides as well as oxygen containing carbonyl compounds is one of the important synthetic reactions. Epoxides and carbonyl compounds have industrial significance, biological activities [172] that are very useful in synthetic organic chemistry, from both industrial [173] and academic points of view. Epoxides are industrially important chemicals [174], and are largely used for the synthesis of several perfume materials, anthelmintic preparations, epoxy resins, plasticizers, drugs, sweeteners, etc. Moreover, styrene oxide is an important organic intermediate in the synthesis of fine chemicals and pharmaceuticals, and has been synthesized using an epoxidation of styrene which is commercially important reaction [175].

Epoxidation of styrene is commercially important reaction for the production of styrene oxide, an important organic intermediate. Earlier studies reported for the epoxidation of styrene were based on the use of TS-1 [176-178], Ti–SiO₂ [179, 180], Ti–MCM-41 [177], and TBS-2 and TS-1 catalysts, using different oxidizing agents, such as TBHP [179], aqueous H₂O₂ [176], [180] and urea–H₂O₂ adduct [179]. For all the above catalysts, the use of aqueous H₂O₂ resulted in a very poor selectivity for styrene oxide. High-styrene oxide selectivity (≥80%) could be obtained using urea–H₂O₂ adduct [177] and TBHP [179] as the oxidizing agents but only at a low-styrene conversion (18 and 10%, respectively). The styrene oxide is traditionally produced by epoxidation of styrene using stoichiometric amounts of peracids as the oxidizing agent [181]. Peracids, however, are very expensive, hazardous to handle, non-selective for the epoxide formation and also lead to formation of undesirable products, creating a lot of waste. It is, therefore, of great practical interest to find a much better catalyst for the epoxidation of styrene. Recently,
Mandelli et al. [182] have observed a good activity and selectivity for γ-alumina in the epoxidation of limonene, cyclohexene and 1-octene by anhydrous H₂O₂. However, they observed catalyst deactivation due to accumulation of the reaction water: after a certain reaction period (5 h), the catalyst was deactivated. They can easily be prepared by the conversion of alkenes into a halohydrin followed by base-induced cyclization [183]. This route is very attractive compared to traditional methodologies as it avoids the utilization of hazardous per acids and analogues [184] or the expensive metal-based molecular O₂ or H₂O₂ oxidation, which frequently suffers from formation of undesirable oxygenated by-products [185]. The groups of Venturello [186] and Ishii [187] independently developed highly effective and mechanistically closely related polyoxometalates-based catalyst systems for alkene epoxidation by hydrogen peroxide. The major drawbacks to the Venturello–Ishii epoxidation are the use of toxic and carcinogenic chlorocarbons (chloroform and 1,2-dichloroethane) as solvents and catalyst deactivation causing difficulty in catalyst reuse [188].

The catalytic potentials of these complexes have been demonstrated by studying the oxidation of styrene, cyclohexene and ethyl benzene. Styrene oxide, an oxidation product of styrene, is an important intermediate in organic synthesis and in the manufacture of the perfumery chemical, phenylethyl alcohol. Epoxidation of styrene has been reported using homogeneous catalysts [189, 190], titanosilicate zeolites [191], heteropolytungstates [192] and zeolite-encapsulated metal complexes [193, 194]. Amongst the various oxidation products of cyclohexene, cyclohexene epoxide is a highly reactive and selective organic intermediate widely used in the synthesis of enantioselective drugs, epoxy paints and rubber promoters. Acetophenone, the valuable product of the selective oxidation of ethylbenzene, has also attracted interest [195, 196]. This is a useful intermediate in pharmaceuticals, resins, alcohols, esters, aldehydes and tear gas and is also used as a component in perfumery, in a drug to induce sleep, and as a solvent for cellulose ethers.

In order to overcome these limitations, environmentally benign catalytic methods for epoxidation with clean oxidants are actively investigated. The employment of hydrogen peroxide is an attractive option on both environmental and economical ground since it is cheap, readily available and gives water as the only byproduct [197, 198].
1.9.2 Degradation of pollutants

In recent years, metal-on-oxide systems have received considerable attention. A detailed understanding of the processes occurring at the metal/oxide interfaces is crucial in order to improve their efficiency and performance towards specific applications. Unfortunately, in comparison with other hybrid systems, the development of elaborate metal-semiconductor oxide nanoarchitectures has achieved only limited success. The synthesis of metal-loaded semiconductor oxide materials by conventional physical blending or chemical precipitation followed by surface adsorption usually yields insoluble materials for which control over the size, morphology and dispersion of the metal component remains inherently difficult [199]. Various core–shell systems have also been created by either epitaxial deposition or assembly of oxide nanostructures onto suitably functionalized metal nanoparticles [200]. The metal core in such composite gains stability against light damage without losing its catalytic activity, but unfortunately the preparative protocols usually involve many delicate steps whose accurate control is not straightforward. Another approach is based on the mixing of surfactant-capped metal and oxide nanocrystals synthesized separately [201]. A drawback of this method is that organic ligands on the particle surface can block a number of active sites and/or can be susceptible to severe degradation under photolysis [202]. Therefore, to date the preparation of novel functional oxide–metal heterostructures still remains an active research area.

On the other hand, organic dyes such as synthetic azo-dyes are extensively used for various industrial applications including textile dying, photographic, coating and photochemical industries. The degradation by-products of these dyes have dangerous impacts on the environment since it contains toxic aromatic amine compounds and the removal rate of these materials during aerobic waste treatment are still low [203]. A variety of physical, chemical and biological methods are used for treatment of textile waste water although most of them were found to be not effective and expensive [204, 205]. It has been reported that photo catalysis techniques can be used to destroy waste materials of dyes using semiconductor catalysts under light irradiation. Hisao et al. [206] studied photochemical decomposition of environmentally persistent short-chain
perfluorocarboxylic acids (PFCAs) in water mediated by iron (II)/(III) redox reactions. The catalysis process was explained by photoredox reactions between PFCA, Fe$^{3+}$/Fe$^{2+}$, and oxygen via photo-induced complexation of Fe$^{3+}$ with the PFCAs. Gondal et al. [207] investigated the laser induced photocatalytic splitting of water into hydrogen and oxygen. The activity of pure Fe$_2$O$_3$ catalyst and various electron capture agents under the irradiation of a strong laser beam has been investigated. The amount of hydrogen and oxygen produced within a short span of time were quite substantial and the photonic efficiency achieved using pure Fe$_2$O$_3$ was much higher than the reported conventional lamp based photo catalysis techniques.

1.10 Nature of present problem

There is lot of work done by the various research groups on the synthesis, characterization and catalytic activity. Most of the groups have prepared transition metal oxides, mixed transition metal oxides and used as catalysts in various organic transformations as well as degradation reactions as explained in previous section.

Our aim is to prepare the catalyst by using a simple chemical like metal nitrates via environment friendly method like sol-gel combustion method. Very few groups have focused their attention towards the alkaline earth metal oxides as well as iron based alkaline earth metal oxides. During the survey it was found that barring one or two most of the researchers have synthesized the perovskite type (ABO$_3$) of ferrite material, while few of them prepared hexaferrites (AB$_{12}$O$_{19}$). So our interest developed in the synthesis of spinel type soft (AB$_2$O$_4$) and pure alkaline earth metal ferrites like CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ by using sol-gel combustion method for the selective oxidation of various organic substrate like styrene, cyclohexene etc. After the synthesis of pure alkaline earth metal (AEM) ferrites, we have synthesized the substituted or modified alkaline earth metal ferrites like strontium substituted calcium ferrite Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$, where $x = 0 \leq x \leq 1$, barium substituted calcium ferrite Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$, where $x = 0 \leq x \leq 1$, and barium substituted strontium ferrite Ba$_x$Sr$_{1-x}$Fe$_2$O$_4$, where $x = 0 \leq x \leq 1$ in order to increase the catalytic efficiency of catalyst towards the epoxidation instead of simple oxidation by imparting the synergism between AEM ions and Fe$^{3+}$ ions. These substituted AEM
ferrites are prepared by citrate-gel combustion: sucrose assisted combustion and ultrasonicated citrate-gel method. The substitution enhance the catalytic efficiency of ferrite material it may be due to the synergistic effect of M-Fe where, M = divalent alkaline earth metal, as well as the site preference energy of the alkaline earth metal ions towards the octahedral site of catalyst. As the metal ion ratio play an important role in the catalytic activity we have synthesized the series of catalyst to check which composition of alkaline earth metal ion play decisive role in the organic transformation as well as degradation reactions.

The synthesized precursor of all parent as well as substituted alkaline earth metal ferrites are characterized by TG-DTG-DSC method to find out the formation temperature of catalyst. The precursors are burnt in silica crucible then calcined in furnace at different temperature to form a stable oxide. These oxides are well characterized by FT-IR. X-ray diffraction (XRD). X-ray florescence (XRF). Scanning electron microscopy (SEM). energy dispersive X-ray diffraction (EDX). Transmission electron microscopy (TEM). Brunauer, Emmett and Teller (BET). etc.

Styrene epoxidation is of interest to both academic and commercial fields for the synthesis of two important products, styrene oxide and benzaldehyde, in the presence of hydrogen peroxide. The use of hydrogen peroxide for oxidizing organic substrates generates various types of products, depending on the catalyst and the reaction conditions used. Epoxides are well known as one of the most valuable building blocks, which can be used as intermediates and precursors for chemical production. From an industrial point of view, epoxides are largely used for the synthesis of perfume materials, anthelmintic preparations, epoxy resins, plasticizers, drugs, sweeteners, etc.

The well characterized catalyst is used further in selective oxidation of styrene to benzaldehyde. selective epoxidation of styrene as well as cyclohexene. The products obtained in the styrene and cyclohexene oxidation reaction were analyzed by gas chromatography and mass spectroscopy GCMS). The influence of the catalyst, reaction time, temperature, amount of catalyst, styrene/ H₂O₂ molar ratio, oxidizing agents, effect of chemical composition of catalyst, method of preparation of catalyst, substrate/ oxidant molar ratio and solvents on the conversion and product distribution were also studied.
The substituted alkaline earth metal ferrites used for the degradation of Rhodamine-6G, one of the toxic and fluorescent dyes were also studied. The extent of degradation of rhodamine-6G (Rh-6G) as well as methylene blue (MB) is determined by using UV spectroscopy. The reuse of catalyst is also investigated by using the same catalyst for number of cycles.

The aims of our investigation were (i) to comparatively investigate the catalytic behavior of the pure and modified or substituted alkaline earth metal ferrites for selective oxidation of styrene, epoxidation of styrene, selective epoxidation of cyclohexene and degradation of toxic and carcinogenic dyes. (ii) to observe the effect of $M^{2+}$ ($M = \text{Ca, Sr and Ba}$) on the catalytic behavior for selective oxidation of styrene, cyclohexene in oxygen rich (combustion) and oxygen poor (OCM) atmospheres, and (iii) to get a better understanding on the generation, nature and role of lattice defects on the catalytic reactivity.
1.1 References:


