1

Introduction

1.1 Catalysis

A catalyst always helps a reaction to alter its rate. The history of catalysis began from 1796 with the studies by von Marum on the dehydrogenation of alcohol using metals. However, the term catalysis was defined by J. J. Berzelius in 1836 as a process in which a relatively small amount of a foreign material, called a catalyst, augments the rate of the reaction without being consumed in the reaction. 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.

Modern industries are learning more and more about the applications and benefits of catalysts and the different ways to bring down the cost of production. The specificity of a catalyst enables a chemical process to proceed more efficiently with less waste. 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 more well defined areas of industrial catalysis are petroleum, pharmaceutical and environmental catalysis. In the present day, catalysis research and industrial catalyst development are dependent largely upon the impulses and the needs of the market, the ecological circumstances, i.e., environmental protection, the extensive utilization of the starting materials and above all, the development of reaction specific catalysts. We must expect that in the 21st century energy production, various modes of transport, chemical and petroleum industry, metallurgy and other industries involving chemical treatment will become world wide and more safe by the use of catalytic technologies leading to the purification of exhaust gases, waste water and other harmful by-products. 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.
Traditionally, this field is divided into homogeneous and heterogeneous catalysis. By definition, a catalytic reaction in which the reactants and the catalyst are in the same phase, is homogeneous catalysis and if the reactants and the catalysts are in different phases, it is heterogeneous catalysis. Each of these catalytic processes possesses its own advantages and disadvantages. The strongest impulse for developing new, more efficient and more selective catalyst systems is related to environmental compatibility. Looking at the different industrial areas, in particular in the production of fine chemicals and in the pharmaceutical industry, a lot of by-products and wastes are produced. The so called E-factor i.e., the ratio of the amount of by-products to the amount of product is not acceptable. The reason is the use of stoichiometric amount of homogeneous Brönsted acids such as HF, H₂SO₄, H₃PO₄, HNO₃, etc. and Lewis acids such as AlCl₃, BF₃, FeCl₃, etc. By-products in the form of salts due to the neutralization of the acids are also produced. That is also true for the application of Brönsted and Lewis bases in the field of organic multi-step syntheses and in each step there is a loss of starting material. The synthesis of fine chemicals and pharmaceuticals generates large amounts of wastes, which is due in particular to the fact that most of the reactions are stoichiometric 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. Due to these striking properties, the field of heterogeneous catalysis is one of the rapidly expanding areas in chemical industry.

In recent years, considerable advances have been achieved in the study of surface structure and mechanism of the catalytic reaction. A heterogeneous catalyst performs by providing an alternative reaction pathway with lower energy of activation. Heterogeneous catalysts interact with reactants and enhance the rate of chemical reactions. This interaction may be chemical and physical processes, which are fundamental to any heterogeneous catalytic system. The overall catalytic reaction rate depends on these chemical and physical processes or steps. Each of these steps contributes to a greater or lesser extent to the overall reaction rate.
The general steps involved in heterogeneous catalysis are:

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

From experience, it is possible to narrow the range of solids that are likely to catalyze a certain type of chemical reactions. Heterogeneous catalysts can be classified according to their electrical conductivity as conductors, semiconductors, and insulators. Table 1.1 shows such classification and the type of reactions for each type of catalyst.

**Table 1.1 Classification of heterogeneous catalysts.**

<table>
<thead>
<tr>
<th>Classification</th>
<th>Conductor</th>
<th>Semiconductor</th>
<th>Insulator</th>
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<tbody>
<tr>
<td><strong>Materials</strong></td>
<td>Metals</td>
<td>Metal oxides and</td>
<td>Metal oxides</td>
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<tr>
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<td></td>
<td>sulphides</td>
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<tr>
<td><strong>Examples</strong></td>
<td>Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt, Ag, Cu.</td>
<td>NiO, CuO, ZnO, Cr₂O₃, V₂O₅, etc., WS₂, MoS₂, etc.</td>
<td>Zeolites, Al₂O₃, SiO₂-MgO, Al₂O₃ + Cl or F</td>
</tr>
<tr>
<td><strong>Types of Reactions</strong></td>
<td>Hydrogenation, Oxidation, Reduction, Hydrogenation, Dehydrogenation, Oxidation, Reduction</td>
<td>Dehydrogenation, Polymerization, Cracking, etc.</td>
<td>Desulphurization, etc.</td>
</tr>
</tbody>
</table>

From experience, it is possible to narrow the range of solids that are likely to catalyze a certain type of chemical reactions. Heterogeneous catalysts can be classified according to their electrical conductivity as conductors, semiconductors, and insulators. Table 1.1 shows such classification and the type of reactions for each type of catalyst.
1.2 Transition metal oxides as catalysts

Transition metal oxides are technologically important materials that have found to be relevant in chemical applications. Transition metal oxides are the proficient components in catalysts employed in many reactions such as oxidation, reduction, oxidative and non-oxidative dehydrogenation, ammoxidation, metathesis and water gas shift reaction for the production of hydrogen.

Many transition metal oxides are non-stoichiometric. It is known that the interaction of the oxide with its constituents in the gas phase generates defects or coordinatively unsaturated sites. These defects or coordinatively unsaturated sites are important in surface chemistry, which are mainly responsible for the adsorptive and catalytic properties of the transition metal oxides. Due to the formation of these defects, various cations may be differently distributed between the surface and bulk of the single as well as in the multi-component transition metal systems. When the concentration of the defects at the surface of the oxide surpasses a certain critical value, ordering of defects or formation of new bi-dimensional surface phase may occur, resulting often in a dramatic enhancement of catalytic activity and selectivity [1-3]. As an example, nickel oxide mixed with SiO$_2$ [4], SiO$_2$-Al$_2$O$_3$ [5] and NiSO$_4$ [6] are highly active for the dimerization of olefins and the active site for this reaction is found to be the low valent nickel at the surface of the system.

Transition metal oxides possess acid-base properties. Titania and zirconia attracted much attention because these are good supports for metal catalysts and change to super acids on combining with small amount of sulphate. Hydrated Nb$_2$O$_5$ and Ta$_2$O$_5$ are making an impact for their application as unusual solid acids and showed excellent stability as a catalyst for esterification, hydrolysis and hydration reactions [7-11]. Oxides of Cr, Mo and W are seldom used as single oxides but are used as mixed oxides with alumina and silica for hydrogenation, dehydrogenation, skeletal isomerization of hydrocarbons, polymerization of olefins and hydrodesulphurization [12-16]. Probably due to the high oxidation activity of manganese oxides, very few studies have been reported for their acid-base properties. MnO$_2$ has been claimed to be efficient for the hydration of nitriles to amides, in which the acidic character of the catalyst is involved.
[17, 18]. Re₂O₇ supported on alumina exhibited strong acid sites and are efficient catalysts for the metathesis of olefins [19]. Fe₂O₃ is regarded to be weakly acidic and basic and Fe₂O₃ obtained by heat-treating of FeSO₄ showed maximum acidity and catalytic activity at the calcination temperature of 700°C for several reactions [20-24]. The acidic sites in Co and Ni oxides are due to the presence of coordinatively unsaturated Co and Ni ions and are established to be active for the dimerization of olefins [4-6]. ZnO is considered as amphoteric and the acidity and basicity increase when ZnO is mixed with other oxides [25-28] and thereby the catalytic activity is enhanced.

Analysis of the voluminous patent literature concerning the selective oxidation of hydrocarbons clearly indicates that majority of the efficient catalysts for these processes are transition metal oxides. Their efficiency in oxidation reactions depends not only on their redox properties but also on their acid-base properties. Numerous works are reported to correlate the acid-base properties of mixed transition metal oxides with the catalytic activity/selectivity in selective oxidation of hydrocarbons [29, 30].

The catalytic abatement of NOₓ has engrossed the interest of many laboratories world wide because of the stringent regulations for the NOₓ emissions. Transition metal oxides (for example, oxides of Cu, Co, Fe, Mn, Ti, and V) show promising results when added as promoters or co-catalysts [31-34].

Transition metal oxides are efficient systems in relation to their adsorption behaviour of reaction products. Their catalytic oxidation of CO is performed by a series of reaction steps, while the adsorption of CO proceeds quickly and is limited only by the desorption of CO₂. It has been known for a long time that copper oxides display high catalytic activity for the oxidation of CO [35-38]. A number of other transition metal oxide systems, Cu-Cr-O, Cu-Al-O, Mn-Mg-Al-O, Mn-Al-Mg-O, Mn-perovskite and Ni-Cu-Cr-O also have been identified to be active over a wide range of compositions [39].

Ternary transition metal oxides with general formula AB₂O₄, where A and B are the metal cations, having the spinel structure show greater structural stability and catalytic activity. In the present investigation, manganese-iron based spinel oxides of chromium, cobalt, nickel, copper and zinc are chosen.
1.3 Ferrites

Mixed metal oxides with iron (III) oxides as their main component are known as ferrites. Ferrites crystallizes in three different crystal types namely, magnetoplumbite, garnet and spinel and accordingly they can be classified into three groups (Table 1.2).

Table 1.2 Crystal type of ferrites.

<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
<th>General Formula</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetoplumbite</td>
<td>Hexagonal</td>
<td>$\text{A}^{III}\text{Fe}<em>{12}\text{O}</em>{19}$</td>
<td>$\text{BaFe}<em>{12}\text{O}</em>{19}$</td>
</tr>
<tr>
<td>Garnet</td>
<td>Cubic</td>
<td>$\text{Ln}^{III}\text{Fe}_2\text{O}_4$</td>
<td>$\text{Ln}^{III} = \text{Y}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm} \text{and Lu}$</td>
</tr>
<tr>
<td>Spinel</td>
<td>Cubic</td>
<td>$\text{A}^{II}\text{Fe}_2\text{O}_4$</td>
<td>$\text{A}^{II} = \text{Cd}, \text{Co}, \text{Mg}, \text{Ni} \text{and Zn}$</td>
</tr>
</tbody>
</table>

1.4 Spinels

The simplest among the ferrites are the spinel type. Simple ferrospinels ($\text{A}^{III}\text{Fe}_2\text{O}_4$), as well as mixed ferrospinels of the general composition $\text{A}_x\text{B}_{1-x}^{III}\text{Fe}_2\text{O}_4$ are known. The interesting structural, electrical, magnetic and catalytic properties of these compounds are governed by their chemical composition. So special care must be taken in the preparation stages of these compounds to get ferrospinels with specific properties.

1.5 Methods of preparation

Ferrites can be prepared by almost all the existing techniques of solid state chemistry, leading to a wide variety of forms: thin and thick films, single crystals and polycrystalline aggregates. The ideal characteristics of ferrite powders are:

- Small particle size
- Narrow distribution in particle size
- Dispersed particles
- High purity
- Homogeneous composition
For the exact reproducibility of the ferrite particles utmost care must be taken during the preparation stages. Minor changes in the preparation method can drastically alter their properties.

The oldest method of preparation of ferrites is the *ceramic method*. The precursor compounds are usually iron oxide (α-Fe₂O₃) and oxides or carbonates of the other cations in the desired ferrite and these are ground well by mechanical milling. But this method cannot produce fine particles and extended milling introduces significant quantities of undesired impurities and the distribution in particle size becomes extremely wide. The major drawback found for this method is the lack of homogeneity of the material prepared. Again, the high temperature (1200 K) required to complete solid state reactions leads to drastic decrease in surface area of the resulting material by sintering.

Ferrite powders with all the ideal characteristics mentioned above can be prepared by various new methods. Their common feature is that the mixing of components takes place at the atomic or molecular scale. *Co-precipitation* is a very suitable method for the creation of homogeneous catalyst components or for the moulding of precursors with a definite stoichiometry, which can easily be converted to the active catalyst [40]. This method is based on the stoichiometric mixing of aqueous solutions of chlorides, nitrates and sulphates of Fe³⁺, and of divalent Ni, Co, Mg, Ba, Sr, etc., in the concentrations required for the ferrite composition and their simultaneous precipitation in the form of hydroxides by NaOH [41-45]. This is followed by filtration, washing and calcination of the product to form the oxide. The morphology, the texture, the structure and the size of the particles can be accurately controlled by altering the pH of the solution, temperature and nature of the reagents [46]. By this method ferrite particles with a narrow size distribution in the range 50-500 nm may be obtained, with high purity.

The *precursor method* allows the preparation of ferrites with a precise stoichiometry. It involves the synthesis of a compound (precursor) in which the reactants are present in the required stoichiometry. Upon heating in air (1200-1500 K), the precursor decomposes to yield the ferrite [47-49]. Particles with high magnetization, high purity and size in the range 20-60 nm can be obtained by this method.
Sol gel techniques are receiving much attention because they can be applied to a wide variety of materials; they offer the possibility of controlling not only the size and distribution of particles, but also their shape. A broad range of ferrites with any desired shape can be prepared by this technique [50-52]. The process involves the preparation of a sol, which is a dispersion of a solid and a dispersed phase in a liquid (dispersion medium). The sol is prepared by mixing concentrated solutions containing the cations of interest, with an organic solvent as dispersion medium. The sol is then destabilized by adding water, leading to the formation of a gel. This is transformed to the solid phase by high pressure heating whereby the liquid contained in the gel is transformed into supercritical vapours.

Spray-drying technique of preparation of ferrites involves precipitation from a concentrated solution of cations by solvent evaporation. To ensure that the particle size remains small, the concentrated solution is atomized at high pressure into fine droplets of 100-500 µm diameter; the solvent is rapidly evaporated by an upward stream of hot gas. Several alternative methods are currently under development, as an efficient way to control the texture, composition, homogeneity and structural properties of the ferrite particles [53-57].

In freeze drying method, the aqueous, concentrated solution is atomized into fine droplets, and are rapidly frozen by blowing into low temperature bath such as ice-acetone, or liquid nitrogen. The droplets are then dried in vacuum and the anhydrous salts are calcined to produce fine powders. Ni-Zn ferrites have been obtained from freeze-drying with high density and small and uniform grain size [58].

Combustion synthesis is a novel method for the preparation of fine particles of ferrites making use of the exothermic redox reaction between metal nitrate and tetraformal triazine or oxalic acid dihydrazine [59]. In this process stoichiometric ratio of nitrates is dissolved in the minimum amount of water in a pyrex dish; the fuel is added and is heated at 350°C in a muffle furnace. A heating rate of 75°C/min is used to obtain good combustion. This method can be used for the synthesis of Ni-Zn and Co spinels.

In addition to the above-discussed methods, some other methods like molten salt synthesis [60] and shock wave synthesis [61] are also applied in the ferrite synthesis.
1.6 Spinel structure

The spinel structure was first determined by Bragg and Nishikawa [62]. The unit cell of a spinel contains eight formula units and hence can be represented as $8[\text{AB}_2\text{O}_4]$. The 32 oxygen anions per unit cell form a face centered cubic (fcc) lattice in which two kinds of interstitial sites are present namely, (i) 64 tetrahedral sites, surrounded by 4 oxygens (A site) and (ii) 32 octahedral sites, surrounded by 6 oxygen ions (B sites). Of these, 8 tetrahedral holes ($1/8^{th}$ of the tetrahedral interstices) and 16 octahedral interstices ($1/2$ of the octahedral interstices) are occupied by metal ions. The unit cell of an ideal spinel structure is shown in Fig. 1.1. It is convenient to divide the unit cell into eight edges of length $a/2$ to show the arrangements of the A and B sites (Fig. 1.2). The space group is Fd3m (Oh$^7$). The oxygen atoms have four-fold coordination, formed by three B cations and A cation. The nearest neighbours of a tetrahedral site, octahedral site and oxygen anion site are shown in Fig.1.3.

Fig. 1.1 The unit cell of an ideal spinel structure. Hatched circles indicate A cations, unhatched circles indicate B cations and large unhatched circle indicate oxygen anions.
Fig. 1.2 The spinel structure. The unit cell can be divided into octants; tetrahedral cations A, octahedral cations B and oxygen atoms (large circles) are shown in two octants.

Fig. 1.3 Nearest neighbours of (a) a tetrahedral site, (b) an octahedral site and (c) oxygen anion.
The ideal situation is never realized as the oxygen anions in the spinel structures are generally not located at the exact positions of the fcc sublattice. The interstices available in an ideal close packed structure of rigid oxygen anions can incorporate only those metal ions with radius $r_{\text{tetra}} \leq 0.30 \text{ Å}$ in tetrahedral sites and only those ions with radius, $r_{\text{octa}} \leq 0.55 \text{ Å}$ in octahedral sites. So in order to accommodate larger cations such as Co, Cu, Mn, Mg, Ni and Zn, the lattice has to be expanded. The difference in the expansion of the octahedral and tetrahedral sites is characterized by a parameter called oxygen parameter ($u$). In all ideal spinels, the parameter '$u$' has a value in the neighbourhood of 0.375. But in actual spinel lattice this ideal pattern is slightly deformed, usually corresponds to $u > 0.375$. 'u' increases because the anions in the tetrahedral sites are forced to move in the [111] direction to give space to the larger A cations, but without changing the overall 43m symmetry. Octahedra become smaller and assume 3m symmetry. In Table 1.3, interatomic distances are given as a function of the unit cell parameter 'a' and the oxygen parameter '$u$' [63, 64].

Table 1.3 Interatomic distances and site radii in spinels $\text{AB}_2\text{O}_4$ as a function of unit cell edge (a) and oxygen parameter ($u$).

<table>
<thead>
<tr>
<th></th>
<th>a ($3/4$)$^{1/2}$</th>
<th>a ($11/8$)$^{1/2}$</th>
<th>a ($2/4$)$^{1/2}$</th>
<th>a [3($u$-0.25)]$^{1/2}$</th>
<th>a ($3u^2$-2.75 $u$ + 43/64)$^{1/2}$</th>
<th>a ($5/8$-$u$)</th>
<th>a ($2(2u-0.5)$)$^{1/2}$</th>
<th>a [2(1-2$u$)]$^{1/2}$</th>
<th>a ($4u^2$-3$u$ + 11/16)$^{1/2}$</th>
<th>a [3($u$-0.25)]$^{1/2}$ - $R_0$</th>
<th>a ($3u^2$-2.75$u$ + 43/64)$^{1/2}$ - $R_0$</th>
<th>a ($5/8$-$u$ ) - $R_0$</th>
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<td>Tetra-tetra separation A-A</td>
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<td>Tetra - octa separation A-B</td>
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<td>Octa - octa separation B-B</td>
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<td>Tetra - O separation A-O</td>
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<td>Octa - O separation B-O</td>
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<td>O-O tetrahedral edge O-O</td>
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<td>O-O shared octa edge O-O</td>
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<td>O-O unshared octa edge O-O</td>
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<td>Tetrahedral radius</td>
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<td>Octahedral radius</td>
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$u$ is defined with unit cell origin at an A site and $R_0$ is the oxide ion radius.
1.6.1 Distribution of metal ions over different sites

*Normal, Inverse and Random Spinels*

The interesting and useful electrical, magnetic and catalytic properties of the spinels are governed by the distribution of metal ions among the octahedral and tetrahedral sites of the spinel lattice. As mentioned earlier, the general formula of the spinel is $A_B^{204}$, where $A$ and $B$ cations occupy the tetrahedral and octahedral sites respectively. Many different cation combinations may form a spinel structure and it is almost enough to combine any three cations with a total charge of eight to balance the charge of the anions. The following combinations

- $A = ^{+2}, B = ^{+3}$ as in $\text{NiFe}_2\text{O}_4$
- $A = ^{+4}, B = ^{+2}$ as in $\text{Co}_2\text{GeO}_4$
- $A=^{+1}, B=^{+3,4}$ as in $\text{LiFeTiO}_4$
- $A = ^{+1}, B = ^{+3}$ as in $\text{Li}_{0.5}\text{Fe}_2.5\text{O}_4$
- $A = ^{+1}, B = ^{+2,5}$ as in $\text{LiNiVO}_4$

and

- $A = ^{+6}, B = ^{+1}$ as in $\text{Na}_2\text{WO}_4$, are known.

The structure and the cation distribution of the spinels have been discussed by Verway and Heilman [65]. If $A$ denotes a divalent cation and $B$, a trivalent one, the cation distribution is usually indicated as $(A)\{B_2\}O_4$, where the square brackets indicate the octahedral site occupancy and the cation in the parenthesis are located in the tetrahedral sites. This is the so called *normal* distribution, in which the tetrahedral sites are occupied only by the $A$-type ions and the octahedral sites by the $B$-type ions. The $A$ ions of a normal spinel occupy the 8 tetrahedral sites of the Oh$^7$ space group and have a point symmetry $T_d$. The $B$ ions of a normal spinel occupy the 16 octahedral sites of the Oh$^7$ space group and have point symmetry $D_{3d}$. Another extreme cation distribution is, $(B)[AB]O_4$, as pointed out by Barth and Posnjak [66]. In this case the $B$ cations occupy the tetrahedral sites and all the $A$ cations together with the other half of the $B$ cations occupy the octahedral sites. This type of spinel configuration is called *inverse* spinels. Datta and Roy [67] and Hafner and Laves [68] have shown that there are many *intermediate* or *random* spinels which are in between the pure normal and pure inverse
arrangements. This can be represented as \((A_{(1-x)}B_x)\ [A_xB_{(2-x)}]O_4\), where \(x\) is the degree of inversion, with a value of zero for normal and one for the inverse distribution. This intermediate spinel structure is due to the average distribution of all the ions about all the spinel cation positions (Table 1.4).

Table 1.4 Cation distribution, lattice parameter \(a\) and oxygen parameter \(u\) for several spinels.

<table>
<thead>
<tr>
<th>Distribution</th>
<th>(a(\text{Å}))</th>
<th>(u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Cd})[\text{Fe}_2])</td>
<td>8.7050</td>
<td>0.3935</td>
</tr>
<tr>
<td>((\text{Zn})[\text{Fe}_2])</td>
<td>8.5632</td>
<td>0.3865</td>
</tr>
<tr>
<td>Inverse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Fe})[\text{CoFe}])</td>
<td>8.3500</td>
<td>0.3810</td>
</tr>
<tr>
<td>((\text{Fe})[\text{CuFe}])</td>
<td>8.3690</td>
<td>0.3800</td>
</tr>
<tr>
<td>((\text{Fe}^{3+})[\text{Fe}^{2+}\text{Fe}^{3+}])</td>
<td>8.3940</td>
<td>0.3798</td>
</tr>
<tr>
<td>((\text{Fe})[\text{Li}<em>{0.5}\text{Fe}</em>{1.5}])</td>
<td>8.3300</td>
<td>0.3820</td>
</tr>
<tr>
<td>((\text{Fe})[\text{NiFe}])</td>
<td>8.3390</td>
<td>0.3823</td>
</tr>
<tr>
<td>Random</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}_{1-x}\text{Fe}_x)[\text{Mg}<em>x\text{Fe}</em>{(2-x)}])</td>
<td>8.3600</td>
<td>0.3820 ((x = 0.10))</td>
</tr>
<tr>
<td>((\text{Mn}_{1-x}\text{Fe}_x)[\text{Mn}<em>x\text{Fe}</em>{(2-x)}])</td>
<td>8.5110</td>
<td>0.3865 ((x = 0.85))</td>
</tr>
<tr>
<td>((\text{Mo}_{1-x}\text{Fe}_x)[\text{Mo}<em>x\text{Fe}</em>{(2-x)}])</td>
<td>8.5010</td>
<td>0.3751 ((x = 0.50))</td>
</tr>
</tbody>
</table>

1.6.2 Factors determining the cation distribution

The physical and chemical properties of spinels depend not only on the kinds of cations in the lattice, but also their distribution over the available crystal sites. It is thus of major importance to understand the factors which influence the site occupancy.

The factors that contribute to the total lattice energy in spinels are:

(i) elastic energy
(ii) electrostatic (Madelung) energy
(iii) crystal field stabilization energy
(iv) polarization effects
The elastic energy refers to the degree of distortion of the crystal structure due to the difference in ionic radii assuming that ions adopt a spherical shape. Smaller cations, with ionic radii of 0.225-0.4 Å, should occupy tetrahedral sites, while cations of radii 0.4-0.73 Å should enter octahedral sites. This distribution leads to a minimum in lattice strain. Since trivalent cations are usually smaller than divalent ones, a tendency towards the inverse arrangement would be expected.

The detailed Madelung energy calculations for spinels [69], show that this energy is dependent on the \( u \) parameter. For \( u > 0.379 \), the normal distribution is more stable, while for lower \( u \) values, the inverse arrangement possesses a higher Madelung constant. The presence of two kinds of cation on octahedral sites in inverse spinels leads to an additional contribution to the Madelung energy. The critical \( u \) value then becomes 0.381 [70]; Madelung energy is higher for the normal spinel if \( u > 0.381 \), and the inverse, ordered spinel is more stable for \( u < 0.381 \).

The application of the crystal field theory to the understanding of cation site preference was first suggested by Romeijn [71]. Dunitz and Orgel [72] and simultaneously McClare [73] have calculated the octahedral site preference energies of transition metal ions in oxides using crystal field theory (CFT) and is given in Table 1.5.

The data show that the systems with \( d^5 \) and \( d^{10} \) configurations have no crystal field stabilization energy and hence no site preference. The \( d \) system has the highest octahedral site preference energy. The \( d^6 \) and \( d^9 \) ions can be further stabilized by Jahn-Teller distortion. In the regular \( O_h \) symmetry, octahedra of surrounding anions is elongated or compressed in the \( z \) direction to give \( D_{4h} \) symmetry, the doublet (\( e_g \)) and triplet (\( t_{2g} \)) levels split [74]. The splitting of the doublet is larger. In the case of elongation, the \( d_{x^2-y^2} \) orbital is stabilized compared to the \( d_{z^2} \) orbital. \( \text{Fe}[\text{CuFe}]_4\text{O}_4 \), \( \text{Mn}[\text{ZnMn}]_4\text{O}_4 \), \( \text{Cr}[\text{NiCr}]_4\text{O}_4 \) and \( \text{Zn}[\text{Mn}^{3+}]_4\text{O}_4 \) are examples of tetragonally distorted spinels.

The last factor to be discussed is polarization effects. Polarization may simply be considered as the degree of distortion of the electronic charge density around an ion. This can arise from the negligible distortion and effective removal of an electron from one ion towards its neighbour, giving rise to a purely covalent bond and a purely ionic
bond, respectively. With regard to transition metal ions in spinels, only spherically symmetric ions (d$^5$ and d$^{10}$) can show tendency for covalency. In this case, tetrahedral sites are preferred. Cations which show covalent affinity for tetrahedral environments are Fe$^{3+}$, Ga$^{3+}$, In$^{3+}$ and, more strongly, Zn$^{2+}$ and Cd$^{2+}$. Spinels with the former cations tend, therefore, to be inverse while those with the latter tend to be normal.

When the various factors are counterbalancing, there can be a completely random arrangement of metal ions among the eight tetrahedral sites and sixteen octahedral sites.

Table 1.5 Crystal field stabilisation energies for transition-metal cations on octahedral and tetrahedral spinel sites.

<table>
<thead>
<tr>
<th>Number of d electrons</th>
<th>Theoretical cfs in terms of Dq</th>
<th>Cations</th>
<th>Estimated octahedral site preference energies, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Octahedral</td>
<td>Tetrahedral</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>6</td>
<td>Ti$^{3+}$</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>12</td>
<td>V$^{3+}$</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>8</td>
<td>V$^{2+}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr$^{3+}$</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>4</td>
<td>Mn$^{3+}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr$^{2+}$</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>Fe$^{3+}$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Mn$^{2+}$</td>
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<tr>
<td>6</td>
<td>4</td>
<td>6</td>
<td>Fe$^{2+}$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Co$^{3+}$</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>12</td>
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</tr>
<tr>
<td>8</td>
<td>12</td>
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<tr>
<td>9</td>
<td>6</td>
<td>4</td>
<td>Cu$^{2+}$</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>Zn$^{2+}$</td>
</tr>
</tbody>
</table>
1.6.3 The surface of catalytically active spinels

The surface structure and properties of spinels are of wide interest. The principal and interesting question to ask is, which plane, which coordination and which valency states are responsible for the catalytic activity and selectivity in spinels? There are many reports that the tetrahedral sites in spinels are not active [75-77]. The fact that the tetrahedral sites are not active could originate from stronger metal-oxygen bonds due to the lower valency and coordination number. Moreover, the tetrahedral sites are not accessible to the reactants [78]. In the literature, usually only the low-index planes are taken into consideration when discussing the surface of spinels [75, 79-81]. Following the suggestion by Knözinger and Ratnaswami [75] and using their notation one can distinguish six different low-index surface planes, which are shown in Fig. 1.4. From the figure it follows that A (111), C (110), E (100), and F (100) planes have both tetrahedral and octahedral sites on the surface, while B (111) and D (110) planes expose only octahedrally coordinated cations.

Fig. 1.4 The low-index planes of a normal spinel structure: (a) A (111), (b) B (111), (c) C (110), (d) D (110), (e) E (100), (f) F (100). The open spheres represent the oxygen anions, the solid spheres the octahedral cations and hatched spheres the tetrahedral cations.
According to Ziolkowski and Barbaux [79], from the theoretical calculations, the A (111) and D (110) planes are preferred in the surface, but these predictions do not form a final conclusion. Shelef and coworkers [80-82] made an experimental attempt to elucidate the surface structure of spinels using the low energy ion scattering (LEIS) and they support the idea that the tetrahedrally coordinated cations are not accessible for the reactant molecules.

Beaufils and Barbaux [76, 77] investigated the surface composition of normal spinel oxides by differential neutron diffraction (D.N.D) techniques and concluded that the surface of spinel consists of a mixture of (110) and (111) planes. By comparing the experimental results of D.N.D with some models involving argon-oxygen distances, they observed that these planes contain only octahedral cations and oxygen anions respectively. Jacobs et al. [78] confirmed this by the LEIS technique. By substitution of the Mn and Co cations in different sites in the spinel structure of MnO4 and Co3O4 by other cations which are not active in the selective reduction of nitrobenzene to nitrosobenzene, they studied the role of these sites in the catalytic reaction. Their results confirmed the idea that octahedral ions are exposed almost exclusively at the surface of the spinel oxide powders and only these sites participate in the reaction. The only two low-index planes of the spinel structure, which can satisfy this condition, are identified as B (111) and D (110). The absence of occupied tetrahedral sites at the surface is a more general property of spinels.

1.7 Spinels as catalysts

Ternary oxides crystallizing with spinel structure exhibit interesting catalytic properties. However, individual metal oxides lose their catalytic activity rapidly owing to ageing and coke formation on the catalyst surface. The spinel lattice imparts extra stability to the catalyst under various reaction conditions, so that these systems sustained activity for longer periods [83]. In spinel systems correlation between catalytic activities and the electric and the magnetic properties are often found; this is a direct consequence of the dependence of both properties on the nature of the ions, their charges, and their distributions among octahedral and tetrahedral sites. Jacobs et al. in their recent work revealed that octahedral sites are exposed almost exclusively at the surface of spinel
oxide and the catalytic activity of such systems is mainly due to the octahedral cations [78]. The tetrahedral ions are either inactive or contributing only a little to the catalytic properties [85]. The lower activity of the tetrahedral ions comes from the fact that the metal oxygen bonds will be stronger due to lower coordination number and hence such cations are less accessible to the reactants.

Among the spinel compounds, ferrites have been used as effective catalysts for a number of industrially important reactions such as oxidative dehydrogenation of hydrocarbons, hydrodesulfurization of petroleum crude, treatment of automobile exhaust gases, oxidation of CO, etc. The catalytic effectiveness of ferrites for many such reactions arises because of the ease with which iron can exchange its oxidation state between 2 and 3. Even if reduction of Fe$^{3+}$ to Fe$^{2+}$ occurs, spinel structure remains unaltered and upon reoxidation the original state can be regained [85].

Many single and mixed oxides have been mentioned as catalysts for the oxidative dehydrogenation (ODH) of olefins. Bajaras et al. reported MgFe$_2$O$_4$ as an efficient catalyst for the oxidative dehydrogenation of hydrocarbons containing 4 to 6 carbon atoms [86]. Gibson and Hightower made kinetic and mechanistic studies of oxidative dehydrogenation of butene to butadiene over magnesium ferrite using deuterium and $^{14}$C labelled isotopic traces [87]. Their kinetic studies showed that the reaction is zero order in oxygen and first order in olefin at low partial pressures of butene. They suggested a modified Rennard-Massoth mechanism for the reaction in which the butene adsorption site is postulated to be an anion vacancy. Zinc-chromium and magnesium-chromium ferrites with spinel structure are superior catalysts for the oxidative dehydrogenation of butene to butadiene [83, 88, 89]. The Cr$^{3+}$ ions, incorporated into octahedral site in spinel lattice, inhibit the bulk reduction of the catalyst and increase its activity and selectivity for the reaction. Cares et al. reported CoFe$_2$O$_4$ as a better catalyst over CuFe$_2$O$_4$ for the dehydrogenation reaction [90]. A probable reason for the difference in activity of two catalysts is the greater reducibility of the copper ions relative to the cobalt ions as suggested by the authors.

Methyl tertiary-butyl ether (MTBE) is an octane number enhancer as well as an emission reducing agent present in much of the unleaded gasoline today. Improvements
in the catalytic higher alcohol synthesis (production of isobutanol and methanol for downstream synthesis to MTBE) from syn gas are necessary in order for the reaction pathway to become economically viable. A commercially available Zn/Cr spinel catalyst is Engelhard Zn-0312. Epling et al. promoted this commercial catalyst with varying amount of potassium and cesium [91-94]. Their results indicate that a better catalyst for the production of an equimolar mixture of isobutanol and methanol can be achieved by promoting the Zn/Cr spinel by Cs rather than K and Cr, which are found to be unnecessary for higher alcohol syntheses and possibly detrimental. Further, the authors prepared a series of Zn/Cr/ Mn spinel catalysts promoted with Cs and Pd in which some of the Cr atoms have been replaced by Mn and the resulting data indicate that Mn improves the catalytic properties of Cs promoted spinels [95, 96].

Another important reaction catalyzed by oxidic spinels is selective reduction of nitrobenzene to nitrosobenzene, which is an intermediate of various organic syntheses leading to widely used antioxidants. Maltha et al. investigated the active sites of some manganese and cobalt spinels in the selective reduction of nitrobenzene and showed that Mn and Co ions in the octahedral positions are responsible for the catalytic activity [97]. Ziolkowski et al. report that spinels of nominal composition Zn(1-x)Mn xAl2O4, (0 ≤ x ≥ 3) are active, selective and are stable catalysts for the selective reduction of nitrobenzene to nitrosobenzene [98]. A series of mixed cobalt aluminium oxides with spinel structure showed high activity for this reaction and the catalytic activity is related to the concentration of cobalt ions on the catalyst surface [99]. This is in agreement with the operation of the Mars-van Krevelen mechanism.

The production of oxygen gas for many years relied on the electrolysis of water. The heterogeneous decomposition of hydrogen peroxide is a convenient alternative to the electrolysis of water for the production and storage of oxygen gas. Cobalt ferrite (CoFe2O4) catalyzes, the decomposition of hydrogen peroxide to the same extent as expensive noble metal oxides such as silver oxide, platinum and palladium black [100]. The high activity of cobalt-iron spinel oxide system towards the peroxide decomposition was explained by a redox-couple mechanism in which the presence of CoII ion at the
octahedral lattice sites of the cobalt spinel oxide structure initiated a cyclic electron transfer process [100-102].

There are many studies in search of a spinel compound with optimum catalytic activity for the peroxide decomposition. Investigations on the catalytic properties of Co$_2$Fe$_3$O$_4$, Ni$_3$Fe$_3$O$_4$ and Cu$_3$Fe$_3$O$_4$ (0 x 3) in strong alkaline media have shown that the activity follows the order Co > Cu > Ni [101, 103-105]. Attempts on the intrinsic catalytic power of ferrospinels with stoichiometry, $M^{II}$Fe$_2$O$_4$ ($M^{II}$ = Mn, Co, Ni, Cu, Zn and Cd) for hydrogen peroxide decomposition in neutral medium (pH = 6.6) have shown that ferrospinels with $M^{II}$ = Mn and Co are highly active and $M^{II}$ = Ni, Cu, Zn and Cd are moderately active [104]. Senguptha et al. tried the peroxide decomposition over a series of manganese ferrospinels, Mn$_2$.Fe$_3$O$_4$ (0 x 3) and out of which Mn$_{2.5}$Fe$_{0.5}$O$_4$ promises to be a potential cost effective substitute for the noble metal oxides [107].

The Fischer-Tropsch synthesis for the production of hydrocarbons from syn gas has been studied over manganese ferrospinels by Maiti et al. and compared its activity and selectivity compared with pure iron oxides or elemental iron [108]. The mixed iron manganese catalysts with spinel phase results in stable activity. The low concentration of manganese promotes the formation of olefins, whereas high manganese catalysts promote the formation of saturated hydrocarbons. In a recent work Cabet et al. and Tihay et al. investigated the catalytic behaviour of Co-Fe oxides with spinel phase in the hydrogenation of carbon monoxide in the Fischer-Tropsch synthesis and they proved the ability of such catalysts to produce C$_2$-C$_4$ olefins [109, 110].

Nitrogen oxides and soot particulates emitted from diesel engine have been causing serious problems to global environment and human health. Ternary AB$_2$O$_4$ (A = Mg, Co, Cu, Ni and Zn and B = Cr, Fe and Mn) spinel type oxides catalyses the simultaneous removal of NO$_x$ and diesel soot to form carbon dioxide, nitrogen and nitrous oxide and the superiority of spinels to constituent simple metal oxides and their mixture is confirmed [111]. The catalytic performance of the spinels depends significantly on the constituent metal cations and CuFe$_2$O$_4$ is the most excellent system with highest selectivity to nitrogen formation, lowest selectivity to nitrous oxide and provides intermediate ignition temperature of soot [112].
Chlorinated organic compounds are highly toxic for the environment. The catalytic hydrodechlorination of polychlorinated aromatic compounds [1,2,4-trichlorobenzene → benzene] using Ni catalysts with spinel structure is found to be a promising attempt to reduce the environmental pollution [113]. NiAl₂O₄ prepared by the low temperature method catalyze the exhaustive dehydrogenation with no loss in activity, which can occur as a result of the toxicity of the hydrogen chloride produced. Nickel spinel systems are also found to be active catalysts for ozone decomposition reaction to obtain highly reactive atomic oxygen, which is able to oxidize harmful organic compounds at room temperature [114].

1.8 Transport studies

Ferrites attracted the attention of physicists and technologists since they are magnetic semiconductors. Both semiconductors and magnetic materials exhibit interesting properties that could be used in electronic devices. Semiconductors find endless uses in electronic devices while ferrites find application as passive devices in a multitude of devices due to their high electrical resistivity, low eddy current losses and appropriate dielectric loss. They are used nowadays in industry as transformer cores, TV yokes, telephone receivers, loud speakers, permanent magnets and memory devices.

Spinel ferrites, in general are semiconductors with their conductivity values varying between 10² and 10¹¹ ohm⁻¹ cm⁻¹. The conductivity is due to the presence of Fe²⁺ and M³⁺ (M = metals like Co, Ni, etc.). The presence of Fe²⁺ results in n-type and presence of M³⁺ in p-type behaviour. The conductivity arises due to the mobility of extra electron (from Fe³⁺) or the positive hole (M³⁺) through the crystal lattice.

The conduction mechanism in ferrites is quite different from that of semiconductors. In semiconductors the charge carriers occupy states in wide energy band. But the charge carriers in ferrites are localized at the magnetic atoms. In ferrites, the cations are surrounded by close-packed oxygen anions and the electrons associated with particular ion will largely remain isolated. Hence a localized electron model is more appropriate in the case of ferrites rather than the electron band model. Also, in ferrites the temperature dependence of mobility affects the conductivity whereas the carrier concentration is unaffected.
Many models have been suggested to account for the electrical properties in ferrites [115-121]. The factors that differentiate electrical behaviour of ferrites from that of semiconductors, led to hopping electron model [122-124]. The conductivity in these systems is found to be due to the electronic exchange between Fe\(^{2+}\) and Fe\(^{3+}\) ions, distributed on crystallographically equivalent lattice points [125]. Niko’skii [126] has shown that the hopping of electrons between Fe\(^{2+}\) and Fe\(^{3+}\) ions, arranged in non-equivalent points (ie. octahedral and tetrahedral sites) could also play a substantial role in the conduction process. The hopping probability depends upon (i) the separation between the ions involved and (ii) the activation energy. Assuming all the Fe\(^{2+}\) ions in the octahedral sites to participate in the hopping transport, the number of charge carriers \((n)\) works out to be of the order of \(10^{22} \text{ cm}^{-3}\). Since mobility is very low, the conductivity is low, even though \(n\) is large.

The electrical properties of the ferrites are affected by the distribution of cations in the octahedral and tetrahedral sites, preparation conditions, particle size and particle growth effects. The electrical properties of manganese ferrites have been studied by many investigators [127-132]. Among them, Lotgerring [132] has investigated the semiconducting properties of the ferrite system, \(\text{Mn}_{\text{II}}\text{Fe}_{\text{III}}\text{O}_4\) and explained the observation on the basis of Verwey hopping mechanism. A systematic study of the electrical conductivity of manganese magnesium ferrites as a function of composition and temperature has been made by Venugopal \textit{et al.} [133]. They divided the mixed ferrites under study into two groups. The mixed ferrites of group I have a slight excess of cations and show n-type conduction, whilst those of group II have a cation deficiency and show p-type conduction. The mechanism of the electrical conduction is explained in terms of the oxidation of Fe\(^{2+}\) ions by Mn\(^{3+}\) ions on octahedral sites. Perchiik \textit{et al.} [134] suggested a hopping theory for the description of transport phenomena in the case of \(\text{Mn}_{0.4}\text{Mg}_{0.6}\text{Fe}_2\text{O}_4\) in the temperature range 300 to 800 K.

Various research groups evaluated certain important parameters of a semiconductor such as the energy gap, lattice frequencies and activation energies involved in the lattice deformation and compared with those obtained in the case of cobalt and nickel ferrite systems [135-137]. Jonker studied the electrical conductivity of
a series of ferrites $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ and observed two regions of conductivity. One region is of low conductivity containing $\text{Co}^{2+}$ and $\text{Co}^{3+}$ ions and is of p-type semiconduction. The other region was of high conductivity containing $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ and it is the n-type semiconduction. The DC resistivity of a nickel ferrite with composition $\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Fe}_{1.8}\text{Mn}_{0.1}\text{O}_4$ has been measured from room temperature to 300°C by Sinha et al. [138]. It was pointed out that large value of dc resistivity indicates low mobilities and high effective mass for the carriers.

Of late, the chemists are interested in the electrical properties of ferrites for the kinetic and mechanistic studies of various reactions. Narasimhan et al. studied the decomposition of isopropyl alcohol on $\text{MgAl}_{2-x}\text{Fe}_x\text{O}_4$ ($0 \leq x \geq 2$) and correlated the catalytic activity with the electrical conductivity of the systems [85]. Their results showed that there is no correlation between the dehydration activity and electrical conductivity. Thus electrical properties of the catalysts do not seem to play any role in the dehydration reaction. But the dehydrogenation activity varies linearly with activation energy for conduction. The higher the degree of n-type conductivity, the higher is the dehydrogenation activity.

Cares and Hightower supported the Rennard-Kehl mechanism of zero order oxygen dependence on oxidative dehydrogenation of butene to butadiene by the electrical conductivity measurements on cobalt ferrite [90]. Ghorpade et al. prepared a series of $\text{CuCr}_{2-x}\text{Fe}_x\text{O}_4$ ($0 \leq x \geq 2$) and evaluated the electrical conductivity and correlated the activation energy for conduction with the liquid-phase benzene alkylation reaction [139]. The activation energy goes on decreasing as ‘$x$’ increases from 0 to 1 and the decrease in activation energy increases the formation of diphenylmethane. The small magnitude of the activation energy or the energy gap rules out the possibility of holes taking part in the reaction.

In the present investigation manganese ferrospinels of Cr, Co, Ni, Cu and Zn are chosen. The materials are prepared by the soft-chemical route and their electrical properties such as conductivity, carrier mobility and hole effects are correlated to various reactions studied.
1.9 Acid-base properties

Surface acidity and basicity investigations have received considerable attention in recent years, since they play important role in many catalytic reactions. In the case of reactions that have been recognized to be catalyzed by acid sites on a catalyst surface, basic sites also act more or less as active sites in cooperation with acid sites. The catalyst having suitable acid-base pair sites sometimes show pronounced activity, even if the acid-base strength of a bi-functional catalyst is much more weaker than the acid or base strength of simple acid or base. For example, ZrO₂, which is weakly acidic and basic show higher activity for C-H bond cleavage than highly acidic SiO₂-Al₂O₃ or highly basic MgO [140]. A systematic investigation of the activity and selectivity of a catalyst and acid-base property (strength, amount and type) enabled the development of an optimum catalyst with desired acid-base properties for a specific reaction. Development in this area has given rise to numerous methods for exploring these properties.

1.9.1 Surface electron donating properties

The electron donor strength of the metal oxide can be defined as the conversion power of an electron acceptor adsorbed on the surface into its anion radical [141]. The electron donor sites are associated with surface hydroxyl groups and with defect centres involving oxide ions. Study of electron donor properties of metal oxides by the adsorption of electron acceptors of various electron affinity values has been a well established technique. The first work of this type is the one reported by Flockart et al. [142], who investigated the electron donor properties of an alumina surface by the adsorption of tetracyanoethylene (TCNE). Similar studies on single metal oxides and binary metal oxides have also been reported by several other workers [143-148].

If a strong electron acceptor is adsorbed on the metal oxide, its anion radical is formed at strong as well as weak donor sites present on the surface. On the other hand, if a weak electron acceptor is adsorbed, the formation of anion radical is expected only at the strong donor sites. In the case of a very weak electron acceptor adsorption, its anion radical will not be formed even at the strongest donor sites. The electron donating capacity can be expressed as the limiting electron affinity value at which free radical
anion formation is not observed at the metal surface. Thus by comparing the limiting amount of the electron acceptor adsorbed on the catalyst surface and the electron affinity values of the respective electron acceptor used, it is possible to get an insight into the strength and distribution of the electron donor sites on the surface.

A detailed investigation of electron donating sites on oxide surfaces has been carried out by Cordishi et al. [149, 150]. They correlated electron donating sites on the surface with the Lewis basicity. The donor sites is proposed to be a coordinatively unsaturated oxygen ion, \((O^2_{\text{cus}})\) associated with a nearby \(\text{OH}^-\) group, whose proton interacts with the radical anion formed giving stability. Thus Brönsted acidity stabilized the radical ion formed and the active site can be considered as acid-base pair as shown below.

\[
O^2_{\text{cus}} \quad M^{m} \quad \text{OH}^- \quad + \text{A} \quad \text{A}^- \quad \text{H}^+
\]

Meguro et al. reported adsorption of electron acceptors on alumina and according to them surface hydroxyl groups are responsible for the electron donating properties of the oxides [148]. The ionization potential of hydroxyl group is comparatively small (about 2.6 eV in gas phase) [151], and therefore an oxidation-reduction process of the type, \(\text{OH}^- + \text{EA} \rightarrow \text{OH} + \text{EA}^-\), where \(\text{EA}\) is an electron acceptor can be included.

Electron acceptors such as 7,7,8,8-tetracyanoquinidodimethane (TCNQ), 2,5-dichloro-p-benzoquinone (DCQ), \(p\)-dinitrobenzene (PDNB) and \(m\)-dinitrobenzene with electron affinity values 2.84, 2.30, 1.77 and 1.26 eV respectively are extensively used for probing electron donor sites on the surface [141]. Esumi et al. carried out the adsorption of 2,3,5,6-tetrachloro-p-benzoquinone (chloranil) with electron affinity value 2.40 eV from acidic and basic solvents on metal oxides such as alumina and titania. They could successfully correlate the amount of chloranil adsorbed with acid-base interaction at the interface. Meguro et al. studied the adsorption of electron acceptors with electron affinity values from 1.26 to 2.84 eV on the surface of alumina by measuring the adsorption isotherms, esr and electronic spectra [152]. They observed that radical
concentration decreased as the electron affinities of electron acceptors decreased from 2.84 to 1.77 and thus it was noted that the radical concentration formed were directly related to the electron affinity values of the respective electron acceptor employed.

Esumi and coworkers investigated the solvent effects on the acid-base interaction of the electron acceptors (TCNQ and chloranil) with the metal oxide such as alumina and titania [153, 154]. They could see that the amount of electron acceptors adsorbed and the concentration of anion radicals formed decreased with an increase in acid-base interaction between the electron acceptor and the organic solvents used. Drago equation [155] was applied to understand the nature of interaction of different solvents with TCNQ. It was observed that acid-base enthalpy between TCNQ and the organic liquids increased in the order 1,4 dioxane > ethyl acetate > acetonitrile. So the electron acceptor adsorption is greatly depressed by the interaction between TCNQ and acetonitrile.

The effect of calcination temperature on the electron donating property of zirconia was studied by Esumi et al. [156]. An increase of calcination temperature reduces the amount of electron acceptor adsorbed indicating the reduction of OH⁻ on the surface. Above 900°C the amount of adsorbed species again increased due to the formation of surface oxide ions.

Sugunan et al. investigated the electron donor properties of rare earth oxides such as Pr₆O₁₁ [157], CeO₂ [158], Sm₂O₃ [159], La₂O₃ [160] and Nd₂O₃ [161, 162] and their mixed oxides with alumina as a function of composition and activation temperature. It was found that the number of both strong and weak donor sites was increased with increase in calcination temperature. The extent of electron transfer was characterized by magnetic measurements. During adsorption, magnetic moment decreased and reached a limiting value at the same concentration at which the limiting amount of electron acceptor was adsorbed.

1.9.2 Temperature programmed desorption studies

Temperature programmed desorption of basic molecules such as ammonia, pyridine, n-butylamine, etc. is an accepted technique extensively used to characterize the acid strength as well as acid amount on a solid catalyst surface [163-166]. When gaseous
bases are adsorbed on acid sites the one which is adsorbed on a strong acid site is more stable than the one which is adsorbed on a weak acid site and is more hard to desorb. As elevated temperatures stimulate the evacuation of the adsorbed bases from the acid sites, those at weaker sites will be evacuated preferentially. Thus, the proportion of the adsorbed base evacuated at different temperatures can give a measure of acid strength. Also, the amount of gaseous base, which a solid acid can adsorb chemically from the gaseous state can be taken as a measure of the amount of acid sites on its surface. The advantage of TPD method over the other techniques is that it allows the study of the catalyst under conditions more or less similar to that of reaction and that the acid amount for a solid at high temperatures (several hundred degree centigrade) can be determined.

The NH₃-TPD method is widely employed to characterize the acidity of solid catalysts [167-178]. Ammonia is an excellent probe molecule for testing the acidic properties of solid catalysts, because its strong basicity and small molecular size allow the determination of acidic sites of any strength and type [167, 168]. Though ammonia-TPD method is unable to distinguish the type of acid sites (Lewis and Brønsted acidic sites) it gives the total acidity and acidity of solid catalyst at any temperature region. The NH₃-TPD spectra are often poorly resolved and experimental artifacts such as change in the activation treatment and curve deconvolution methods can give insights on site distribution and heat of desorption. Thus, on the basis of complementary characterization results, a fairly reliable interpretation of the NH₃-TPD pattern can be attained [178].

Generally, IR spectroscopy [173, 174], calorimetric [172] and TPD techniques are employed to achieve information on the interaction of NH₃ with solid acids. Kijenski et al. [179] reported that when NH₃ is chemisorbed on a surface having acidic properties, it can interact with acidic protons, electron acceptor sites and hydrogen from neutral or weakly acidic hydroxyls. The NH₃ adsorbed on a surface can be retained either by hydrogen bonding via one of its hydrogen atoms to a surface oxygen atom or oxygen of the hydroxyl group or by the transfer of protons from surface OH to ammonia [180]. These two interactions involve neighbouring anions or OH groups. The strongest interaction is the coordination to an electron deficient atom. The dissociative adsorption
in the form of surface NH$_2$ or NH and OH is also possible. Another mode of interaction is the complete transfer of H$^+$ from Bronsted sites to produce NH$_4^+$. Trombetta et al. made NH$_3$-TPD study on mono and bi-pillared smectites [181]. The desorption of ammonia was run between 373 and 873 K to allow the total evacuation of ammonia molecules. By this technique they work out the total acidity per unit area of montmorillonite and saponite. From the relative amounts of ammonia desorbed at different temperatures (measure of the strength of the adsorbing site), they observed that pillared montmorillonite carry stronger sites than the layer surface, while the reverse is observed for the saponite. In all the samples they observed that majority of NH$_3$ desorbed between 473 and 573 K.

Sato et al. studied the TPD of ammonia adsorbed on cation-exchanged ZSM-5 [182]. The TPD spectrum of ammonia showed two distinct peaks for H-ZSM-5, indicating the existence of strong (a peak at 723 K) and weak (a peak at 463 K) acid sites. Hashimoto et al. describes a method which calculates the density function of activation energy for desorption of ammonia by analyzing the TPD spectrum of ammonia [183].

The heat of adsorption of a base is clearly a measure of the acid strength on a solid surface [164]. Tsutsumi et al. plotted differential heat of adsorption for ammonia on SiO$_2$-Al$_2$O$_3$ and SiO$_2$ against the surface coverage [184]. Heat of adsorption corresponding to acid strength increases with increasing alumina content in SiO$_2$-Al$_2$O$_3$.

Arena et al. made a characterization study of the surface acidity of solid catalysts by temperature programmed desorption of basic probe molecules such as ammonia, pyridine and benzene [178]. According to them, TPD of adsorbed ammonia is a reliable method to feature the strength but not the nature (Lewis and Brønsted) of surface acid sites in solid acid catalysts. Mathematical analysis of NH$_3$-TPD spectra highlights the presence of weak, medium and strong acid sites on all the catalysts and also enables their quantitative estimation. A comparative evaluation of the TPD patterns of ammonia, pyridine and benzene sheds light on the nature (Lewis and Brønsted) of the acidic sites.
1.9.3 Thermogravimetry of desorption of basic molecules

The thermogravimetry (TG) of desorption of basic molecules is an existing method for the estimation of the acid amount together with the acid strength of a solid catalyst [164]. Pyridine has been the most widely used base for the acid characterization purposes, due its interaction with both Brönsted and Lewis acid sites [185-191]. The thermodesorption study of the pyridine adsorbed samples gives the total acid amount on the solid surface. Thus this method supports the results obtained from NH$_3$-TPD method.

Recently, it has been shown that sterically hindered dimethylpyridines can be used successfully to characterize acid surfaces through their chemisorption measurements [190]. The adsorption of 2,6-dimethylpyridine (2,6-DMP) is weaker than that of pyridine, even though the former is a stronger base. This indicates the presence of steric hindrance of methyl groups adjacent to nitrogen atom for the adsorption of methylpyridines [191]. The most important features of these molecules, when compared with pyridine, are their higher basicity (the p$K_a$ is 6.7 for 2,6-DMP and 5.2 for pyridine) and their specificity for protonic centers. In the case of an acid catalyst, fluorinated γ-Al$_2$O$_3$, which contains both Brönsted and Lewis acid sites, pyridine fails in titrating the Brönsted acidity mainly due to the low surface concentration of these sites capable of interacting with pyridine. 2,6-DMP is a more convenient probe molecule for the specific determination of Brönsted acidity [192, 195].

The possibility of determination of Brönsted acidic sites in solid catalysts using 2,6-dimethylpyridine as a probe molecule is established by several authors [189-191, 193, 194]. Satsuma et al. examined the possibility of use of dimethylpyridines (2,6-DMP and 3,5-DMP) as probe molecules on metal oxides for the determination of the acid strengths of Brönsted and Lewis acid sites [196]. From the IR spectra of 2,6-DMP adsorbed on alumina, they showed that 2,6-DMP is held coordinatively on Lewis acid sites at lower temperature. By employing the appropriate purging temperature, 2,6-DMP is eliminated selectively from the Lewis acid sites and selective adsorption of 2,6-DMP on Brönsted acid sites is achieved. It is also demonstrated that the profiles of TPD studies of both 2,6- and 3,5-DMP ensure the measurement of the amount of Brönsted and Lewis acid sites on solid catalysts.
1.9.4 Cyclohexanol decomposition

Alcohols are amphoteric and they interact with both acidic and basic sites. The utility of alcohol decomposition as a test reaction for acid-base property studies of metal oxides is well established [27, 29, 197-202]. It was observed that metal oxides catalyze both dehydration and dehydrogenation of alcohols. Dehydration of alcohol leads to an olefin and dehydrogenation forms an aldehyde (in the case of primary alcohols) or a ketone (in the case of secondary alcohols) and hydrogen. At elevated temperatures, decomposition may involve C-C bond cleavage giving products like CO, CO₂, etc. At near ambient temperatures ether can be a major product.

According to the generally accepted concept, dehydration is an acid catalyzed reaction whereas dehydrogenation, which proceeds by a concerted mechanism, is due to the combined effect of both acidic and basic sites on the system. Thus, dehydration activity gives the direct measure of the acidity of the system, whereas the ratio of the dehydrogenation activity to the dehydration activity gives the basicity of the system [85, 203].

One of the most widely studied alcohol decomposition reaction for the acidity-basicity correlation is the cyclohexanol decomposition. The amphoteric nature of cyclohexanol permits its interaction with both acidic and basic sites. As a result of this, dehydration and dehydrogenation are catalyzed by the oxide systems forming cyclohexanol and cyclohexanone (Fig. 1.5).

Fig. 1.5. Scheme of decomposition of cyclohexanol
Bezouhanava et al. have noticed cyclohexanol decomposition as an easy and reliable method to determine the functionality of metal oxide catalysts [204]. They correlated the dehydrogenation activity to the existence of basic sites originating from the lattice oxygen. Stronger acid sites are needed for dehydration of cyclohexanol compared to other secondary and tertiary alcohols like isopropyl alcohol or tertiary butyl alcohol. The test reaction of cyclohexanol decomposition was done over HZSM-5, HY, SAPO, MAPO molecular sieves and commercial chromite catalysts to characterize their acid-base properties [205].

Rachel et al. have studied the selectivity for dehydrogenation reaction in the decomposition of cyclohexanol as a function of copper loading assisted by the predominantly basic character of ZrO2 in CuO/ZrO2 catalyst [206]. The influence of copper ions in the octahedral sites of spinel catalysts on the transformation of cyclohexanol to cyclohexanone was studied by Jebarathinam et al. also. Their investigation indicates that Cu⁺ at the octahedral sites is more active than Cu⁰ for the dehydrogenation of cyclohexanol [207]. The same authors studied the effect of Zn²⁺ in NiFe₂O₄ matrix on the catalytic decomposition of cyclohexanol. Introduction of Zn²⁺ in NiFe₂O₄ matrix creates strong basic sites and facilitates the dehydrogenation of cyclohexanol to cyclohexanone [208].

Aramendia et al. observed an increase in selectivity towards cyclohexanone in the decomposition reaction of cyclohexanol by doping sodium carbonate in zinc phosphate. Addition of Na₂CO₃ during the synthetic procedure increases the surface basicity of the resultant solids and it enhances the dehydrogenation rate of cyclohexanol [209]. Catalytic decomposition of cyclohexanol over Mgₓ₋ₓZnxAl₂O₄ reported by Joshi and coworkers established the correlation among transport properties, surface acidity and catalytic behaviour [210]. Investigations on alumina by Pines et al. spot out to the formation of methylcyclopentene on stronger acidic sites, which is formed by the isomerization of cyclohexene [211].
1.10 Reactions selected for the present study

(a) Acylation of aromatic compounds

Benzoylation under Friedel-Crafts acylation reactions are important in organic synthesis and provide fundamental and useful method for the preparation of aromatic ketones in chemical industry, which are used in the manufacture of weed killers, dye intermediates, etc. An attempt is made to eliminate the disadvantages of homogeneous catalytic processes by replacing the hazardous homogeneous catalysts such as AlCl₃, TiCl₄, FeCl₃, SnCl₄, etc. by solid acid catalysts. A detailed description of these reactions is given in chapter 4.

(b) Alkylation of aniline and phenol

Alkylation of aniline and phenol are industrially outstanding reactions due to the numerous use of the alkylated products. Alkylation of aniline gives both C-alkylated and N-alkylated products and of these, N-alkylated ones such as N-methylaniline and N,N-dimethylaniline are more synthetically valuable. Alkylation of phenol gives a wide range of products and among them, cresols and xylenols are the most important ones. Chapter 4 deals with a detailed discussion of each type of these reactions.

(c) Phenol hydroxylation

Phenol hydroxylation is one of the industrially important reactions as the products namely catechol and hydroquinone are extensively used as photographic developers, ingredients for food and pharmaceutical applications and antioxidants. This reaction has an added importance for the reduction of phenolic pollutants in the aqueous effluents from industries such as pharmaceutical, chemical, petrochemical, etc. Chapter 5 covers a thorough discussion of this reaction.

(d) Oxidative dehydrogenation of ethylbenzene

Oxidative dehydrogenation of ethylbenzene is an industrially important process for the production of styrene. In chapter 5, we discuss the correlation between acid-base properties of the catalyst and selective formation of styrene from ethylbenzene.
1.11 Objectives of the present work

Mixed metal oxides having spinel structure exhibit interesting structural, electrical, magnetic and catalytic properties. These systems have been found to possess extra stability under various reaction conditions and have sustained activity for longer periods. These spinel oxides are cheap and their preparation method is simple. These attractive features of spinel oxides prompted us to prepare manganese ferrospinels via low temperature co-precipitation method and investigate their catalytic properties for various reactions. The main objectives of the present work can be summarized as follows:

- To prepare manganese ferrospinels containing Cr, Co, Ni, Cu and Zn by low temperature co-precipitation method and characterize these by adopting various physico-chemical methods such as XRD, ICP, BET surface area, DRIFT, TGA, DC conductivity measurements and Hall effect measurements.
- To evaluate the surface basicity using electron acceptors of various electron affinity values.
- To estimate the surface acidity by the temperature programmed desorption of ammonia (NH$_3$-TPD) and by the thermodesorption studies of pyridine and 2,6-dimethylpyridine adsorbed samples.
- To study the vapour-phase cyclohexanol decomposition reaction and to correlate the results with surface acid-base properties.
- To assess the catalytic activity of the samples towards the industrially important reaction, namely Friedel-Crafts benzoylation of aromatic compounds.
- To evaluate the catalytic activity of the systems for aniline and phenol alkylation using methanol as the alkylating agent.
- To study the phenol hydroxylation reaction over all the prepared systems.
- Another important objective of the present work was to evaluate the catalytic activity of the systems for the oxidative dehydrogenation of ethylbenzene and to optimize the process parameters to get the synthetically valuable styrene as the major product.
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