CHAPTER 1

INTRODUCTION

1.1 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 catalyze. The phrase catalysis was coined by Jöns Jakob Berzelius in 1835 who was the first to note that certain chemicals speed up a reaction. Other early chemists involved in catalysis were Alexander Mitscherlich who in 1831 referred to contact processes and Johann Wolfgang Döbereiner who spoke of contact action and whose lighter based on hydrogen and a platinum sponge became a huge commercial success in the 1820's. 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 more well defined areas of industrial catalyst are petroleum, pharmaceutical and environmental catalysis. The petroleum processing catalysts that have aroused the greatest interest and that constituted

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a major advancement when they are first introduced in the 1960s are the molecular sieves or zeolites. Catalysis is a very important process from an industrial point of view since the production of most industrially important chemicals involves catalysis. The earliest commercial processes are the Haber process for ammonia synthesis and the Fischer-Tropsch synthesis. Research into catalysis is a major field in applied science, and involves many fields of chemistry, notably in organometallic chemistry, and physics. 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. Biocatalysis is 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. Examples of homogeneous catalysts are $\text{H}^+$ (aq) which acts as a catalyst in esterification, and chlorine free radicals in the break down of ozone. Chlorine free radicals are formed by the action of ultraviolet radiation on chlorofluorocarbons (CFCs). They react with ozone forming oxygen
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molecules and regenerating chlorine free radicals. The synthesis of fine chemicals and pharmaceuticals generates large amount of waste, 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.

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. Bonds in the substrate become weakened sufficiently for new bonds to be created. The bonds between the products and the catalyst are weaker, so the products are released. The nature of interaction may be chemical or physical process. 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:

- 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.
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- 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.

1.2 Solid acids as catalysts

Solid acid catalysts are appealing since the nature of acid sites is known and their chemical behavior in acid catalyzed reactions can be rationalized by means of existing theories and models. It is possible to modify the acid properties of these materials by adopting various synthesis and post synthesis routes. Solid acid catalysts in many commercial processes have proved to be more economical and often produce better quality products. Being stronger acids, they have a significantly higher catalytic activity compared to conventional acid catalysts and above all they provide clean environment.

1.2.1 Zeolites

A number of reactions that are catalyzed by acids and bases in solution are also catalyzed by solids having acidic and basic properties. The most important catalysts belonging to this class are aluminosilicates. The surface hydroxyl group of a single element, for example, silica or alumina have poor acidic behavior and are of little importance as catalysts. Binary oxides in
which the two elements are in two different oxidation states have good acidic properties and make good catalysts. The catalytic properties of zeolites depend on the pore diameter and the number and strength of acid sites.

1.2.2 Heteropoly acids

Heteropoly acids are solid acid compounds and they offer appealing characteristics as heterogeneous as well as homogeneous catalysts. Various types of heteropoly compounds are known each having its own characteristic structure. Heteropoly acids are highly acidic and the acidity of these compounds is higher than that of well known solid acid catalysts such as alumina-silica and the free acid of the heteroatom. The acid sites of heteropoly acids are found to be Brönsted type.

1.2.3 Mesoporous Materials

These materials have potential applications in the field of catalysis, mainly because of their thermal and hydrothermal stabilities and large surface areas. M41S members are of great utility as materials on which catalytically active phases such as heteropoly acids, transition metal complexes and oxides can be supported. It is possible to generate Brönsted acid sites on the surface of these materials and by the exchange of these protons by alkaline metal ions; one can visualize mild basicity which will be useful for base catalyzed reactions. The acidity of MCM-41 is comparable to that of amorphous silica-alumina, both in number and acid strength distribution. The mild acidity in combination with large pores has been successfully employed for reactions such as Aldol condensation, Friedel-Crafts alkylation etc. The large pores of MCM-41 combined with acidity on the walls are extensively utilized as catalysts for cracking large molecules.
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1.2.4 Transition metal oxides

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, metathesis and water gas shift reaction for the production of hydrogen. Transition metal oxides are known for their redox properties and for their capacity to catalyze oxidation reactions of hydrocarbons\textsuperscript{4,5}. The defect in the form of non-stoichiometry for transition metal oxides or co-ordinatively unsaturated sites are important in surface chemistry, which are mainly responsible for the adsorptive and catalytic properties of transition metal oxides. Due to the formation of the 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\textsuperscript{6-8}.

Transition metal oxides possess acid-base properties. It is well known that the most active homogeneous and heterogeneous catalysts for alkane and alkene oxidation, are those based on transition metals of group 4 (Ti), 5 (V and Nb) and 6 (Mo)\textsuperscript{9-13}. Their efficiency in oxidation reactions depends not only on their redox properties but also on their acid-base properties. Numerous work are reported to correlate the acid-base properties of mixed transition metal oxides with the catalytic activity/selectivity in selective oxidation of hydrocarbons\textsuperscript{14,15}. 

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Titania and zirconia have attracted much attention because they are found to be good supports for metals and in combination with small amount of sulphate, they will change to super acids. Hydrated $\text{Nb}_2\text{O}_5$ and $\text{Ta}_2\text{O}_5$ are making an impact for their application as unusual solid acids and showed excellent stability as a catalyst for esterification, hydrolysis and hydration reactions.$^{16,17}$

Transition metal oxides are efficient systems for the oxidation of CO. A number of transition metal oxide systems such as Cu-Cr-O, Cu-Al-O and Mn-Al-Mg-O have been identified to be active for over a wide range of compositions.$^{18}$

1.3 Spinels

Mixed oxides having the formula $\text{AB}_2\text{O}_4$ are known as spinels where A and B are metal cations with charge +2 and +3 respectively. There are simple spinels and mixed spinels. Mixed metal oxides possessing spinel structure have been investigated by a number of workers as they exhibit interesting structural, electrical and magnetic properties. Mixed metal oxide materials are good alternatives to both zeolites and aluminium phenolate for many alkylation reactions. Individual metal oxides loose their catalytic activity rapidly owing to aging and formation of coke over the catalyst surface. The spinel lattice imparts extra stability to the catalyst under various reaction conditions so that these systems have sustained activities for longer periods. Spinels with B ion as $\text{Fe}^{3+}$ are known as ferrites and those with $\text{Co}^{3+}$ as B ion are known as cobaltites. The spinels chosen for the present study were ferrites and cobaltites. 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 spinels with specific properties.

1.3.1 Methods of Preparation

There are various methods for the preparation of spinels leading to a wide variety of forms: thin and thick films, single crystals and poly crystalline aggregates. For the exact reproducibility of the spinel particles utmost care must be taken during the preparation stages. Minor changes in the preparation method can drastically alter their properties. Small particle size, homogeneous composition, narrow particle size distribution, high purity and dispersed particles are the ideal characteristics of spinel particles.

The oldest method of preparation of spinels is the ceramic method. The precursor compounds are oxides or carbonates of cations in the desired spinel 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 (~1200K) required to complete solid state reactions leads to drastic decrease in surface area of the resulting material by sintering.

Co-precipitation is a very suitable method for the creation of homogeneous catalyst components or for the moulding of the precursors with a definite stoichiometry, which can easily be converted to the active catalyst\(^\text{19}\). This method is based on the stoichiometric mixing of aqueous solutions of chlorides, nitrates or sulphates of divalent and trivalent ions in the concentrations required for the spinel composition and their simultaneous
precipitation in the form of hydroxides by NaOH$^{20,21}$ or NH$_4$OH$^{22,23}$. This is followed by filtration, washing and calcinations of the product to form the oxide. The morphology, the texture, the structure and size of the particles can be accurately controlled by altering the pH of the solution, temperature and nature of the reagents$^{24}$. By this method spinel particles with a narrow size distribution in the range 50-500 nm may be obtained with high purity. Ferrites used in catalytic applications are generally synthesized by low temperature co-precipitation methods$^{25-27}$. Co-precipitation method generates Brönsted acid sites in different cationic environments in addition to the Lewis sites, which makes the catalyst active and effective for many organic transformations.

The method of precipitation from solution under hydrothermal conditions is of current interest and attractive for the direct synthesis of crystalline ceramic particles during the reaction at relatively low temperatures. It has been reported that uniform ferrite particles with controlled size, shape and stoichiometry can be produced by controlling the hydrothermal conditions. Hydrothermal reactions in general are carried out in an autoclave at temperatures between the boiling and critical points of water (100-374 °C) and at elevated pressures (up to 15 MPa). The powder synthesized by this method has excellent homogeneity and particle uniformity. It enables one to synthesize a material at a far lower temperature than those in the conventional solid state reaction methods$^{28}$. Further more, crystalline powders are directly prepared in the hydrothermal treatment; the need for the high temperature treatment as in the sol-gel route and in turn, the resulting aggregation and the subsequent grinding processes are eliminated$^{29}$. In this method the metal sulphates were dissolved in distilled water in a Teflon vessel, then desired
amount of aqueous ammonia (28 wt %) was poured into this solution to control the pH. This mixed solution with the desired concentration was then placed in a stainless steel vessel. After sealing the vessel, it is placed in a thermostated oven, and heated at 150 to 240 °C for 5 to 50 h with constant rotation. The precipitated solid product was separated by centrifuging, washed and then dried in an oven. This hydrothermal method has been used for the synthesis of fine oxide powders and their particle size and morphology are well controlled. So far, considerable progress has been made by employing this solution technique in obtaining spinel oxides for high performance electrode materials.

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 spinels with any desired shape can be prepared by this technique. The process involves the preparation of a sol, which is a dispersion of a solid and 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 transferred to the solid phase by high pressure heating where by the liquid containing in the gel is transformed into supercritical vapours.

Combustion synthesis is a novel method for the preparation of fine spinel particles making use of exothermic redox reaction between metal nitrate and tetraformal triazine or oxalic acid dihydrazine. In this process stoichiometric ratio of nitrates is dissolved in the minimum amount of water in
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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 Ni-Zn and Co spinels.

Spray drying technique of preparation of spinels involves precipitation from a concentrated solution of cations by solvent evaporation. To ensure that the particle remains small, the concentrated solution is atomized at high pressure into fine droplets of 100-500 μm diameter; the solvent is 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 spinel particles\textsuperscript{39-43}. In freeze drying method, the aqueous concentrated solution is atomized into fine droplets, and is 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\textsuperscript{44}. In addition to the above discussed methods, several other methods like pulsed wire discharge\textsuperscript{45}, shock wave synthesis\textsuperscript{46} and sonochemical method\textsuperscript{47} are also applied in spinel synthesis.

1.3.2 Spinel structure

The spinel structure was first determined by Bragg and Nishikawa\textsuperscript{48}. The unit cell of a spinel contains eight formula units and hence can be represented as $8[AB_2O_4]$. The 32 oxygen ions per unit cell form a face centered cubic (fcc) lattice in which two kinds of interstitial are present. In the former the cation is surrounded by four oxygen ions located at the corners of a
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tetrahedron and in the latter by six oxygen ions located at the corners of an octahedron. These are called tetrahedral ($T_d$) and octahedral ($O_h$) sites respectively and are often represented to as A and B sites. There are 64 tetrahedral sites and 32 octahedral sites per unit cell. Of these, 8 tetrahedral holes ($\frac{1}{8}$ of tetrahedral interstices) and 16 octahedral interstices ($\frac{1}{2}$ 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 ($O_h^7$). 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 circles 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.
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The spinel structure is very flexible with respect to the cations it can incorporate; there are over 100 known compounds. In particular, the A and B cations can mix. In other words, the composition with respect to one unit cell can be

- \((A_8)(B_{16})O_{32}\), or
- \(B_8(A_8B_8)O_{32} = B(AB)O_4\) in regular chemical spelling, or
- \((A_{8/3}B_{16/3})(A_{16/3}B_{32/3})O_{32}\)

and so on, with the atoms in the brackets occupying the respective site at random. Few examples: Magnetite-\(Fe^{3+}(Fe^{2+}Fe^{3+})O_4\); Spinel-\(Mg^{2+}(Al^{3+})O_4\); Chromite-\(Ni^{2+}(Cr^{3+})O_4\); Jacobsite-\(Fe^{3+}(Mn^{2+}Fe^{3+})O_4\).

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 sub lattice. 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. Octahedra become smaller and assume 3m symmetry.
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In Table 1.1, interatomic distances are given as a function of the unit cell parameter ‘a’ and the oxygen parameter ‘u’.49,50

Table 1.1 Interatomic distances and site radii in spinels AB₂O₄, as a function of unit cell edge (a) and oxygen parameter (u)

<table>
<thead>
<tr>
<th>Description</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetra-tetra separation A-A</td>
<td>a (3/4)½</td>
</tr>
<tr>
<td>Tetra-octa separation A-B</td>
<td>a (11/8)½</td>
</tr>
<tr>
<td>Octa-octa separation B-B</td>
<td>a (2/4)½</td>
</tr>
<tr>
<td>Tetra-O separation A-O</td>
<td>a [3(u-0.25)]½</td>
</tr>
<tr>
<td>Octa-O separation B-O</td>
<td>a (3u²-2.75u + 43/64)½        a (5/8-u)</td>
</tr>
<tr>
<td>O-O tetrahedral edge O-O</td>
<td>a [2(2u-0.5)]½</td>
</tr>
<tr>
<td>O-O shared octa edge O-O</td>
<td>a [2(1-2u)]½</td>
</tr>
<tr>
<td>O-O unshared octa edge O-O</td>
<td>a [4u²-3u + 11/16]½</td>
</tr>
<tr>
<td>Tetrahedral radius</td>
<td>a [3(u-0.25)]½-R₀</td>
</tr>
<tr>
<td>Octahedral radius</td>
<td>a [3u²-2.75u + 43/64]½-R₀ a (5/8-u)-R₀</td>
</tr>
</tbody>
</table>

u is defined with unit cell origin at an A site and R₀ is the oxide ion radius.

The spinel structure is also interesting because it may contain vacancies as regular part of the crystal. For example, if magnetite is slowly oxidized by lying around a couple of billion years, or when rocks cool, Fe²⁺ will turn into Fe³⁺. If all Fe²⁺ is converted into Fe³⁺, charge balance requires a net formula of Fe₂₁.₆₇O₃₂ per unit cell and this means that 2.33 sites must be vacant - we have what is called a defect spinel. In a way, the composition is now Fe₂₁.₆₇Vac₂.₃₃O₃; having lots of vacancies as an integral part of the structure.
1.3.3 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 $\text{AB}_2\text{O}_4$, where A and B cations occupy the tetrahedral and octahedral sites respectively.

The structure and cation distribution of the spinels have been discussed by Verway and Heilman\textsuperscript{51}. If A denotes a divalent cation and B a trivalent one, the cation distribution is usually indicated as $(\text{A})(\text{B}_2)\text{O}_4$, 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\textsuperscript{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\textsuperscript{7} space group and have point symmetry $D_{3d}$.

Another extreme cation distribution is, $(\text{B})(\text{AB})\text{O}_4$ as pointed out by Barth and Posnjak\textsuperscript{52}. In this case the B cation 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 the spinel configuration is called inverse spinels. Datta and Roy\textsuperscript{53} and Hafner and Laves\textsuperscript{54} have shown that there are many intermediate or random spinels which are in between the pure normal and pure inverse arrangements. They can be represented as $(\text{A}_{(1-x)}\text{B}_x)(\text{A}_x\text{B}_{(2-x)})\text{O}_4$, where $x$ is the degree of inversion, with a
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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 1.2).

Table 1.2 Cation distribution of some of the spinels

<table>
<thead>
<tr>
<th>Spinel</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>(Zn) [Fe₂]</td>
</tr>
<tr>
<td></td>
<td>(Ni) [Cr₂]</td>
</tr>
<tr>
<td>Inverse</td>
<td>(Fe) [NiFe]</td>
</tr>
<tr>
<td></td>
<td>(Co) [NiCo]</td>
</tr>
<tr>
<td></td>
<td>(Fe) [Li₀.₅ Fe₁.₅]</td>
</tr>
<tr>
<td>Random</td>
<td>(Mo₁₋ₓ Feₓ) [MoₓFe₂₋ₓ]</td>
</tr>
<tr>
<td></td>
<td>(Mn₁₋ₓ Feₓ) [MnₓFe₂₋ₓ]</td>
</tr>
<tr>
<td></td>
<td>(Mg₁₋ₓ Feₓ) [MgₓFe₂₋ₓ]</td>
</tr>
</tbody>
</table>

1.3.4 Factors determining cation distribution

Diverse properties of the spinel compounds are derived from the possibility of synthesis of multicomponent spinel by partial substitution of cations in position A and B of spinel structure. Among the spinels, inverse spinels have got special attention due to redox nature of the metal ions and the lack of site preference of cations, which enable them to redistribute between
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octahedral ($O_h$) and tetrahedral ($T_d$) sites during the course of catalytic transformation keeping the spinel structure intact. This accounts for the variety of reactions in which they have been used as catalysts. In these compounds the physical and chemical properties are controlled by the nature of ions, their charge and site distribution among $O_h$ and $T_d$ 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 ions, a tendency towards the inverse arrangement would be expected.

The detailed Madelung energy calculations for spinels\textsuperscript{55} 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 possess a higher Madelung constant. The presence of two kinds of cation on octahedral

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sites in inverse spinels leads to an additional contribution to the Madelung energy. The critical $u$ value then becomes 0.381$^{56}$. Madelung energy is higher for the normal spinel if $u > 0.381$, and the inverse, ordered spinel is more stable for $u < 0.381$.

Romeijn$^{57}$, Adaunitz and Orgel$^{58}$ have first suggested the application of crystal field theory to understand the site preference of cations. McClare$^{59}$ has calculated the octahedral site preference energies of transition metal ions in oxide using crystal field theory and is given in Table 1.3

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 $d^3$ system has the highest octahedral site preference energy. The $d^4$ and $d^9$ ions can be further stabilized by Jahn-Teller distortion. In the regular $O_h$ symmetry, octahedra of surrounding anion is elongated or compressed in the z direction to give $D_{4h}$ symmetry, the doublet ($e_g$) and triplet ($t_{2g}$) levels split$^{60}$. The splitting of the doublet is larger. In the case of elongation, the $d_{z^2}$ orbital is stabilized compared to $d_{x^2-y^2}$ orbital. Fe[CuFe]O$_4$, Mn[ZnMn]O$_4$, and Zn[Mn$_2$]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 the transition metal ions in spinels, only spherically symmetric ions
Table 1.3 Crystal field stabilization energies for transition metal cations on tetrahedral and octahedral spinel sites.

<table>
<thead>
<tr>
<th>Number of d electrons</th>
<th>Theoretical CFSE 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>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn$^{2+}$</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>6</td>
<td>Fe$^{2+}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Co$^{3+}$</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>12</td>
<td>Co$^{2+}$</td>
</tr>
<tr>
<td>8</td>
<td>12</td>
<td>8</td>
<td>Ni$^{2+}$</td>
</tr>
<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>
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(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 counteracting, there can be a completely random arrangement of metal ions among the eight tetrahedral sites and sixteen octahedral sites.

1.3.5 The surface of catalytically active spinels

The surface structure and properties of spinels are of wide interest. The principle 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\textsuperscript{61-63}. The fact that the tetrahedral sites are not active could originate from the stronger metal-oxygen bonds due to the lower valency and coordination number. Moreover, the tetrahedral sites are not accessible to the reactants\textsuperscript{64}. In the literature, usually only the low index spinels are taken into consideration when discussing the surface of spinels\textsuperscript{61,65-67}. Following the suggestion by Knozinger and Ratnasami\textsuperscript{61} 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.
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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 Barboux\textsuperscript{65}, 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 co-workers\textsuperscript{66-68} made an experimental attempt to elucidate the surface structure of spinels using the low energy ion scattering (LEIS) and they support the data that the tetrahedrally coordinated cations are not accessible for the reactant molecules.
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Beaufils and Barbaux\textsuperscript{62,63} investigated the surface composition of normal spinel oxides by differential neutron diffraction (DND) techniques and concluded that the surface of spinel consists of a mixture of (110) and (111) planes.

By comparing the experimental results of DND with some models involving argon-oxygen distances, they observed that these planes contain only octahedral cations and oxygen anions respectively. Jacobs et al.\textsuperscript{64} confirmed this by LEIS technique. By substitution of Mn and Co cations in different sites in the spinel structure of Mn\textsubscript{3}O\textsubscript{4} and Co\textsubscript{3}O\textsubscript{4} 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 almost exposed 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.

The important factors that determine the structural and magnetic properties of spinel ferrites are the cation arrangement in spinel ferrite, the radius of cations, charge and site preference energy. It is well known that the properties of non stoichiometric oxides and/or mixed oxides depend considerably on the degree of non stoichiometry\textsuperscript{69,70}. Recently reported examples of these unusual solids include the non stoichiometric spinel type (NSS) mixed oxides mainly employed as catalysts for hydrogenation reactions\textsuperscript{71}. The specific physicochemical and catalytic properties of NSS solid
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depends on the presence of excess divalent ions and/or ions with unusual co-

Depending upon the nature of the metal ion occupying the B site, there
are different types of spinels-ferrites (Fe in B site), cobaltites (Co in B site),
manganites (Mn in B site), aluminates (Al in B site), chromites, (Cr in B site),
galates (Ga in B site), gadolinites (Gd in B site) etc. Transition metal spinel
oxides are an important class of compounds having large variety of electronic,
magnetic and catalytic properties. Soft ferrites have been actively used for
many kinds of magnetic devices such as transformers, induction and magnetic
heads for high frequency because their electrical resistivity is higher than those
of the soft magnetic alloys. Some spinels are super conductors with a
relatively high transition temperature and some spinel ferrites exhibit magnetic
properties which make them applicable in technology and industry as magnetic
storage devices, microwave devices etc. Ultra fine ferrite particles has been
extensively investigated in recent years because of their potential applications
in high density magnetic recording, magnetic fluids, ferrofluid technology,
magnetocaloric refrigeration, magnetic resonance imaging enhancement,
magnetically guided drug delivery etc.

1.3.6 Spinels as catalysts

Unlike single oxides or their mixture, the single phase spinel type
binary and ternary oxides show, extra stability and exhibit interesting catalytic
properties. These compounds have attracted much attention due to their
remarkable transport, magnetic and electric properties. In these compounds,
the properties are controlled by the nature of ions, their charge and site
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distribution among the tetrahedral \([T_d]\) and octahedral \([O_h]\) sites. In spinel systems containing iron, Fe\(^{3+}\) ion can be easily replaced between \(O_h\) and \(T_d\) sites by stoichiometrically varying the concentration of other cations. This peculiar structural feature enables ferrospinels to withstand even extremely reducing atmospheres\(^{84}\). Another important attribute to these materials, from the commercial standpoint, is that spinel structure provides high stability so that these materials can withstand extremely reducing conditions. Even if reduction of Fe\(^{3+}\) to Fe\(^{2+}\) occurs, spinel structure remains unaltered and upon reoxidation the original structure can be retained.

Spinels containing transition metal ions can act as efficient catalysts in a number of heterogeneous chemical processes such as CO oxidation\(^{85}\), catalytic combustion of hydrocarbons\(^{86}\) or selective oxidation and reduction of several organic molecules\(^{87-89}\). For these applications of metal oxides as heterogeneous catalysts, high surface area and accessible porosity are relevant properties.

Transition metal oxide or mixed oxides have now been established as inexpensive alternatives to precious metal and noble metal containing catalysts\(^{90}\). Copper manganese oxide mixture based on CuMn\(_2\)O\(_4\) is a long established catalyst for the removal of toxic gases and vapour since its discovery in 1920\(^{91}\). These catalysts are still the general choice for respiratory protection in mining industry to remove CO at near ambient temperatures. Moreover, these spinel catalysts are very effective catalysts at elevated temperatures of 200-500 °C for combustion of over 35 organic compounds and nitrogen containing compounds\(^{92}\). Transition metal oxides like hamatite can be converted to spinel ferrite by adding Zn, Mg, Ni or Co to it, and can be
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used for the oxidative dehydrogenation of hydrocarbons\textsuperscript{93}, for transformation of butane\textsuperscript{94-96} and ethyl benzene\textsuperscript{97}.

For reactions such as 1-butene oxidative dehydrogenation, the catalytic activity of a ferrite strongly depends on the cation distribution in lattice\textsuperscript{98,99}. For instance; MgFe\textsubscript{2}O\textsubscript{4}, which has an inverted spinel structure, is having higher catalytic activity than the one of stoichiometric ZnFe\textsubscript{2}O\textsubscript{4} ferrite, whose crystalline structure is not inverted\textsuperscript{100}. These results suggest that the distribution of iron in the tetrahedral and octahedral sites of a ferrite could determine their catalytic activity.

Spinels have been conveniently used as catalysts for a variety of industrially important reactions. They can effectively replace conventional Friedel and Crafts catalysts for many aromatic alkylation reactions, for the production of aromatic alkyl derivatives is un-economic and acid-waste makes the process non-economic. The increasing demands of environmental legislation have been prompting the chemical industry to minimize or preferably eliminate waste production in chemical manufacture. Solid acid catalysts are very important alternatives to the above. The global demand of solid acid and solid base catalysts has increased considerably in recent years since such systems often give value added products with improved yield without creating major burdens on the environment. Among the various solid acid catalysts, the oxides and mixed oxides\textsuperscript{101-103} are the best for the alkylation reactions. Although there are a number of catalysts like Th/Al oxides, Fe-Si-Mg oxides, phosphoric acid, SiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, magnetite, hydrotalcite, Al\textsubscript{2}O\textsubscript{3} oxides\textsuperscript{103,104-106}, these catalysts possess one or more of the drawbacks such as low conversion, severe operative conditions, poor selectivity due to

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number of side products and lack of reproducibility. Recently Rao and co-workers established the idea of using spinels for aromatic C and/or N methylation of compounds like pyridine, aniline, phenol etc. It is to be noted that Fe$_2$O$_3$ in combination with other oxides such as CdO, SnO$_2$, CeO$_2$, NiO, CoO, Cr$_2$O$_3$ and ZrO$_2$ are highly active for the alkylation reactions. Diverse properties of the spinel compounds are derived from the possibility of synthesis of multi-compound spinel by partial substitution of cations in position A and B.

Spinel oxides, having cation distribution in two crystallographic environments, are reported to be more active for the dehydrogenation of hydrocarbons, isopropyl alcohol and cyclohexanol. Ferrites are very much effective for many of those reactions as mentioned above. 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. Another important attribute of these materials, from commercial standpoint, is their stability under extremely reducing conditions, which is due to the spinel structure. Thus the reduction of Fe$^{+3}$ to Fe$^{+2}$ takes place without altering these lattice configurations so that upon reoxidation, the original state is retained. In contrast to the spinel ferrites, the catalyst Fe$_2$O$_3$ loses its activity as it is reduced to FeO and metallic iron.

Recent studies on spinels show that they can be used as supports for homogeneous catalysts. Spinels like ZnAl$_2$O$_4$ which have high thermal stability, high mechanical resistance, or inertness to water vapour make it an attractive material both as a catalyst as well as a carrier for active metal to substitute for the more traditional systems. Rhodium complexes supported
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on ZnAl$_2$O$_4$ are reported to be good catalysts for the hydroformylation and hydrogenation$^{123}$. Not only this, certain organic transformations can be carried out over spinels. Anisole can be transformed into other industrially important derivatives using ZnAl$_2$O$_4$ and Fe$_2$O$_3$/ZnAl$_2$O$_4$.$^{123}$ ZnAl$_2$O$_4$ has been shown to be active for the synthesis of styrene from acetophenones$^{124}$ or for the double bond isomerization process of alkenes$^{125}$. It is also promising support for catalysts such as Pt$^{126}$ or Pt/Sn$^{127}$ (dehydrogenation process), and Cu$^{128}$ (low pressure synthesis of methanol) and in the synthesis of compounds like indenes from indanones$^{129}$.

Spinels play important role in the production of fuels. Fuel production in effective and economical route is one of the problems faced by world today. In the last two decades, methanol decomposition into CO and H$_2$ is considered as a promising way to produce an effective and ecological fuel for vehicles, gas turbines and fuel cells.$^{130,131}$ Catalysts with high activity, selectivity and stability under lower temperatures are needed but the problem is not solved enough. Recently Manova et al.$^{132}$ reported their study on nano dimensional iron-cobalt spinel oxides as catalysts for methanol decomposition. A significant methanol conversion with H$_2$ and CO being the main products is registered for the above spinel just above 500-580K. The heterogeneous decomposition of H$_2$O$_2$, though a convenient alternative to the electolysis of water for the production and storage of O$_2$ gas needs a cost effective and high performance catalyst. The selectivity of the H$_2$O$_2$ decomposition catalysts has proved difficult as the suitable ones, silver oxide, Pt and Pd blacks are expensive. Among the inexpensive corrosion resistant catalysts$^{133-140}$, the
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Binary ferrospinels seem to be potential alternatives to the noble metal catalysts. Chemical composition, crystal structure and microstructural factors have been found to contribute to the overall activity of the catalysts\textsuperscript{137}. Cobalt ferrite catalyses the decomposition of H\textsubscript{2}O\textsubscript{2} to the same extent as the noble metal catalysts\textsuperscript{133}. Sengupta and Lahiri reported their study on manganese ferrospinel systems for H\textsubscript{2}O\textsubscript{2} decomposition and these are promises to be a potential cost effective substitute for the noble metal catalysts.

The production of isobutanol and metahanol from syn gas (CO and H\textsubscript{2}) feed stream has received considerable attention recent years. Types of higher alcohol synthesis (HAS) catalysts include modified Fischer-Tropsch and methanol synthesis catalyst. These types of catalysts typically are composed of a Zn/Cr spinel structure which is promoted with Cs or K\textsuperscript{141-146}, and the addition of Cs usually results in better catalysts. Epling et al. reported the production of isobutyl alcohol and methanol from syngas using K and Pd promoted Zn/Cr/Mn spinel\textsuperscript{147-149}.

Alkylation of benzene and substituted benzenes are attracting special attention since the products obtained from these reactions find application in a number of fields such as agrochemicals, pharmaceuticals, pesticides, herbicides, plastics, special grade paints and in the manufacture of a variety of chemicals. Conventional Friedel-Crafts catalysts can be effectively replaced by spinels. Rao et al. conducted a number of studies on the alkylation reactions of phenol, aniline etc\textsuperscript{150-156}. They have employed ferrospinel based on copper and cobalt, Cu\textsubscript{1-x}Co\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4}, and showed an excellent performance towards phenol methylation both in terms of conversion and ortho selectivity.
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The catalytic effectiveness of these systems is due to the ability of the metallic ions to migrate between the sub lattices without altering the structure, which makes the catalyst efficient for many organic transformation reactions. These spinel oxide materials are good alternatives to both zeolites and aluminium phosphate for selective o-alkylation using olefins and alcohols\textsuperscript{157}. Many ferrospinels based on Cu, Co, Cr, Mn and Zn are proved to be highly active for the production of N-methyl aniline, N, N-dimethyl aniline, 2,6-xylenol etc. by the methylation of aniline and phenol\textsuperscript{155,156,158-160}. Sugunan et al. also reported the benzoylation of benzene using benzyl chloride catalyzed by ferrospinels\textsuperscript{161,162}.

Styrene production and styrene oxidation can be conveniently carried out by spinels. The catalytic dehydrogenation of ethyl benzene is of industrial importance in the manufacture of styrene as it is extensively used as an intermediate in the manufacture of polystyrene. Spinels such as MgFe$_2$O$_4$ and ZnFe$_2$O$_4$ are reported as highly active catalysts for the oxidation of styrene to bezaldehyde\textsuperscript{163-166}.

The reduction of NO$_x$ emission from automobile exhaust and removal of N$_2$O and CO remains a challenging problem to both academic and automobile industry. Because of the inefficiency of the conventional three way catalyst in converting NO under lean burn conditions, the selective catalytic reduction of NO with hydrocarbons is believed to be a promising alternative to eliminate NO. Recently spinels, mainly cobalt spinels are introduced for the removal of NO$_x$\textsuperscript{167,168}. The cobalt oxide spinel Co$_3$O$_4$ is one receiving considerable interest. Yan et al. reported spinel oxide with partial replacement of Co$^{2+}$ by Zn$^{2+}$ in Co$_3$O$_4$ which are highly active for N$_2$O.
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decomposition into N₂ and O₂. Magnesium cobaltite spinels prepared by hydrothermal method shows excellent catalytic activity for N₂O decomposition.

Copper Manganese oxide mixture based on CuMn₂O₄ is a long established catalyst for the removal of toxic gases and vapours. These catalysts are still the general choice for respiratory protection in mining industry to remove CO at near ambient temperatures. Spinels like NiMn₂O₄ and CuCo₂O₄ show high activity in the catalytic CO oxidation.

Photocatalysis is the important field where spinels find immense application. Spinels as such or in the composite form are used for the production of H₂ and for the degradation of environmentally pollutant organic chemicals. Hydrogen gas is an important chemical feedstock and is highly valued as a nonpolluting renewable fuel, its production from cheap raw materials like water has been actively studied and is currently a subject of much interest. Suspension of CuMn₂O₄ or ZnMn₂O₄ in aqueous solutions containing S²⁻/SO₃²⁻ will generate hydrogen photochemically. Their narrow energy band gap and relative inertness toward photo corrosion make them attractive materials in photoelectrocatalytic systems. Solid solutions such as Zn₁₋ₓNiₓMn₂O₄ and ZnFe₂O₄ used to convert H₂S wastes to less harmful products namely polysulfides with a gain of storable form of power (hydrogen). The spinel with a relatively small band gap, especially nanometer sized ZnFe₂O₄, is a potentially useful solar energy material for photocatalytic conversion and photochemical hydrogen production from water, whose advantages are to absorb visible light and to not be sensitive to photoanodic corrosion. Nanocomposites of ZnFe₂O₄ and TiO₂
with useful characteristics making them suitable for far reaching applications in photocatalysis. ZnFe$_2$O$_4$/TiO$_2$ nanocomposite is a more effective photocatalyst for the photodegradation of phenol than TiO$_2$ alone\textsuperscript{170}. Application of these nanocomposites for the photocatalytic decomposition of phenol gives an increased photocatalytic activity relative to TiO$_2$ only nanomaterials. These nanocomposites are promising solar energy materials for applications in photocatalysis as well as in photo electrochemical conversion.

1.4 Acid-base properties

Surface acidity and basicity investigations have received considerable attention in recent years because they can provide significant information in determining the behaviour of solid surfaces. Determination of strength of acid sites exposed on the solid surface as well as their distribution is a necessary requirement to understand the catalytic properties of acidic solids. The conversion and selectivity of a reaction are influenced not only by the nature of the acidic sites but also by their number and their strength. A variety of physico-chemical methods have been developed and widely applied to evaluate the structure and the amount of surface acid sites on catalysts, and a large variety of probe molecules have been utilized to both qualitatively ascertain in the acidity and provide a measure of the number of these acid sites. Some of the physico-chemical methods used to characterize acid sites are amine, pyridine and ammonia titrations, potentiometric titrations, spectroscopic investigations, thermal desorption and gravimetric desorption measurements. They differ from each other in their physical and chemical principles and this makes it difficult to compare the acidic results. The
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temperature programmed desorption method is most promising, facilitating the direct determination of the distribution of the strength of the acidic sites. Basic sites were characterized by using electron acceptors which will accept electrons from basic sites. Cyclohexanol decomposition and cumene cracking were the test reactions suggested to get a qualitative idea about the acid-base properties. Acidity and basicity depend on the nature of the oxide and on the charge and radius of the metal ions. Other factors influencing the character of metal – oxygen bond are the co-ordination number, the filling of the d orbitals and the nature of other ligands.

1.4.1 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. The electron donor sites are associated with surface hydroxyl groups and with defect centers 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 electron donor properties of alumina surface have been investigated by Flockart et al., by the adsorption of tetracyano ethylene.

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.

Cordishi et al.\textsuperscript{178,179} have correlated the electron donating sites on the surface with Lewis basicity. The donor site is proposed to be a coordinatively unsaturated oxygen ion, $\text{O}^{2-}_{\text{cus}}$ 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.

Surface electron donating properties have been studied by various electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,5-dichloro-$p$-benzoquinone (DCQ), $p$-dintrobenzene (PDNB) and $m$-dinitrobenzene with electron affinity values 2.84, 2.30, 1.77 and 1.26 eV respectively\textsuperscript{180}. Adsorption study of 2,3,5,6-tetrachloro-$p$-benzoquinone (chloranil) with electron affinity of 2.40 eV from acidic and basic solvents on alumina and titania have been carried out by Esumi et al. and they correlated the amount of chloranil adsorbed with the acid-base interaction at the interface. By measuring the electronic spectra, esr and adsorption isotherms,
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Meguro et al.\textsuperscript{181} have studied the adsorption of electron acceptors with electron affinity values from 1.26 to 2.84 eV on the surface of alumina. Radical concentration formed were found to be directly related to the electron affinity values of the respective electron acceptor adsorbed since the radical concentration decreased as the electron affinities of electron acceptors decreased from 2.84 to 1.77.

It was found that the calcination temperature has an effect on the electron donating property of metal oxide as shown by the studies on zirconia by Esumi et al.\textsuperscript{182}. An increase of calcination temperature reduces the amount of electron acceptor adsorbed indicating the reduction of OH\textsuperscript{-} on the surface. Above 900 °C the amount of adsorbed species again increased due to the formation of surface oxide ions.

Solvent effects on the acid-base interactions of the electron acceptors (TCNQ and chloranil) with the metal oxides such as alumina and titania have been investigated by Esumi and co-workers\textsuperscript{183,184}. They observed 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. Using Drago equation\textsuperscript{185}, 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.

Sugunan et al. investigated the electron donor properties of rare earth oxides such as Pr\textsubscript{6}O\textsubscript{11}\textsuperscript{186}, CeO\textsubscript{2}\textsuperscript{187}, Sm\textsubscript{2}O\textsubscript{3}\textsuperscript{188}, La\textsubscript{2}O\textsubscript{3}\textsuperscript{189} and Nd\textsubscript{2}O\textsubscript{3}\textsuperscript{190,191} and
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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 is 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.

1.4.2 Temperature programmed desorption studies

Temperature programmed desorption of basic molecules such as ammonia, pyridine, n-butylamine etc. is an accepted technique used to characterize the acid strength as well as acid amount on a solid catalyst surface\(^{192,193}\). 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 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 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 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 higher temperatures (several hundred degree centigrade) can be determined.

The \(\text{NH}_3\)-TPD method is widely employed to characterize the acidity of solid catalysts\(^{194,195}\). Ammonia is an excellent probe molecule for testing
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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\textsuperscript{194,195}. Though ammonia TPD method is unable to distinguish the type of acid sites (Lewis and Brönsted acidic sites), it gives the total acidity and acidity of solid catalyst at any temperature region. The NH\textsubscript{3}-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 NH\textsubscript{3}-TPD pattern can be attained\textsuperscript{196}.

Information on the interaction of ammonia with solid acids can be generally achieved by IR spectroscopy\textsuperscript{197}, calorimetric\textsuperscript{198} and TPD techniques. When ammonia is chemisorbed on acidic surfaces, it can interact with acidic protons, electron acceptor sites and hydrogen from neutral or weakly acidic hydroxyls\textsuperscript{199}. The ammonia 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\textsuperscript{200}. 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\textsubscript{2} or NH and OH is also possible. Another mode of interaction is the complete transfer of H\textsuperscript{+} from Brönsted sites to produce NH\textsubscript{4}\textsuperscript{+}.

By analyzing the TPD spectrum of ammonia it is possible to calculate the density function of activation energy for desorption of ammonia as described by Hashimoto et al.\textsuperscript{201}. Sato et al. studied the TPD of ammonia
adsorbed on cation-exchanged ZSM-5\textsuperscript{202}. 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. The heat of adsorption of a base is clearly a measure of the acid strength on a solid surface\textsuperscript{192}. Tsutsumi et al. plotted differential heat of adsorption for ammonia on SiO$_2$-Al$_2$O$_3$ and SiO$_2$ against the surface coverage\textsuperscript{203}. 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 TPD of basic probe molecules such as ammonia, pyridine and benzene\textsuperscript{196}. According to them, TPD of adsorbed ammonia is a reliable method to feature the strength but not the nature (Lewis and Brönsted) 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 shed light on the nature (Lewis and Brönsted) of the acid sites.

1.4.3 Cyclohexanol decomposition

Alcohol decomposition reaction has been widely studied because it is a simple model reaction to determine the functionality of an oxide catalyst, to be chosen for industrial process. Decomposition of isopropanol and cyclohexanol (CHOL) are the most widely studied reactions in this category. 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
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Studies of metal oxides is well established. Dehydration of an alcohol leads to an olefine 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, CO$_2$ etc. At near ambient temperatures ether can be a major product.

Dehydration activity is linked to the acidic property and dehydrogenation activity to the combined effects of both acidic and basic properties of the catalyst. Thus dehydrogenation activity gives the direct measure of the acidity of the system, where as the ratio of the dehydrogenation activity to the dehydration activity gives the basicity of the system. Decomposition of alcohols is one among the many classes of reactions catalyzed by oxidic spinels. Studies on the decomposition of isopropanol, benzyl alcohol, and CHOL by spinel oxides have been reported.

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 cyclohexene and cyclohexanone.

Jebarathinam et al. studied the transformation of cyclohexanol to cyclohexanone over the spinel catalysts to investigate the influence of copper ions in the octahedral sites. Their observation indicates that Cu$^+$ at the octahedral sites is more active than Cu$^0$ for the dehydrogenation of cyclohexanol. They have also studied the effect of Zn$^{2+}$ substitution on NiFe$_2$O$_4$ for the decomposition of cyclohexanol. Introduction of Zn$^{2+}$ ions...
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into the NiFe$_2$O$_4$ matrix has facilitated the dehydrogenation of cyclohexanol to cyclohexanone by creating strong basic sites. Joshi et al. studied the catalytic decomposition of cyclohexanol over Mg$_{1-x}$Zn$_x$Al$_2$O$_4$ and established correlation among transport properties, surface acidity and catalytic behaviour$^{212}$.

According to Bezouhanava et al., decomposition of cyclohexanol is a reliable method to determine the functionality of metal oxide catalysts$^{211}$. 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 or tertiary butyl alcohol. On stronger acid sites, formation of methyl cyclopentane, which is formed by the isomerization of cyclohexene, has been observed over alumina catalyst by Pines et al$^{213}$.

1.4.4 Cumene cracking

Catalytic cracking uses a solid acid catalyst and moderately high temperatures to aid the process of breaking down large hydrocarbon molecules into smaller ones. Cumene cracking reaction is generally used as a test reaction to get a qualitative idea about the Lewis and Brønsted acid sites. The cracking of alkyl aromatic compounds is a very specific reaction. Cumene is a conventional model compound for testing the catalytic acidity since it undergoes different reactions over different type of acid sites. $\alpha$-methyl styrene and benzene are the major products of the reaction where as toluene, ethyl benzene and styrene are grouped into minor products.
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The major reactions occurring during cumene conversion may be grouped into dealkylation (cracking) and dehydrogenation. Another possibility is the cracking of the alkyl chain to give ethyl benzene which on dehydrogenation gives styrene. Cracking of cumene to benzene is generally attributed to the action of Brönsted sites by a carbonium ion mechanism\textsuperscript{214,215}. Dehydrogenation of cumene yields α-methyl styrene as the major product, the formation of which has been ascribed to the Lewis acid sites\textsuperscript{214}. Boorman et al. prepared a series of catalysts containing fluoride, cobalt and molybdenum as additives to γ-alumina, both individually and in combination. The surface acidity of these systems was correlated with their reactivity for cumene conversion\textsuperscript{216,217}. Sohn and Jang\textsuperscript{218} correlated the activity for cumene dealkylation with both acidity and acid strength distribution of sulphated ZrO\textsubscript{2}-SiO\textsubscript{2} catalysts.

1.5 Reactions selected for the present study

(a) Alkylation reactions

Alkylation is the transfer of an alkyl group from one molecule to another. The alkyl group may be transferred as an alkyl carbocation, a free radical or a carbanion. It is one of the most important research targets in organic chemistry. Alkylation is accomplished by using the functional groups as alkyl electrophile, alkyl nucleophile or sometimes as alkyl radical. In this work we have discussed the alkylation reactions of aniline, phenol and m-cresol. The alkylating agents used were methanol, tert-butyl alcohol and isopropyl alcohol. The reactions were conducted in vapour phase. Alkylation of aniline and phenols are
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industrially outstanding reactions due to the numerous uses of the alkylated products. Alkylation of aniline gives both C-alkylated and N-alkylated products and of these, N-alkylated ones such as N-methyl aniline and N,N-dimethyl aniline are synthetically more valuable. Alkylation of phenols gives a wide range of products and among them cresols, xylenols, thymol, tertiary butyl derivatives are the most important ones. A detailed description of these reactions has been given in chapter 4.

(b) Oxidation Reactions

The activation and functionalization of paraffins is one of the world wide pursuit research directions with a high potential for the development of new catalytic process technologies. The selective oxidation of hydrocarbons, which requires activation of the relatively inert carbon-hydrogen bond, is an important commercial reaction for functionalizing hydrocarbons to yield products that are important themselves or as intermediates for other chemicals. The reactions selected for the present study were styrene oxidation, cyclohexane oxidation and benzyl alcohol oxidation using hydrogen peroxide as the oxidizing agent. The products of these reactions namely benzaldehyde, cyclohexanol and cyclohexanone have numerous applications in industry. The oxidation reactions were conducted in liquid phase. These reactions are discussed in chapter 5.

1.6 Objectives of the present work

The main objectives of the present work can be summarized as follows:
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➢ To prepare ferrospinels and cobaltite spinels by co-precipitation method. The prepared spinels were nickel ferrites, copper cobaltites and nickel cobaltites. Ferrites were prepared by low temperature co-precipitation method whereas cobaltites were prepared by high temperature co-precipitation method using NaOH.

➢ To improve the surface and electronic properties of spinels by incorporating various ions and by changing the stoichiometry of ions. Ferrospinels were modified by replacing iron by chromium and gadolinium. Cobaltite spinels were modified by changing the stoichiometry of nickel, copper and cobalt.

➢ Characterization of the prepared spinels by various methods such as XRD, DRIFT, TG, BET surface area, SEM, EDAX, Mössbauer spectroscopy etc.

➢ To evaluate the surface basicity using electron acceptors of various electron affinity values.

➢ To determine the total acidity by the temperature programmed desorption of ammonia (NH₃-TPD) and qualitative estimation of acidity by IR studies of pyridine adsorbed samples.

➢ To evaluate the Lewis acidity by perylene adsorption studies.

➢ To study the cyclohexanol decomposition reaction and cumene cracking reaction and to correlate the results with the surface acid-base properties.

➢ To study the catalytic activity of the prepared spinels towards industrially important reactions which include various alkylation and oxidation reactions.
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