

**SURFACE ELECTRON DONATING PROPERTIES
AND CATALYTIC ACTIVITY OF FERROSPINELS
CONTAINING Co, Zn AND Ni**

THESIS SUBMITTED TO THE
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

IN THE FACULTY OF SCIENCE

BY

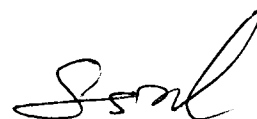
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CERTIFICATE

This is to certify that the thesis herewith is an authentic record of research work carried out by the author under my supervision, in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.



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PREFACE

Binary and ternary oxides possessing spinel structure have attracted much attention due to their remarkable transport, magnetic and catalytic properties. Spinel oxides containing iron are called ferrospinels. Simple ferrospinels, $A^{II}B_2O_4$, as well as mixed ferrospinels of the general formula $A^{II}B^{III}Fe_2O_4$ are known. The catalytic effectiveness of ferrites for many reactions arises because of the ease with which iron can change oxidation state between 2 and 3. However, the most important property of these materials is their stability to withstand under extremely reducing conditions. Thus the reduction of Fe^{3+} to Fe^{2+} takes place without altering the lattice configurations so that upon reoxidation the original state can be regained.

Ferrites are generally produced by the conventional ceramic processes involving high temperature (≥ 1200 °C) solid state reaction between the constituent oxides or carbonates. This method provides non-homogeneous, coarser ferrite particles with very low surface areas; thus the material does not match with the properties essentially required for a good catalyst. Recently reported, low temperature controlled co-precipitation methods have overcome these drawbacks and produced homogeneous, fine and reproducible ferrite powders with significantly high surface areas.

This work is oriented to evaluate the catalytic activities of ferrospinels containing Zn, Co and Ni prepared via low temperature route. The major reactions carried out were methylation of aniline and phenol, oxidative dehydrogenation of ethyl benzene to styrene and alcohol decomposition. Various physico-chemical methods have been adopted for the characterization of the systems.

The last chapter of the thesis summarises the general conclusions drawn by us from the results presented in the earlier chapters. These materials offer interesting opportunities as potential catalysts in alkylating both aniline and phenol. There is plenty of scope for further research in this field for alkylating various substituted phenols and anilines, and also various heterocyclic compounds.

CHAPTER I

INTRODUCTION & LITERATURE SURVEY

1.0 INTRODUCTION

Catalyst development and synthesis have become a wide spread research field because of the increasing global demand for better systems in chemical industry. Today, the chemical industry has been blamed for producing environmentally hazardous substances, which cause acid rain, a reduction of stratospheric ozone levels and so on. Many industrial processes have become a burden on the environment, and, therefore, must be essentially replaced by more eco-friendly or compatible processes. In addition to this, disposing of by-products or converting them into environmentally nonhazardous substances consume much energy. The successful exploitation of a material as a catalyst will give value-added products with improved yields and also eliminate or minimize environmental pollutants.

The two catalyst systems, homogeneous and heterogeneous, have been implemented widely in chemical industries. Although, well known homogeneous catalytic systems such as ‘Wacker’ and ‘oxo’ processes have been successfully used on an industrial scale, there are ever increasing problems associated with these catalytic reactions. Homogeneous systems often perform better selectivity, activity and reproducibility, however, they are more vulnerable to extraneous materials. Low thermal stability and shorter catalyst life-time amplify the cost of production. Synthesis of new heterogeneous systems to replace the existing homogeneous systems has become a challenging task in the catalytic field.

1.1 HETEROGENEOUS CATALYSIS

The field of heterogeneous catalysis is one of the most rapidly expanding fields of chemistry. The world market for heterogeneous catalysts is expected to reach highest peak in the coming years. Here reactants and catalysts are present in different phases. Commonly, the catalyst is a solid, and the reactants are either gases or liquids. Chemisorption of the substrates on the surface of the catalyst is the first step in heterogeneous catalysis, which is followed by the reaction of the chemisorbed molecules and the diffusion of the products away from the active sites of the catalyst. The main advantage of the heterogeneous catalytic process is that it can be operated

continuously in a reactor without interruption. Since the catalyst is present in a phase different from the reactants and the products, the separation of the catalyst from the final reaction mass is also quite easy.

A commercial catalyst should be stable, active and selective. Sufficiently high surface area, good porosity and stable mechanical strength are essential for an effective heterogeneous catalyst. The properties of a heterogeneous catalyst for industrial use can be classified broadly into two [1]:

1. Properties which determine directly catalytic activity and selectivity: Here factors such as bulk and surface chemical composition, local microstructure and phase composition are important.
2. Properties which ensure their successful implementation in the catalytic process: Here thermal, mechanical and chemical stability, porosity, shape and dimension of catalyst particle enter.

Experiments show that in the majority of cases the chemical composition of the principal component of a catalyst exerts considerably greater influence on its catalytic activity than the method of preparation.

Heterogeneous catalysts are classified into several ways. Based on their physico-chemical nature they can be classified as follows:

1. Metal oxides: Simple metal oxides, mixed metal oxides, supported metal oxides, modified metal oxides.
2. Supported metals / bimetallic catalysts.
3. Zeolites / molecular sieves.
4. Clays and hydrotalcites.
5. Solid supported heteropoly acids.

A wide range of reactions can be catalysed by heterogeneous systems. However, heterogeneous based reactions can be separated mainly into two types[2].

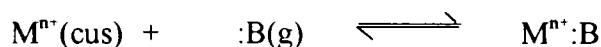
1. Oxidation-reduction (electronic): Reactions pertaining to this type are those of oxidation, reduction, hydrogenation, dehydrogenation, decomposition of unstable oxygen containing compounds and others. The reactions are catalyzed by solids possessing free or easily excited electrons *i.e.* metals and semiconductors. The mechanism of these reactions is a characteristic transfer of electron in an elementary act of catalysis from the catalyst to the reacting substance or vice versa.

2. Acid-base (ionic): Catalytic cracking, hydration, dehydration, hydrolysis, many reactions of isomerization, and a series of other reactions pertaining to this type. Such reactions are accelerated under the influence of acid or base. For this type of reactions the elementary act is the characteristic transfer of proton or the production of heteropolar donor-acceptor pair. Acid-base property of a heterogeneous surface is the important factor in determining the catalytic efficiencies for these type of reactions. Many chemical reactions are initiated by acid-base interactions followed by catalytic cycles. In acid catalyzed reactions, reactants act as bases toward catalysts which act as acids. On the other hand in a base catalyzed reaction reactants act as acids toward catalysts which act as bases.

1.1.1 Solid acid-base concept in heterogeneous catalysis:

A large number of solids have surface acidic and /or basic properties. Many materials possess inherent acid-base centers. Activity and selectivity of these systems for particular reactions depend predominantly on the strength and distributions of the acid-base centers. The inherent acid-base properties can be further improved by adopting some surface modification techniques and also by adopting proper synthesis/post-synthesis treatments. These solid acids and bases have usually been employed as catalysts on various acid-base catalyzed reactions. Surface hydroxyl groups and coordinatively unsaturated metal cations and oxygen anions are responsible for the surface acidity and basicity on a partially hydroxylated oxide surface. Exposed

coordinatively unsaturated (cus) cations may act as acceptors for free electron pairs of adsorbed molecules.

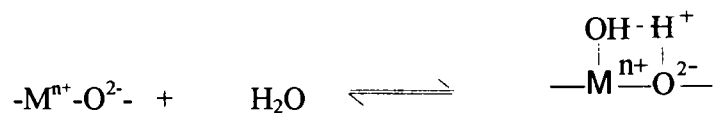


Such cations are Lewis acid sites. The strength of these acid sites depends on the charge and size of the cations. According to the concept of hard and soft acids, cations of a higher oxidation states are harder.

Surface hydroxyl groups may act as Brønsted acid sites. They may dissociate to protonate adsorbed bases:



The resulting conjugate acids and bases are stabilized on the surface by electrostatic interaction with the oxide. Brønsted acid sites are present only when hydroxyl groups are present. Therefore, the number of such sites depends on the extent of hydroxylation of the surface. Hydroxylation and dehydroxylation involve the interaction between a water molecule and surface coordinately unsaturated cations and oxygen anions:



This means that both dehydroxylation and disappearance of Brønsted acidity are responsible for the formation of Lewis acid sites, and vice versa. However in some cases this interconversion may not be demonstrated so readily due to the fact that the surface oxygen anion is very strongly basic such that its protonated form is only a very weak Brønsted acid and it protonates only strongly basic molecules.

An exposed coordinatively unsaturated oxygen ion participates in an acid base reaction acting as a base.

Heterogeneous acid catalysis attracted much attention primarily because in petroleum industry, heterogeneous acid catalysts are used as the main catalyst in the cracking process which is the largest process among the industrial chemical processes. Extensive studies of heterogeneous cracking catalysts undertaken during 1950s revealed that the essential feature of cracking catalysts is acidity, and, therefore, generation of acidic sites on the solids was extensively studied. As a result, amorphous silica-alumina was utilized as a cracking catalyst, and crystalline aluminosilicate (zeolite) was used afterwards.

In many cases good correlation has been found between the total amount of acid (Brønsted + Lewis) and catalytic activities of solid acids. For example the rates of both catalytic decomposition of cumene [3] and polymerization of propylene [4] over $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts were found to increase with increasing acid amounts. Uchida and Imami have found that both the ethylene polymerization activity of $\text{SiO}_2\text{-Al}_2\text{O}_3$ and its acid amounts are increased by the addition of nickel oxide [5]. Alumina's catalytic activity in a range of reactions such as isomerization of hydrocarbons, the polymerization of olefins, etc have been attributed to the acidic properties of the surface [6,7]. Another important observation was the higher activity of $\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ compared to $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ in the trans alkylation of aromatic compounds and in the Beckmann rearrangement of cyclohexanone oxime. This higher activity seems to be due to the higher concentrations of acid sites on $\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ [8].

In contrast to these extensive studies of heterogeneous acidic catalysts, fewer efforts have been given to the study of heterogeneous basic catalysts. The first study of heterogeneous basic catalysts, that sodium metal dispersed on alumina acted as an effective catalyst for double bond migration of alkenes, was reported by Pines *et al.* [9].

The various types of heterogeneous basic catalysts are [10]:

1. Single component metal oxides, alkaline earth oxides, alkali metal oxides and rare earth oxides.

2. Zeolites and alkali ion-exchanged zeolites.
3. Supported alkali metal ions, alkali metal ions on alumina and silica and alkaline earth oxides
4. Clay minerals, hydrotalcite and Sepiolite
5. Non-oxide and KF supported on alumina

Following the report by Pines *et al.*, the 1-butene isomerization over calcium and magnesium oxide was recognized as a base catalyzed reaction in which the reaction was initiated by the abstraction of a proton from 1-butene by the basic site on the catalyst surfaces [11]. The catalytic activities of basic zeolites were also reported during this period. The first reported base catalyzed reaction by alkali-cation exchanged zeolite was the side chain alkylation of toluene as reported by Yashima *et al.* [12].

In addition to the above mentioned catalysts, a number of materials have been reported to act as heterogeneous base catalysts. Except for non-oxide catalysts, the basic sites are believed to be surface O atoms. Oxygen atoms existing on any materials may act as basic sites because any O atoms would be able to interact attractively with a proton.

1.1.2 Methods of preparation:

For the exact reproducibility of the heterogeneous catalysts, utmost care must be taken during the preparation stages. In metal oxide catalysts, both composition and preparation methods are equally crucial in determining their properties. Even minor variation in the preparation method can drastically alter their catalytic properties irrespective of their composition. Therefore, designing metal oxide catalyst involves a judicious selection of metal components and the preparation method. The most common preparation methods are precipitation, co-precipitation, sol-gel method, complexation method, and ceramic method

The formation of a precipitate from the homogeneous liquid phase may occur as a result of the addition of bases, acids or by the use of complex forming agents. In

almost all cases, the formation of a new solid phase in a liquid medium results from two elementary processes; nucleation (*i.e.*, the formation of the smallest elementary particles of the new phase) and growth or agglomeration of the particles. Supersaturation, pH, temperature, nature of the reagents, presence of impurities and the method of preparation are the critical factors in determining the morphology, the texture and the structure of the particles [13].

In the co-precipitation method, hydroxides or carbonates of metal ions are precipitated out of a solution containing the precursor compounds [14,15]. This is followed by filtration, washing and calcination of the product to form the oxide. In a system with two or more metallic compounds, the composition of the precipitate depends on the difference in solubility between the components. When there is a large difference in the solubility products of the compounds involved, the sequential precipitation route can be adopted [16].

Sol-gel method involves the continuous transformation of a solution into a hydrated solid precursor [17]. This method allows control of texture, composition, homogeneity and structural properties of the finished solids. This method generally involves controlled hydrolysis and polymerization of ionic species in aqueous media. The preliminary stage involves the formation of hydrosols, and this is followed by aggregation of primary particles. The discovery of new and faster methods to produce aerogels substantially enhanced the popularity of this method, as an efficient way to control the texture, composition, homogeneity and structural properties of the catalyst materials.

The complexation method involves chemical reactions which transform slowly and without physical discontinuity the homogeneous solution of catalyst precursor into a homogeneous or amorphous phase [18]. The resulting precursor is then dried and decomposed to yield better intermixed and more highly dispersed oxides than those prepared by usual precipitation routes [19]. The multifunctional organic chelating agents will perform smooth gelation of the homogeneous solution of catalyst precursors.

Ceramic method involves the direct calcination of appropriately mixed metal salts at high temperatures. Metal salts (usually oxalates or carbonates) are ground well in wet or dry condition [20]. Solid solutions of the spinel and perovskite type oxides are generally prepared by ceramic route.

In addition to the above discussed common methods, some other methods like combustion synthesis, freeze drying technique, spray drying technique and hydrothermal method are also applied in catalyst synthesis.

1.1.3 Transition metal oxides as catalysts:

The high catalytic activity of transition metals appears to be one of the most significant facts of heterogeneous catalysis. Not only do the transition metals themselves possess high catalytic activity, but also do their alloys and compounds with nonmetals, sulfides and oxides etc. Transition metal oxides are the functional components in catalysts used in a large number of reactions such as oxidation, oxidative and non-oxidative dehydrogenation, reduction, ammoxidation, metathesis (production of long chain alkenes) and water gas shift reaction (production of hydrogen). Of these, selective oxidation, ammoxidation and selective dehydrogenation constitute the most important catalytic uses of transition metal oxides [21]. Another important application of transition metal oxides is that these can be used as precursors for other important catalysts. Cobalt-molybdenum sulfide catalyst for hydro desulphurization of petroleum crude and chromium based catalysts are examples. The important properties of transition metal oxides, that make these systems catalytically important material, are summarized below.

1. Presence of cations and anions in stoichiometric ratios and in well-defined spatial (structural) relationships
2. Possibility of covalent and ionic bonding between cations and anions
3. Presence of strong electric field normal to the surface due to the coulombic nature of the ionic lattice
4. Presence of charged adsorbed species
5. Presence of surface acidity and basicity

6. Presence of cationic and anionic vacancies
7. Ability of cations to undergo oxidation and reduction
8. High mobility of lattice oxygen and the possibility that the lattice oxygen are reactants in a reaction

Generally transition metal oxides in the series Ti → Cu, Zr → Ag, and Ta → Au, are especially active in reactions of the oxidation-reduction class. Many workers have explained the high catalytic activity on the basis of the fact that the cations exert an abnormally strong deforming action and that there is a gradual decrease in the potential of the chemical forces in bonds that are formed by d-electrons, in comparison with bonds formed by s- and p-electrons.

The developments in surface science techniques have provided very detailed idea about the surface structures, chemical composition and electronic properties of the surfaces. In particular, the advances in instrumentation and experimental techniques have made it possible to study the chemistry of the interface between the transition metal oxide and the fluid phase in greater detail than ever before.

Corundum, rocksalt, wurtzite, spinel, perovskite, rutile and layer structure are the important structural classes of transition metal oxides. In addition to these structures, there exist many other structures such as schelite, pyrochlore and wolframite. The difference in these structures is mainly due to difference in the close packing of oxygen anions. Ionic radius of transition metals are smaller than O^{2-} . Thus the oxygen ions are usually close packed with smaller metal ions situated in the octahedral and tetrahedral holes among the oxygen ions.

In the present investigation, iron based spinel oxides of Co, Ni and Zn are chosen. Materials are prepared by soft-chemical route, and their surface properties and catalytic applications are discussed in the present study. A detailed account of the catalyst systems and literature overview are given below.

1.2 DISCUSSION OF THE SPINEL STRUCTURE

Spinel is the structure type of a wide variety of compounds with the general formula AB_2O_4 . The spinel structure can be approximated by a cubic close packing of O^{2-} ions in which A and B ions occupy certain interstices. The unit cell of a spinel contains 8 formula units and, hence, can be represented as $8[AB_2O_4]$. The 32 oxygen anions per unit cell form a face centered cubic cage, while the metallic cations occupy interstitial sites. In an ideal spinel the metallic cations represented as A occupy tetrahedral (Tet.) sites and comprises the tetrahedral sublattice, while those metallic cations represented as B occupy octahedral (Oct.) sites, and comprise the octahedral sublattice. Close packing of 32 O^{2-} ions form 64 tetrahedral interstices and 32 octahedral interstices. Of these, 8 Tet. holes and 16 Oct holes are occupied by cations. In other words, 1/8 of the Tet. interstices and 1/2 of the Oct. interstices are occupied by cations. The unit cell of an ideal spinel structure is shown in Fig.1.2.1. The non-ideal structure is derived from the ideal one by moving the anion from the ideal position in a (111) plane away from the nearest T- ion. The deviation of the ideal pattern is given by the oxygen parameter 'u' (*the difference in the expansion of octahedral and tetrahedral sites, in order to accommodate larger cations (such as Co, Cu, Mg, Mn, Ni and Zn) is characterized by a parameter, and it is generally represented as oxygen parameter 'u'. The tetrahedral interstices in an ideal close packed structure can accommodate only those metal ions with a radius $r_{tet} \leq 0.30 \text{ \AA}$ and in the octahedral sites only ions with a radius $r_{oct} \leq 0.55 \text{ \AA}$. Hence the lattice has to be expanded to accommodate larger cations*). In all ideal spinels the parameter 'u' has a value in the neighbourhood of 0.375. But in actual spinel lattices this ideal pattern is slightly deformed, usually corresponds to $u > 0.375$ [23-25].

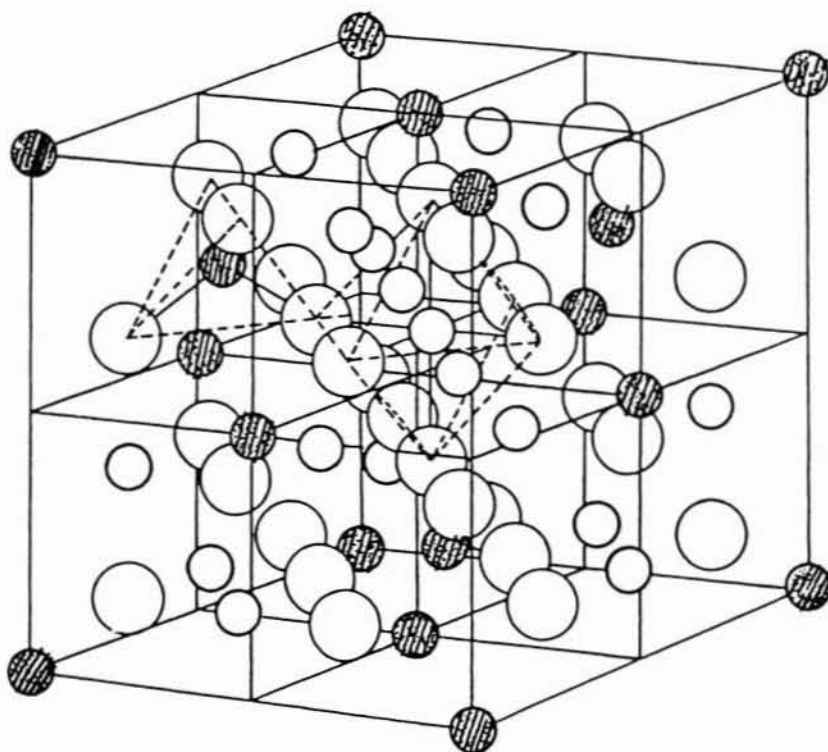


Fig. 1.2.1. The unit cell of an ideal spinel structure. Hatched circles indicate A cations, small unhatched circles indicate B cations and large unhatched circles indicate oxygen anions.

Fig. 1.2.2 represents the immediate neighbours of an anion in the spinel structure. One A and three B cations are around each anion as represented in the figure. If 'a' denotes the cell edge of the spinel unit cell, the AX distance is $a(u-1/4)$ and BX distance is $a(5/8-u)$ for small deviations from the ideal lattice. The angle AXB is about 125° and the angle BXB about 90° .

$$AX = a(u-1/4),$$

$$BX = a(5/8-u).$$

But for an ideal spinel 'u' = 0.375. Hence,

$$AX = a(0.375-1/4)$$

$$= 0.125 a,$$

$$BX = a(5/8-0.375)$$

$$= 0.25 a.$$

This difference in the bond length of two types of cations with the anions is an important factor in determining their electrical and catalytic properties [25].

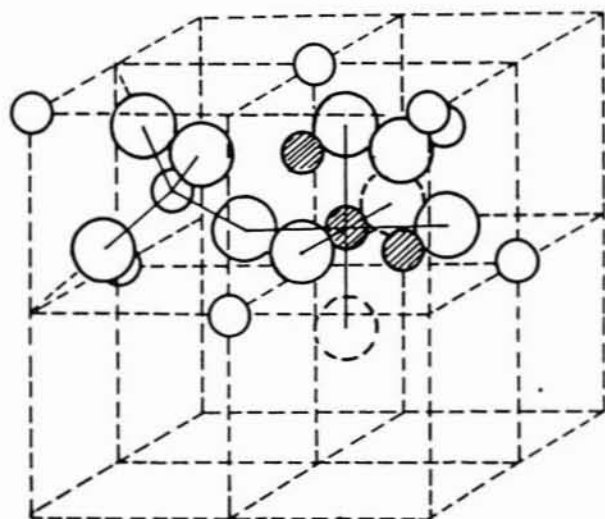


FIG. 1.22. UNIT CELL OF THE IDEAL SPINEL STRUCTURE. THE POSITION OF THE IONS IN ONLY TWO OCTANTS SHOWN. THE DASHED CIRCLES BELONG TO OTHER OCTANTS. LARGE CIRCLES: ANIONS; SMALL HATCHED CIRCLES B-SITE CATIONS; SMALL UNHATCHED CIRCLES: A-SITE CATIONS.

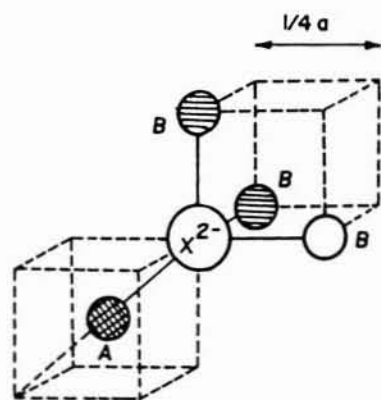


FIG. 1.23. THE NEAREST NEIGHBOURS OF ANION IN THE SPINEL STRUCTURE: X: ANION, A: A-SITE CATION, B: B-SITE CATION, a : CELL EDGE.

1.2.1 Normal and inverse spinels:

As mentioned above the general formula of a spinel can be represented as AB_2O_4 . Mainly three different valency distribution for the cations are possible.

1. $A = +2$ $B = +3$
2. $A = +4$ $B = +2$
3. $A = +6$ $B = +1$

However, the third possibility represented as $A = +6$ and $B = +1$ is very rare.

A spinel is called “normal” if the Tet. sites are occupied only by A-type ions and the Oct. sites by B-ions. The A ions of a normal spinel occupy the 8 Tet. sites of the O_h^7 space group and have a point symmetry T_d . The B ions of a normal spinel occupy the 16 Oct. sites of O_h^7 and have a point symmetry D_{3d} . But Barth and Posenjak [26] pointed out a second possibility, in which half of the B cations occupy the Tet. sites and all A cations together with the other half of the B cations in the Oct. sites. This type of spinel configuration is called “inverse” spinels. Recent work such as that of Datta and Roy [27] and Hafner and Laves [28] have shown that there are many “intermediate” or “random” spinels which are in between the pure normal and pure inverse arrangements. This intermediate spinel structure is due to the averaged distribution of all ions about all spinel cation positions (Table 1.2.1).

Type	Structure	Examples
Normal	$(A^{+2})[B_2^{+3}]O_4$	$ZnFe_2O_4$, $ZnCrFeO_4$, $ZnCr_2O_4$, $MgCr_2O_4$
Inverse	$(B^{+3})[A^{+2}B^{+3}]O_4$	$MgFe_2O_4$, $NiFe_2O_4$, $CoFe_2O_4$
Random	$(A_x^{+2}B_y^{+3})[A^{+2}_{1-x}B^{+3}_{2-y}]O_4$	$MgCrFeO_4$

Table 1.2.1. Examples of some normal and inverse spinels.

