CAPTER ONE

INTRODUCTION

1. Introduction

1.1 Ferrites

Ferrites or ferromagnetic oxides (also known as ceramics containing compounds of iron) are dark brown or gray in appearance and very hard and brittle in physical character. They are prepared by heat-treating various transition metal oxides or alkaline earth oxides with the ferric oxides (Snoek 1947). The magnetic behavior exhibited by the ferrites is quite different form ferromagnetism that is exhibited by metallic materials. Ferrites are non-conducting magnetic media so eddy current and ohmic losses are less than for ferromagnetic materials. Ferrites are often used as transformer cores at radio frequencies (RF). Ferrites are most common in nature. From the daily iron oxide Fe_3O_4 (magnetite) formed at the surface of many iron containing objects like fences, cars, doors, barbecue grills.

Ferrite exhibits ferrimagnetism due to the super-exchange interaction between electrons of metal and oxygen ions. The opposite spins in ferrite results in the lowering of magnetization compared to ferromagnetic metals where the spins are parallel. Due to the intrinsic atomic level interaction between oxygen and metal ions, ferrite has higher resistivity compared to ferromagnetic metals. This enables the ferrite to find applications at higher frequencies and makes it technologically very valuable. Their magnetic properties can greatly vary from one element to another, since the microscopic (atomic) structure is composed of two or more magnetic sublattices.

1.1.2 Composition and properties

Many ferrites are spinels with the formula AB_2O_4, where A and B represent various metal cations, usually including iron Fe. Spinel ferrites usually adopt a crystal motif consisting of cubic close-packed (fcc) oxides (O^{2-}) with A cations occupying one eighth of the tetrahedral holes and B cations occupying half of the octahedral holes. If one eighth of the tetrahedral holes are occupied by B cation, then one fourth of the octahedral sites are occupied by A cation and the other one fourth by B cation and it's called the inverse spinel structure. It's also possible to have mixed structure spinel ferrites with formula $[M^{2+}{}_{1-\delta}Fe^{3+}{}_{\delta}][M^{2+}{}_{\delta}Fe^{3+}{}_{2-\delta}]O4$ where δ is the degree of inversion. The magnetic material known as "ZnFe" has the formula $ZnFe_2O_4$ with Fe^{3+} occupying the octahedral sites and Zn^{2+} occupy the tetrahedral sites. This material is an example of normal structure spinel ferrite (Shriver et al 2006).

1.1.2.1 Crystal chemistry of spinel ferrites

The structure of spinel ferrites is derived from that of the mineral spinel $MgOAl_2O_4$. The structure is complex, in that there are 8 molecules per unit cell (8_x AFe_20_4) where A is the divalent metal ion. The 32 large Oxygen ions form a face centered cubic lattice in which two kinds of interstitial sites are present. The smaller metal ions occupy the interstitial spaces. These spaces are of two kinds. One is called tetrahedral 'A' sites because it is located at the center of a tetrahedron whose corners are occupied by oxygen ions. There are 64 tetrahedral sites surrounded by 4 oxygen ions. The other is called an octahedral or B site, because the oxygen ions around it occupy the corners of an octahedron. There are 32 octahedral sites surrounded by 6 oxygen ions. The crystallographic environments of A and B sites are therefore distinctly different.

Only one eighth of the A sites and one half of the B sites are occupied by the metal ions. In the chemical formula of $MO.Fe_2O_3$ if M^{2+} are in A sites and Fe^{3+} in B

sites then this structure is normally referred to as the normal spinel structure. When the divalent metallic ion M^{2+} occupies the B site and the Fe^{3+} ions equally divided between A and B sites then this configuration is called inverse spinel. $ZnFe_2O_4$ is a normal spinel, while $NiFe_2O_4$ is an inverse spinel. The normal and inverse structure is to be regarded as extreme cases, because X-ray and neutron diffraction have shown that intermediate structures can exist. The distribution of the divalent ions on A and B sites in some ferrites can be altered by heat treatment, it depends on whether the material is quenched from a high temperature or annealed.

The various factors determining the cation distribution includes the size of the cation, valency of the cation and the oxygen parameter of the anions. Large divalent ions tend to occupy tetrahedral sites as this is favored by polarization effects. If the A site ions have a lower valency and the B site ions have a higher valency then the intermediate O^{2-} ion will become polarized towards B sites. Thus polarization favours normal spinel configuration. It has been proved that the inverse structure has the lowest lattice energy for u parameter ($u < 0.379$), whereas, the normal structure has the lowest energy when $u > 0.379$. These factors alone cannot give consistent picture of the observed cation distribution in spineI ferrites. For instance, $CoFe_2O_4$ is an inverse spinel, while $ZnFe_2O_4$ crystallizes in normal spinel structure although Zn^{2+} and Co^{2+} have almost the same ionic radii. These discrepancies can be explained by an individual site preference of the various ions as a result of their electronic configuration. In order to explain the site preference of transition metal ions in oxides, two theories have been proposed, which differ in the concept of chemical bonding in oxides. The first theory is based on crystal field theory, which is purely ionic type of bonding. The second one is a simplified molecular orbital theory, based on the covalent bonding between oxygen and transition metal atoms.

1.1.2.2. Magnetic properties of ferrites

It is known that in ferrimagnetic materials, the magnitude of the magnetic moments oriented in either way differ, so that there always exists a resultant uncompensated magnetic moment. The various factors that determine the magnetic

properties of these ferrites are the nature of cations, heat treatment, preparative methods, site preference energy of cations and madelung energy. According to Neel (1948), ferrites exhibit a magnetic structure distinctly different from any previously recognized structure. Neel (1948) explained the spontaneous magnetisation of these ferrites on the basis of Heisenberg's exchange forces. According to this theory the exchange energy between two adjacent atoms having spin angular momentum is given by equation 1.1.

$$E_{ex} = -2\, J_{ex}\, S_i.S_j \quad \ldots\ldots\ldots\ldots (1.1)$$

Where E_{ex} is the exchange energy, S_i and S_j are the total spins of adjacent atoms and J_{ex} is the exchange integral which represents the probability of exchange of electron. In ferrites three kinds of magnetic interactions are possible, between the magnetic ions, which are occupied in the two crystallographically distinct lattice sites. These interactions are possible through the intermediate O^{2-} ions by super-exchange mechanism. The three possible interactions are A-A interaction, B-B interaction and A-B interaction. The exchange force acting between an ion on A site and an ion on B site is governed by equation 1.1. The interaction is ferri, ferro or antiferro and is determined by the value of J_{ex}. It has been established experimentally that these interaction energies are negative for ferrites and hence induce an anti parallel orientation. However the magnitudes of the A and B sublattice magnetisations are not equal and this will produce a resultant net magnetisation in ferrites. In general, the magnitude of the interaction energy between two magnetic ions depends upon the distance from these ions to the oxygen ion (through which the interaction occurs) and

also the angle< p between the magnetic ions (Me^{I} - O – Me^{II}). An angle of 180° will give rise to the greatest exchange energy and the energy decreases very rapidly with increasing distance. Based on the values of the distance and the angle φ it may be concluded that of the three interactions, the A-B interaction is of the greatest magnitude, the A-A interaction is the weakest. Thus with only A-B interaction predominating, the spins of the A and B site ions in ferrite will be oppositely magnetized in the A and B sublattilces, with a resultant magnetic moment equal to the difference between those of A and B site ions. In general, the value of saturation magnetic moment for the B lattice (M_B) is greater than that of the A lattice (M_A) so that the resultant saturation magnetization (M_S) may be written as $M_S = M_B - M_A$.

1.1.2.3. Electrical properties of spinel ferrites

Spinel ferrites are important over conventional magnetic materials because of their wide variety of applications. These materials have low electrical conductivities when compared to other magnetic materials and hence they find wide use at microwave frequencies. Spinel ferrites, in general are semiconductors with their conductivity lying in between 10^{2} and 10^{-11} Ohm^{-1} cm^{-1}. The conductivity is due to the presence of Fe^{2+} and the metal ions (M^{3+}). The presence of Fe^{2+} results in n-type behavior and of M^{3+} in p-type behavior. The conductivity arises due to the mobility of the extra electron or the positive hole through the crystal lattice. The movement is described by a hopping mechanism, in which the charge carriers jump from one ionic site to the other. In short, one can say that the electrostatic interaction between conduction electron (hole) and nearby ions may result in a displacement of the latter and polarization of the surrounding region, so that the career is situated at the centre of a polaristaion potential well. The career is trapped at a lattice site, if this potential well is deep enough. Its transition to a neighbouring site is determined by thermal activation. This has been described as the hopping mechanism. In such a process the

mobility of the jumping electrons or holes are found to be proportional to $e^{-Q/KT}$, where Q is the activation energy, k Boltzman's constant and T the temperature in degree absolute (Jianjun 1996).

1.1.3 Classification of ferrites

Ferrites are classified according to magnetic properties and their crystal structure. Based on their magnetic properties, ferrites are often classified as "soft" and "hard" which refers to their low or high coercivity of their magnetism, respectively.

1.1.3.1.1Soft ferrites

Soft ferrites are ferrimagnetic materials with cubic crystal structure and they are characterized by a chemical formula $MO{\cdot}Fe_2O_3$, where M is a transition metal ions like Iron, Nickel, Manganese or Zinc. Manganese-Zinc ferrites are used in soft magnetic applications up to high frequencies of 10 MHz. Soft magnetic material is one that can be both easily magnetized and demagnetized, so that it can store or transfer magnetic energy in alternating or other changing wave forms (sine, pulse, square, etc). At high frequency metallic soft magnetic materials simply cannot be used due to the eddy current losses. Therefore, soft ferrites, which are ceramic insulators, become the most desirable material for example in telephone signal transmitters and receivers and in switch mode power supplies (referred as DC-DC converters). For such type of application the driving force to increase frequency is to allow miniaturisation.

1.1.3.1.2 Hard ferrites

Permanent ferrite magnets are made up of hard ferrites, which have a high coercivity and high remanance after magnetization. These ferrites are composed of iron and barium or strontium oxides. In a magnetically saturated state they conduct magnetic flux well and have a high magnetic permeability. This enables these ceramic magnets to store stronger magnetic fields than iron itself. They are cheap, and are

widely used in household products such as refrigerator magnets. The hexagonal ferrite structure is found in both $BaO \cdot 6Fe_2O_3$ and $SrO \cdot 6Fe_2O_3$, but Sr-M hexaferrite has slightly superior magnetic properties.

1.1.3.2Crystal structure of ferrites

Ferrite compounds consist dominant compound of Fe_2O_3. They are divided into four groups, namely, Spinal, Garnet, Ortho and hexagonal or magnetoplumbite ferrites. These ferrites are distinguished with respect to the molar ratio of Fe_2O_3 to other oxide components present in the ceramic as shown in Table 1.1.

Table1.1: Classification of ferrites, (Hench and West 1990)

Types	Molar ratio	Representations
Spinel	$Fe_2O_3.1MO$	MeO is a transition metal oxide
Garnet	$5Fe_2O_3.3M_2O_3$	Me_2O_3 is a rare earth metal oxide
Ortho	$AFeO_3$	A is rare earth elements like HO, Dy, Er, Y, Yb
Hexaferrite	$6Fe_2O_3.1MO$	MeO is a divalent metal oxidefrom group IIA e.g. BaO, CaO, SrO

1.1.3.2.1 Spinel ferrites

Ferrites with the formula AB_2O_4, constitute the first group of ferrites, where A and B represent various metal cations like iron. Spinel ferrites are magnetically soft and they are alternative to metallic magnets such as Fe and layered Fe-Si alloys, but exhibit enhanced performance due to their outstanding magnetic properties (Snelling 1969, Sugimoto 1999). Spinel ferrites have the properties such as high electrical resistivity and low magnetic losse. The two popular ceramic magnets; Nickel-Zinc ferrites and Manganese-Zinc ferrites are the major members of the spinel ferrite family. They have been intriguing ceramic materials due to their high electrical resistivity,

high magnetic permeability and possible modification of intrinsic properties over a wide spectrum (Hench and West 1990).

Members of the spinel group include

1- Aluminium spinels:

Spinel: $MgAl_2O_4$, after which this class of minerals is named. Many aluminium spinels are known, such as, Chrysoberyl ($BeAl_2O_4$), Gahnite ($ZnAl_2O_4$), Hercynite ($FeAl_2O_4$), Galaxite ($MnAl_2O_4$), Pleonaste ($(Mg,Fe)Al_2O_4$).

2- Iron spinels:

Examples of Iron spinels include, Cuprospinel ($CuFe_2O_4$), Franklinite ($(Fe,Mn,Zn)(Fe,Mn)_2O_4$), Jacobsite ($MnFe_2O_4$), Magnesioferrite ($MgFe_2O_4$), Magnetite (Fe_3O_4), Trevorite ($NiFe_2O_4$), Ulvöspinel ($TiFe_2O_4$), Zinc ferrite ($(Zn, Fe) Fe_2O_4$)

3- Chromium spinels:

Many chromium spinel types are known, such as, Chromite ($FeCr_2O_4$), Magnesiochromite ($MgCr_2O_4$), Zincochromite ($ZnCr_2O_4$)

4- Other ferrites with the spinel structure:

These ferrites include, Coulsonite (FeV_2O_4), Magnesiocoulsonite (MgV_2O_4), Ringwoodite ($(Mg,Fe)_2SiO_4$), an abundant olivine polymorph within the Earth's mantle from about 520 to 660 km depth, and a rare mineral in meteorites (Palache et al 1944).

There are many more compounds with a spinel structure, e.g. the thiospinels and selenospinels, that can be synthesized in the lab or in some cases occur as minerals. The heterogeneity of spinel group members varies based on composition with ferrous and magnesium based members varying greatly as in solid solution, which requires

similarly sized cations. However, ferric and aluminium based spinels are almost entirely homogeneous due to their large size difference (Ernst 1969).

1.1.3.2.2 Garnet Ferrites

The second group of ferrites is the garnet type ferrites. Garnets are unique magnetic ceramics, which have optical transparency, and are used in magneto-optical applications (Moulson and Herbert 1990). Yttrium Iron garnet (YIG) is a synthetic garnet with chemical composition $Y_3Fe_5O_{12}$. Yttrium can be replaced by one of the rare earth ions like La^{+3}, $Dy^{+3,}$ Er^{+3}, etc. with an atomic number greater than 61.

1.1.3.2.3 Ortho Ferrites

Ortho ferrites possess extremely high velocities of the domain wall motion and it is used in communication techniques, in optical internet, in sensors of magnetic fields and electrical currents, mechanical quantities etc.

1.1.3.2.4 Hexaferrites:

In 1952, a new class of ferrites having permanent magnetic properties was discovered. Workers at Philips laboratory at Eindhoven in the Netherlands made the developments of hexagonal ferrites possible. Hexagonal ferrites (general formula $MFe_{12}O_{19}$, where M is usually Ba, Sr, Ca or Pb) have been distinguished due to their high uniaxial magneto-crystalline anisotropy which renders them perfect for permanent (hard) magnet applications (Stuijts et al 1954). The crystal structure of hexaferrite is complex but it can be described as hexagonal with a unique c axis, which is the easy axis of magnetization in the basic structure. Hexagonal ferrites are referred to as hard, as the direction of magnetization cannot be changed easily to another axis. Barium ferrite ($BaFe_{12}O_{19}$) and Strontium ferrite ($SrFe_{12}O_{19}$) are the examples of hexagonal ferrites and they have received much interest in recent years because of microwave device applications. Barium hexaferrite is especially of interest for use in hybrid

microwave devices, monolithic microwave integrated circuits or even as a future replacement for Yttrium Iron garnet (Fang & Ong 1999) due to its high uniaxial anisotropy and large resistivity. The next generation of magnetic microwave devices (isolators, filters, phase shifters, and circulators and related components) will be planar, self-biased, and low loss, and operate better than today's devices (Herris et al 2006).

Hexaferrites are subclassified into six subclasses namely; M, W, Y, Z, X and U type according to their crystal structure and arrangement of respective S, R and T blocks. Table 1.2 shows the subclasses of Hexaferrite with their chemical formulae, where, A represents Ba, Pb or Sr and M is a divalent transition metal ion. The crystal structure of these different types of hexaferrite is complex and can be considered as a superposition of S, R and T blocks along the hexagonal c-axis. S block represents a spinel block which consists two oxygen layer (O_4-O_4) with composition Fe_6O_8. R is a three oxygen layer block (O_4-BaO_3-O_4) with composition $BaFe_6O_{11}$. T is a block of four layers of oxygen ions (O_4-BaO_3-Ba_3-O_4) with composition Ba_2 Fe_8O_{14}. Astrik (*) shows that the corresponding block is rotated 180° around the hexagonal c-axis(Zhang et al 1990).

Table 1.2: Subclasses of hexaferrites, (Zhang et alb1990)

#	Hexaferrite type	Chemical formula
1	M-type	$AFe_{12}O_{19}$
2	Y-type	$A_2M_2Fe_{12}O_{22}$
3	W-type	$AM_2Fe_{16}O_{27}$
4	X-type	$A_2MFe_{28}O_{46}$
5	U-type	$A_4M_2Fe_{36}O_{60}$
6	Z-type	$A_3M_2Fe_{24}O_{41}$

1.1.4 Production of ferrites

Ferrites are produced by heating a mixture of finely-powdered precursors pressed into a mold. During the heating process, calcination of carbonates occurs: $MCO_3 \rightarrow MO + CO_2$

The oxides of barium and strontium are typically supplied as their carbonates, $BaCO_3$ or $SrCO_3$. The resulting mixture of oxides undergoes sintering. Sintering is a high temperature process similar to the firing of ceramic ware. Afterwards, the cooled product is milled to particles smaller than 2 μm, small enough that each particle consists of a single magnetic domain. Then the powder is pressed into a shape, dried, and re-sintered. The shaping may be performed in an external magnetic field, in order to achieve a preferred orientation of the particles (anisotropy). Small and geometrically easy shapes may be produced with dry pressing. However, in such a process small particles may agglomerate and lead to poorer magnetic properties compared to the wet pressing process. Direct calcination and sintering without re-milling is possible as well, but leads to poor magnetic properties. Electromagnets are pre-sintered as well (pre-reaction), milled and pressed. However, the sintering takes place in a specific atmosphere, for instance one with an oxygen shortage. The chemical composition and especially the structure vary strongly between the precursor and the sintered product. To allow efficient stacking of product in the furnace during sintering and prevent parts sticking together, many manufacturers separate ware using ceramic powder separator sheets. These sheets are available in various materials such as alumina, zirconia and magnesia. They are also available in fine medium and coarse particle sizes. By matching the material and particle size to the ware being sintered, surface damage and contamination can be reduced while maximizing furnace loading.

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 at most 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 (Takoda 1980). 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 (Takoda and Kiyama 1970; Wikham 1967) or NH_4OH (Mohanunadpour Amini and Torkian 2002; Yang et al 2002). This is followed by filtration, washing and calcinations of the product to form the oxide. The morphology, texture, structure and size of the particles can be accurately controlled by altering the pH of the solution, temperature and nature of the reagents (Marcilly 1984). 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 (Sreekurnar et al 2002; Rao et al 1998). Co-Precipitation method generates Bronsted 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 (Yoshimura 1998).

Furthermore, 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 (Byrappa and Yoshimura 2001). 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 with well controlled particle size and morphology (Dawson 1988; Hirano and Kato 1996). So far, considerable progress has been made by employing this

solution technique in obtaining spinel oxides for high performance electrode materials (Feng et al 1995; Kanasaku et al 1998).

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 (Mccolm and Clerk1988, Brooks and Mmarakoon1991).

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 (Surcsh 1991). In this process stoichiometric ratio of nitrates is dissolved in the minimum amount of water in a pyrex dish; the fuel is added and is heated at 350°C in a muffle furnace. A heating rate of 75 °C/min is used to obtain good combustion. This method can be used for 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 (Matsumota et al 1991, Rothner 1977).

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 (Schnettler and Johnson 1970). In addition to the above discussed methods, several other methods like pulsed wire discharge (Kinemuchi et al 2002), shock wave synthesis (Liu et al 2001) and sonochemical method (Jeevanandam et al 2002) are also applied in spinel synthesis.

1.1.5 Uses

Ferrite cores are used in electronic inductors, transformers, and electromagnets where the high electrical resistance of the ferrite leads to very low eddy current losses. They are commonly seen as a lump in a computer cable, called a ferrite bead, which helps to prevent high frequency electrical noise (radio frequency interference) from exiting or entering the equipment. Early computer memories stored data in the residual magnetic fields of hard ferrite cores, which were assembled into arrays of core memory. Ferrite powders are used in the coatings of magnetic recording tapes. One such type of material is iron (III) oxide. Ferrite particles are also used as a component of radar-absorbing materials or coatings used in stealth aircraft and in the absorption tiles lining the rooms used for electromagnetic measurements. Most common radio magnets, including those used in loudspeakers, are ferrite magnets. Ferrite magnets have largely displaced Alnico magnets in these applications. It is a common magnetic material for electromagnetic instrument pickups. Ferrite nanoparticcles exhibit super paramagnetic properties.

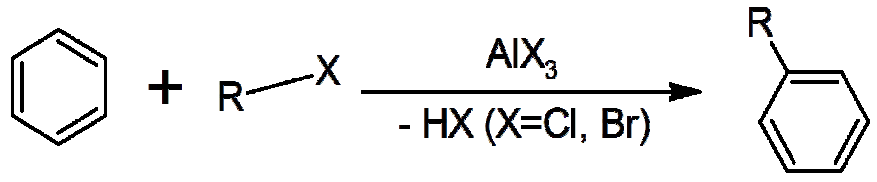
1.1.6 Friedel-crafts alkylation

Friedel-crafts alkylation reaction is a nucleophlic substitution, as it in volves a nucleophlic attack by an aromatic ring on the alkyl group (Morison and Boyd 1973). The first typical friedel-crafts reaction was the reaction of benzene (aromatic) with amyl choride (alkylation agent) in the presence of $AlCl_3$ to product amyl benzene. This reaction was exclusively carried out by charles friedel and his American collaborator james mason crafts in Paris in 1877 (Roberts and Khalaf 1984) The most important alkylation agents are alkyl halides, alkenes and alcohols, but many other types of reagents have also been employed (olah and molnar 2003). The reactivity of friedel-crafts alkylation is based on these alkylating agents.For alkyl halides the reactivity was found to decrease in the order, Allylic > benzylic > tertiary > secanday > primary (Smith and March 2001).

Alkylation of armatic compounds is an important area of industrial research.

Benzylated aromatices, aclass of alkylated aromaties, are very useful intermediates in petrochemicals, cosmeties, dyes, pharmaceuticals and many other chemical in dustries (Olah 1964)

They are formed by replacement of a hydrogen atom of an aromatic compound by benzyl group derived from benzylting agent by means of a catalyst this reaction can be illustrated in scheme 1.1.



{R-X=Benzylation agent, R=benzyl group, (C_6H_5-CH_2-)

Scheme 1.1: Schematic illustration of the Friedel-Crafts benzylation of benzene over AlX_3 using benzyl halide as benzylating agent.

1.1.7 Catalysts

Catalysts are small amounts of certain substances increase the rate of reaction which them self don't take part in the reaction however, the rate of the reaction can be increase by using them (Singh et al 2009). Depending on whether the catalyst and all the reactants belong to a single phase or not, it can be divided in to two categories, namely, (i) homogeneous and (ii) heterogeneous catalysts. For friedel-crafts alkylation reactions and regardless of the type of alkylating agent used, acatalyst in nearly always required. However, a few exceptional cases in which have been reported (Olah and Nishimura 1974; Stang and Anderson 1978).

1.1.7.1 Homogeneous catalysts

When the catalyst and reactants are in the same phase, the process of catalysis is known as homogenous catalysis. The system may consist entirely of gases, or both the catalyst and the reactants are in the solution phase (Singh et al 2009). For instance, Nitric oxide (NO_2) gas catalyses the combination of most sulphure dioxide and oxygen in the lead chamber process for the manufacture of sulphuric acid. Homogenous catalyst in solution is much more common. The most important class of such reactions is those catalyzed by the presence of acids and bases, i.e. acid-base catalysis. However, apart from this class, the Friedel-Crafts reaction is supposed to occur in the presence of $AlCl_3$ catalyst (Singh 2009). Some other Lewis acid catalysts are also involved in this reaction i.e. $AlBr_3$, BF_3, $GaBr_3$, etc. (Olah 1964; Sharman 1962). The acidic strength of the most common Lewis acids decreases in the following order BX_3> AlX_3> FeX_3> GaX_3> SbX_5> InX_3> SnX_4> AsX_5> SbX_3> ZrX_4 (Smith 2002). However, the reactivity decreases in the order: F> Cl> Br >I. An excess of aromatic compounds or solvent i.e. carbon disulphide, CS_2, dichloro methane, CH_2Cl_2, n-hexane, nitro benzene or nitro methane, CH_3NO_2 are used. Olefins and alcohols can be also be employed in place of alkyl halides with protic acid i.e. H_2SO_4, H_3PO_4, HF etc, (Bensal 1978). However,

these catalysts suffer from serveral problems such as corrosion, handling, toxicity, requirements of stochinmetric amounts, and separation disposal of spent catalyst, products isolation and recovery of the catalyst. In order to overcome these problems, many efforts have been done to heterogenize these catalysts by supporting them with many solid porous materials such as zeolites, alumina, clay, mesoporous silica, amorphous silica, etc.

1.1.7.2 Heterogeneous Catalysts

In such catalysis, the catalyst is in a different phase than that of the reactants. The catalysts are usually metal oxides such has NiO, CuO, PtO_2, Ag_2O etc., or metal chlorides such as $HgCl_2$, $TiCl_4$ etc. (Singh et al 2009). Numerous potential advantageous are associated with heterogeneous catalyst for Friedel-Crafts reaction especially for the large scale manufacturing industry these include ease of handling, ease of separation from reaction products ,higher thermal stability ,possibility of regeneration and decrease in cost due to lower loading of active metal and reusability. Some major disadvantages are also encountered such as availability of different environment of active sites, difficulty associated with the proper characterization of the active sites .

1.1.8 Ferrites as catalysts

The use of nanoparticles as catalysts in organic transformation has attracted considerable interest in recent years.

Although using a catalyst in nanometer dimensions may achieve a substantial enhancement in its catalytic activity, the important challenge for green chemistry is the innovation of new technologies for catalyst separation and recycling to replace conventional procedures. In this context, much attention has been paid to the utilization of magnetic metal oxides nanoparticles as heterogeneous and easily recycled catalysts

for various organic reactions (Polshettiwar and Varma 2010; Menini et al 2008; Jacinto et al 2009).

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 distribution among the tetrahedral [T_d] and octahedral (O_h) sites. In spinel systems containing iron, Fe^{3+} ion can be easily replaced between Oh and Td sites by stoichiometrically varying the concentration of other cations. This peculiar structural feature enables ferrospinels to withstand even extremely reducing atmospheres (Viswanathan and Murthy 1990). 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 (Ghose and Murthy 1996), catalytic combustion of hydrocarbons (Guilhaume and Primet 1994) or selective oxidation and reduction of several organic molecules (Yang et al 1991; Sloczynski et al 1999). For these applications of metal oxides as heterogeneous catalysts, high surface area and accessible porosity arc relevant properties.

Transition metal oxide or mixed oxides have now been established as inexpensive alternatives to precious metal and noble metal containing catalysts (Flytzani-Stephanopoulos 2001). Copper manganese oxide mixture based on $CuMn_2O_4$ is a long established catalyst for the removal of toxic gases and vapour since its discovery in 1920 (Lamb et al 1920). 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 compoundsand nitrogen containing compounds (Puckhaber et al 1989). Transition metal oxides like hematite can be converted to spinel ferrite by adding Zn, Mg, Ni or Co to it, and can be used for the oxidative dehydrogenation of hydrocarbons (Kung 1986), for transfonnation of butane (Liaw et al 1989; Yang et al 1984) and ethyl benzene (Hong et al 1984).

For reactions such as I-butene oxidative dehydrogenation, the catalytic activity of a ferrite strongly depends on the cation distribution in lattice (Kung et al 1989; Yang et al 1991). For instance, $MgFe_2O_4$, which has an inverted spinel structure, is having higher catalytic activity than the one of stoichiometric $ZnFe_2O_4$ ferrite, whose crystalline structure is not inverted (Toledo-Antonio et al 2002). These results suggest that the distribution of iron in the tetrahedral and octahedral sites of a ferrite could detennine their catalytic activity.

Both Fe_3O_4 and γ-Fe_2O_4 have been used as catalysts, but compared to $CoFe_2O_4$, show some drawbacks. Fe_3O_4 could be easily prepared and has been efficiently utilized in many organic reactions (Stevens et al 2005; Polshettiwar et al 2009), but it is fairly reactive to acidic and oxidative environment (Wang et al 2006); γ-Fe_2O_4 is also not thermally stable (Sellwood 1956). On the contrary, $CoFe_2O_4$ nanoparticles have a remarkable chemical stability and have been used in various fields (Turtelli and Duong 2008; Murdock et al 1992). However, only a few efforts have been devoted to its catalytic activity in organic reactions.

Senapati et al used a $CoFe_2O_4$ nanocatalyst (40–50 nm) as an efficient catalyst for a Knoevenagel condensation reaction of several aldehydes with ethylcyanoacetate. They could recover the catalyst from the reaction mixture with the aid of an external magnet (Senapati et al 2011). Aerobic oxidation of cyclohexane to cyclohexanol or

cyclohexanon was also reported to be catalyzed by magnetic $CoFe_2O_4$ nanocrystals in solvent free conditions (Tonga et al 2009). In anotherreport, the decomposition of methanol to H_2 and CO was studied by Manova et al. using nanosized iron and iron–cobalt spinel oxides as catalysts (Manova et al 2006).

1.1.9 Ferrites as industrial catalysts

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 (Sato et al 1999; lnove and Emoto 1972) 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_2, Fe_2O_3, Cr_2O_3, magnetite, hydrota1cite, Al_2O_3 oxides (lnove and Emoto 1972; Aleksandrova 1942; Velu and Swamy 2000). These catalysts possess one or more of the drawbacks such as low conversion, severe operative conditions, poor selectivity due to number of side products and lack of reproducibility, Recently Rao and coworkers established the idea of using spinels for aromatic C and/or N methylation of compounds like pyridine, aniline, phenol etc (Sreekumar et al 2000; Rao et al 1998), It is to be noted that Fe_2O_4 in combination with other oxides such as CdO, SnO_2, CeO_2, NiO, CoO, Cr_2O_4 and ZrO_4 are highly active for the alkylation reactions (Grabowska et al 1996; Kotanigawa

1974). 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 (Verwey and Herlman 1947), are reported to be more active for the dehydrogenation of hydrocarbons (Kung 1980), isopropyl alcohol (Balasubramanian and Krishnaswami 1982) and cycohexanol (Chen etbal 1992). 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 (Narasirnhan and Swamy 1982). In contrast to the spinel ferrites, the catalyst Fe_2O_4 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 $ZnAl_2O_4$ 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 on $ZnAl_2O_4$ are reported to be good catalysts for the hydrofonnylation and hydrogenation .Not only this, certain organic transfonnations can be carried out over spinels. Anisole can be transfonned into other industrially important derivatives using $ZnAl_2O_4$ and $Fe_2O_4/ZnAL_2O_4$ (Wrzyszcz 2002). $ZnAL_2O_4$ has been shown to be active for the synthesis of styrene from acetophenones (Roesky et al 1999) or for the double bond isomerization process of alkenes (Welch 1986). It is also promising support for catalysts such as pt (Aguilar-

Rios et al 1992) or Pt/Sn (Miura and Itoh 1999) (dehydrogenation process), and Cu (Kiennemann et al 1990) (low pressure synthesis of methanol) and in the synthesis of compounds like indenes from indanones (Reddy 1999).

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 (Petterson and Sjostrom 1991; Agrell et al 2002). Catalysts with high activity, selectivity and stability under lower temperatures are needed but the problem is not solved enough, Recently (Manova et al 20004). 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_2O_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 perfonnance catalyst, The selectivity of the H_2O_2 decomposition catalysts has proved difficult as the suitable ones, silver oxide, Pt and Pd blacks are expensive. Among the inexpensive corrosion resistant catalysts (Cota et al 1964; Lahiri and Sengupta 1991) , the 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 (Goldstein and Tseunh 1974).Cobalt ferrite catalyses the decomposition of H_2O_2 to the same extent as the noble metal catalysts (Cota et al 1964). Sengupta and Lahiri reported their study on manganese ferrospinel systems for H_2O_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_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 (Forzatti et al 1991; Epling et al 1997), 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 (Epling et al 1999).

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 a1. conducted a number of studies on the alkylation reactions of phenol, aniline etc (Mathcw et al 2004; Srcekumar et al 2000). They have employed ferospinel based on copper and cobalt, $Cu_{1-x}Co_xFe_20_4$, and showed an excellent performance towards phenol methylation both in terms of conversion and ortho selectivity.

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 (Fiege et al). 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 (Srcekumar et al 2000). Sugunan et al. also reported the benzoylation of

benzene using benzyl chloride catalyzed by ferrospinels (Nishamol et al 2004) (Ramankutty and Sugunan 2001).

Styrene production and styrene oxidation can be conveniently carried out by spienls. 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. Spinets such as $MgFe_2O_4$ and $ZnFe_2O_4$ are reported as highly active catalysts for the oxidation of styrene to bezaldehyde (Mathew et al 2003; John Jebarathinam et al 1996).

The reduction of NO_x emission from automobile exhaust and removal of N_2O 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 bum 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 (Liang et al 2003; Chellam et al 2000). The cobalt oxide spinel Co_3O_4 is one receiving considerable interest. Yan et al. reported spinel oxide with partial replacement of Co^{2+} by Zn^{2+} in Co_3O_4 which are highly active for N_2O decomposition into N_2 and O_2 (Liang et al 2003). Magnesium cobaltite spinels prepared by hydrothermal method shows excellent catalytic activity for N_2O decomposition (Chellam et al 2000).

Copper Manganese oxide mixture based on $CuMn_2O_4$ 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 (Paldey et al 2005). Spinels like $NiMn_2O_4$ and $CuCo_2O_4$ show high activity in the catalytic CO oxidation (Fortunato 2001).

Photocatalysis is the important field where spinels find immense application. Spinels as such or in the composite form arc used for the production of H_2 and for the

degradation of environmentally pollutant organic chemicals (Fortunato 2001; Bessekhouad and Tari 20002). 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 $CuMn_2O_4$ or $ZnMn_2O_4$ in aqueous solutions containing S^{2-}/ SO_3^{2-} will generate hydrogen photochemically (Bessekhouad and Tari 20002). Their narrow energy band gap and relative inertness toward photo corrosion make them attractive materials in photoelectrocatalytic systems. Solid solutions such as $Zn_{1x}Ni_xMn_2O_4$ and $ZnFe_2O_4$ are used to convert H_2S wastes to less hannful products namely polysulfides with a gain of storable form of power (hydrogen) (Gautier and Brenet 1984; Lu and Jianjun 1992). The spinel with a relatively small band gap, especially nanometer sized $ZnFe_2O_4$, is a potentially useful solar energy material for photocatalytic conversion and photochemical hydrogen production from water (Yuan et al 1998; De Harrt and Blasse 1985), whose advantages are to absorb visible light and to not be sensitive to photoanodic corrosion. Nanocomposites of $ZnFe_2O_4$ and TiO_2 with useful characteristics making them suitable for far reaching applications in photocatalysis. $ZnFe_2O_4/TiO_2$ nanocomposite is a more effective photocatalyst for the photodegredation of phenol than $Ti0_2$ alone (Fortunato et al 2001). 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.

1.2 Objectives

- To prepare ferrites catalysts (Fe_3O_4, $NiFe_2O_4$, $ZnFe_2O_4$, $BaFe_2O_4$, $CaFe_2O_4$) according to co-precipitation technique.
- To characterize ferrites catalysts by FT-IR spectroscopy.

- To study the catalytic activity of the ferrites were prepared heterogeneous catalysts for the Friedel-Crafts benzaylation reaction of xylene with benzyl chloride.

CHAPTER TWO

EXPERIMENTAI

2. Experimental

2.1 Chemicals & Lab wares

Ferrous sulphate heptahydrate, $FeSO_4.7H_2O$, (Min. assay 98%, Prabhat chemicals).

Barium (II) chloride, $BaCl_2$, (Min. assay 96%, Prabhat chemicals).

Hydrochloric acid HCl, Density 1.18 g/Cm^3, Min. assay 35-38%, Loba chemie Pvt. Ltd, India.

Potassium hydroxide, KOH, Min. assay 85%, Scott science, UK.

Potassium nitrate, KNO_3, Min. assay 87%, Scott science, UK.

Ammonium oxalate monohydrate, $(NH_4)_2C_2O_4.H_2O$, Min. assay 97%, Prabhat Chemicals.

Zinc Sulphate, ZnSO4.

Nickel Sulphate, $NiSO_4$, 98%.

Barium Sulphate, $BaSO_4$.

Calcium Sulphate, $CaSO_4$.

Sulphuric acid solution, H_2SO_4, 10%.

Benzyl chloride, C_7H_7Cl.

Para xylene, C_8H_{10}.

Hot plate stirrer, Bible sterling Ltd, UK. Muffle furnace, Glass wares

2.2 Synthesis of ferrites

2.2.1 Synthesis of magnetite, Fe_3O_4 "$Fe^{II}[Fe_2^{III}O_4]$"

A quantity of 9.265 g of $FeSO_4.7H_2O$ was dissolved in 67 mL of distilled water. Quantities of 0.2827 g of KNO_3 and 5.0269 g of KOH were mixed and dissolved in 33 mL distilled water in a separate beaker. Each solution was heated to about 75 °C then mixed together with vigorous stirring. A thick gelatinous green precipitate was formed. After being stirred at 90 to 100 °C for 10 min, the precipitated turns to finely divided dense black substance. The mixture was cooled to a room temperature then made acidic with little 6M HCl. The precipitate was filtered with help of a filter paper and washed with distilled water until the wash water gave no test for sulfate with $BaCl_2$ solution. The material was dried at 110 °C for more than 1 hour and then weighed.

2.2.2 Synthesis of zinc Ferrite ($ZnFe_2O_4$)

A mixture of 6.214g of $ZnSO_4$, and 6.95 g of $FeSO_4.7H_2O$ and 1 mL of 10% H_2SO_4 was dissolved in 50 mL of distilled water. A quantity of 5.5 g of $(NH_4)_2C_2O_4.H_2O$ was dissolved in 75 mL of warm distilled water. The solution was heated to about 75°C and while stirring vigorously, the oxalate solution was taken and then added to the metal sulfate solution. The mixture was stirred while maintaining the temperature at about 90 to 95 °C for about 5 min. The yellow mixed oxalate precipitate was filtered with help of a filter paper and washed with distilled water until sulfate was no longer detected in the wash (using $BaCl_2$ solution). The oxalate precipitate was dried for one hour at 110 °C then transferred to a porcelain crucible. The crucible was placed and calcined in a muffle at about 700 °C for 3 hours, then allowed to cool to a room temperature and weighed

$$Zn^{+2} + 2Fe^{+2} + 3C_2O_4^{-2} \rightarrow ZnFe2\ (C_2O_4)_3$$

$$ZnFe_2\ (C_2O_4)_{3\ (\Delta)} \rightarrow ZnFe_2O_4 + 2CO_2 + 4CO$$

2.2.3 Synthesis of Nickel Ferrite ($NiFe_2O_4$)

A mixture of 6.219 g of $NiSO_4$, and 6.95 g of $FeSO_4.7H_2O$ and 1 mL of 10% H_2SO_4 was dissolved in 50 mL of distilled water. A quantity of 5.507 g of $(NH_4)_2C_2O_4.H_2O$ was dissolved in 75 mL of warm distilled water. The solution was heated to about 75°C and while stirring vigorously, the oxalate solution was taken and then added to the metal sulfate solution. The mixture was stirred while maintaining the temperature at about 90 to 95 °C for about 5 min. The yellow mixed oxalate precipitate was filtered with help of a filter paper and washed with distilled water until sulfate was no longer detected in the wash (using $BaCl_2$ solution). The oxalate precipitate was dried for one hours at 110 °C then transferred to a porcelain crucible. The crucible was placed and calcined in a muffle at about 700 °C for 3 hours, then allowed to cool to a room temperature and weighed.

2.2.4 Synthesis of barium Ferrite ($BaFe_2O_4$)

A mixture of 6.218g of $BaSO_4$, and 6.95 g of $FeSO_4.7H_2O$ and 1 mL of 10% H_2SO_4 was dissolved in 50 mL of distilled water. A quantity of 5.5 g of $(NH_4)_2C_2O_4.H_2O$ was dissolved in 75 mL of warm distilled water. The solution was heated to about 75°C and while stirring vigorously, the oxalate solution was taken and then added to the metal sulfate solution. The mixture was stirred while maintaining the temperature at about 90 to 95 °C for about 5 min. The yellow mixed oxalate precipitate was filtered with help of a filter paper and washed with distilled water until sulfate was no longer detected in the wash (using $BaCl_2$ solution). The oxalate precipitate was dried for one hour at 110 °C then transferred to a porcelain crucible. The crucible was placed and calcined in a muffle at about 700 °C for 3 hours, then allowed to cool to a room temperature and weighed.

2.2.5 Synthesis of calcium Ferrite ($CaFe_2O_4$)

A mixture of 6.221g of $CaSO_4$, and 6.95 g of $FeSO_4.7H_2O$ and 1 mL of 10% H_2SO_4 was dissolved in 50 mL of distilled water. A quantity of 5.5g of $(NH_4)_2C_2O_4.H_2O$ was dissolved in 75 mL of warm distilled water. The solution was heated to about 75°C and while stirring vigorously, the oxalate solution was taken and then added to the metal sulfate solution. The mixture was stirred while maintaining the temperature at about 90 to 95 °C for about 5 min. The yellow mixed oxalate precipitate was filtered with help of a filter paper and washed with distilled water until sulfate was no longer detected in the wash (using $BaCl_2$ solution). The oxalate precipitate was dried for one hour at 110 °C then transferred to a porcelain crucible. The crucible was placed and calcined in a muffle at about 700 °C for 3 hours, then allowed to cool to a room temperature and weighed.

2.3 Ferrites Characterizations

2.3.1 Fourier Transform Infra-Red spectroscopy

Fourier Transform Infra-Red (FT-IR) data of (Ni-Fer), (Zn-Fer), (Ca-Fer), (Ba-Fer) and (Fe-Fer) were obtained using (Shimadzu, Japan) 8400S FT-IR spectrometer in the wave number range of 400-4000 cm^{-1}, with KBr discs. The KBr disk was prepared at weight ratio of KBr (spectral grade) to ferrite samples of about 20:1.

2.4 Catalytic benzylation reaction

All catalytic benzylation reaction were carried out in round bottom flask (250 mL) equipped with a reflux condenser. The temperature of the reaction vessel was maintained constant 90 °C using prafine oil bath. The reaction were conducted under atmospheric pressure.Typically,3ml of benzyl chloride and 22ml of Para xylene were added to 0.1 g of the catalyst which had been activated one hour at 100 °C.

The reaction mixture was maintained for 3 hour at the predetermined temperature. The sample for analysis was withdrawn from the reaction mixture and analyzed by Gas Chromatography.

2.5 Gas Chromatography (GC) analysis

Gas chromatographic analysis was performed using GC chromatograph equipped with FID detector and capillary column.

Brand: GC 2010

Column type: capillary column BD-210

GC conditions

Column: non polar or intermediate.

Initial temperature: 90˚C.

Initial time: 0 mint.

Ram: 10˚C/mint.

Final temperature: 220˚C.

Final time: 5 mint.

Injector temperature: 250˚C.

Detector temperature: 250˚C.

Carrier gas: Nitrogen.

Flow rate of nitrogen gas: 3ml/mint.

Chapter three

Results and discussion

3.1. Catalyst Characterization

3.1.1. Fourier Transform Infrared Spectroscopy

FT-IR absorption spectra of ferrites samples prepared with surfactant-assisted methods which were recorded in the range of 400-4000 cm-1. On the bases of literature data, in the range of 1000-100 cm^{-1}, the FT-IR bands of solids are usually assigned to vibration of ions in the crystal lattice. In all spinels and particularly in ferrites, two main broad metal oxygen bands are seen in the FT-IR spectra. Therefore the highest one, observed at ν_1 = 600-550cm^{-1}, corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site, (M_{tetra}-O), whereas the lowest band, that observed at ν_2 = 450-385 cm^{-1} is assigned to octahedral metal stretching vibration (M_{Octa}-O). Figure (1-5), shows a difference in the positions and area of ν_1 and ν_2 absorptions bands that may be due to the changed conditions of formation of samples by surfactant assisted process. Because, the positions and intensities of the bands depends strongly on the methods and conditions of preparation. The IR absorption band about 3400 cm^{-1} and weak band about 1600 cm^{-1} are assigned to stretching vibrations of bonded –OH and H–O–H of adsorbed water hydroxyl ions and 1100cm^{-1} to sulphates ions (SO_4) while bands about 1400 cm^{-1} and 882 cm^{-1} may be due to presence of sulphone impurity present in the material.

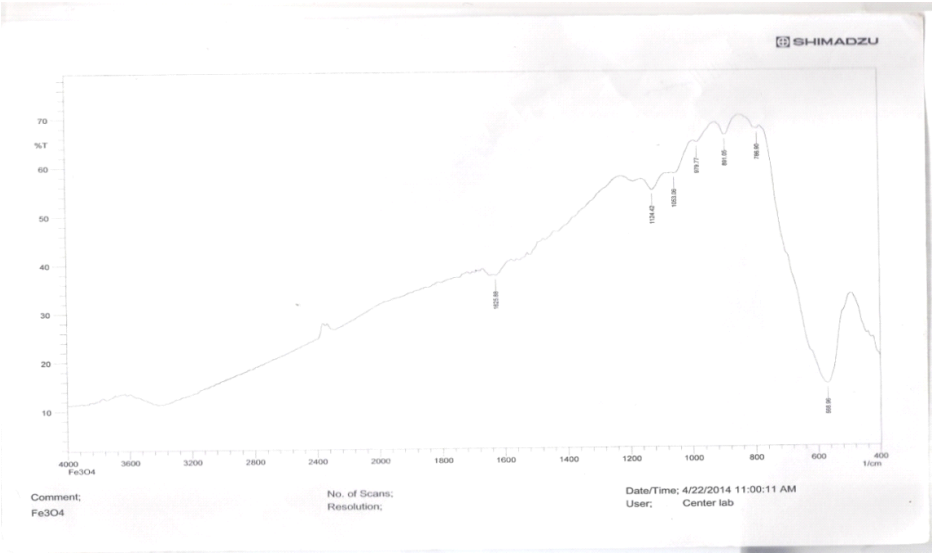


Figure 3.1: FT-IR spectra of the prepared iron ferrite powders

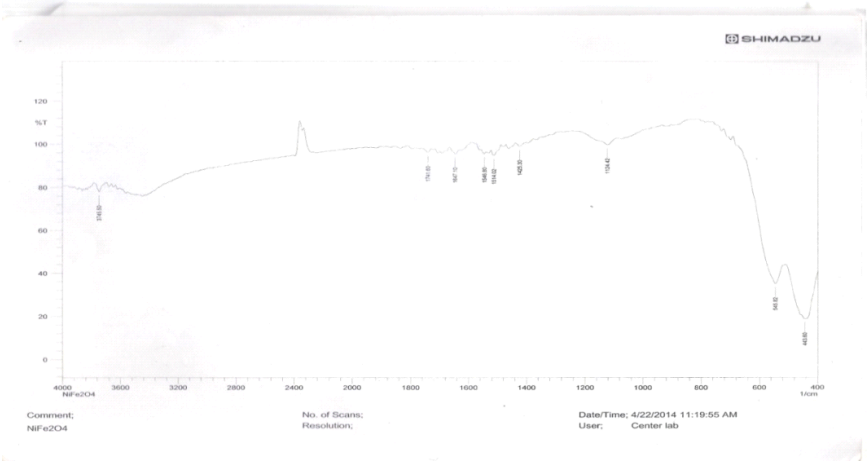


Figure 3.2: FT-IR spectra of the prepare nickel ferrite powders.

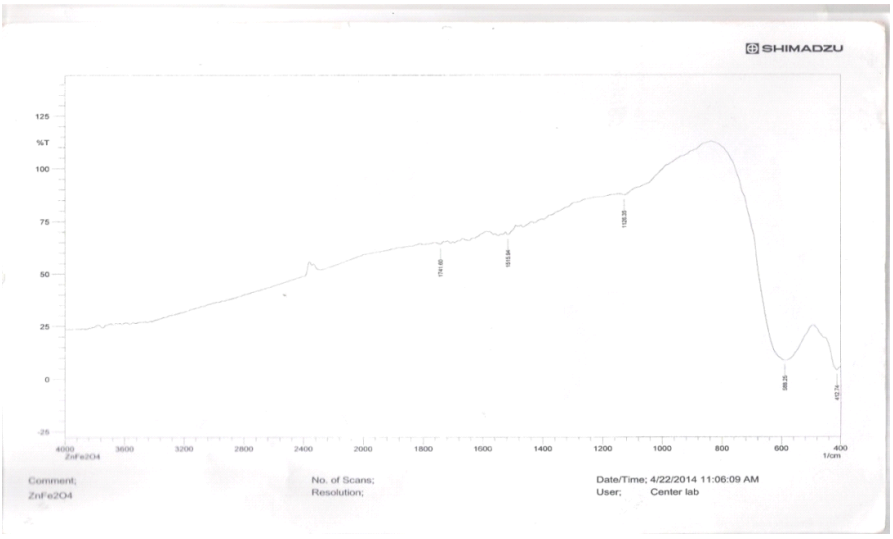


Figure 3.3: FT-IR spectra of the prepare zinc ferrite powders.

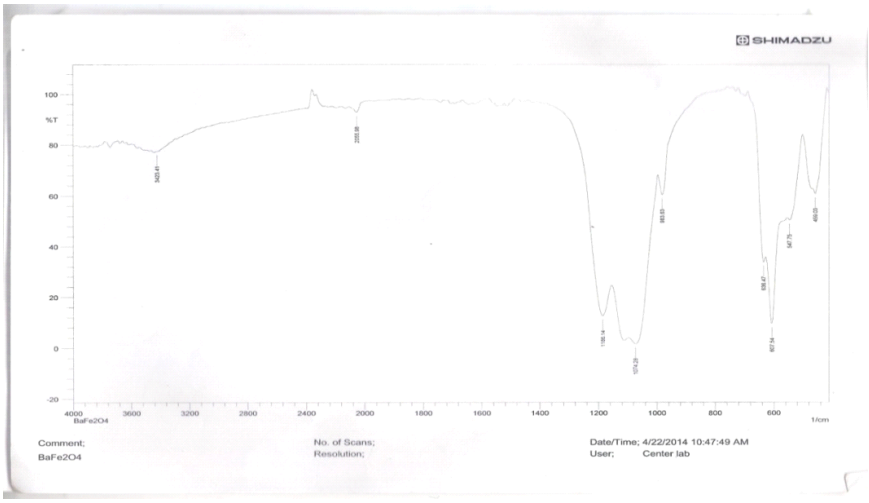


Figure 3.4: FT-IR spectra of the prepare barium ferrite powders.

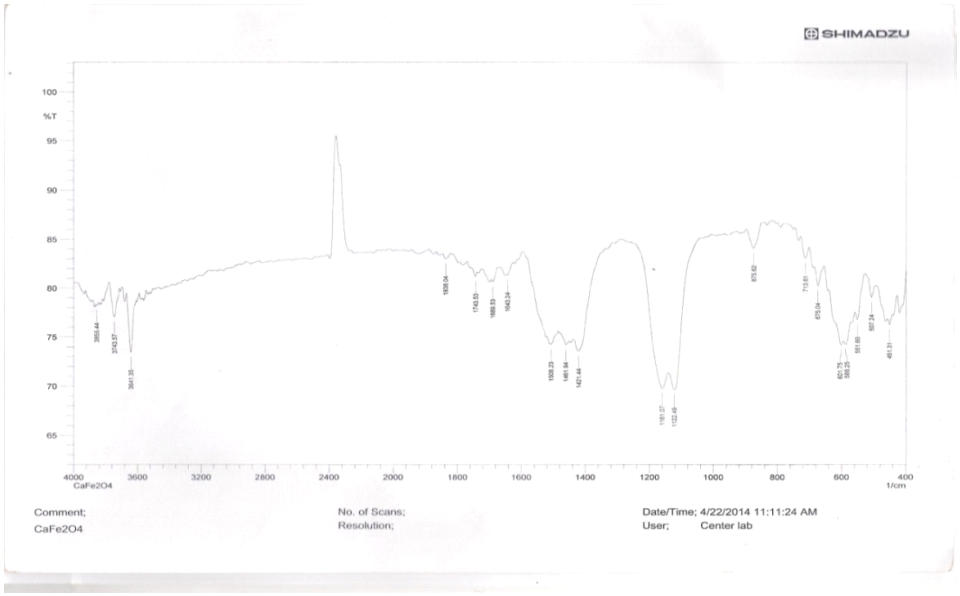
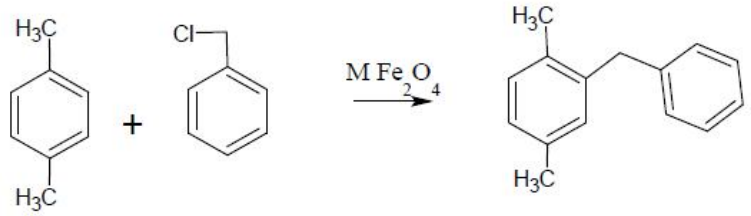


Figure 3.5: FT-IR spectra of the prepare calcium ferrite powders.

3.2. Catalyst Reaction

The liquid phase benzylation of p-xylene was conducted over the synthesized ferrite catalysts at 90˚C using benzylchloride as benzylating agent. The reaction was schematically illustrated in Scheme 3.1.



Scheme 3.1: Schematic illustration for the bezylation of p-xylene with benzylchloride over ferrite catalysts.

The results of the bezylation reactions are listed in Table 3.1. The products of this reaction were detected by GC chromatograph and the result is illustrated in Figures 3.6 – 3.12.

Table 3.1: The benzylation of p-Xyl with benzyl chloride at 90 C over ferrite catalysts.

Catalysts	Conversion of BC (%)	Selectivity of benzylated xylene (%)
Fe_3O_4	100	100
$NiFe_2O_4$	100	100
$BaFe_2O_4$	100	100
$CaFe_2O_4$	100	100
$ZnFe_2O_4$	_	_

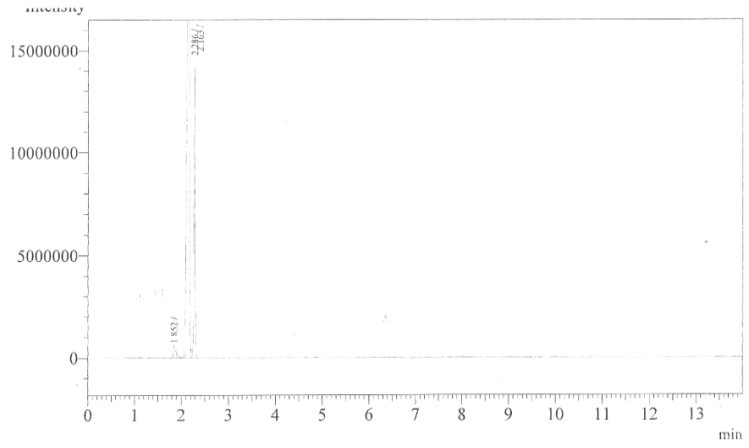


Figure 3.6: The chromatogram of the p-xylene.

From Figure 3.6, it is obvious that the *p*-xylene used in the reaction is not pure and rather associated with the others two xylene isomers i.e. *m*-xylene and *o*-xylene. Three signals were detected at the xylene positions. These signals could be assigned to the three isomers. The peak at retention time (rt) 1.9 min indicates the separation of *o*-xylene, whereas, the signal at rt 2.2 min indicates the separation of m-xylene, and the signal at 2.3 indicates the separation of *p*-xylene. The peak observed at rt of 1.8 min indicates the presence of some impurities such as toluene.

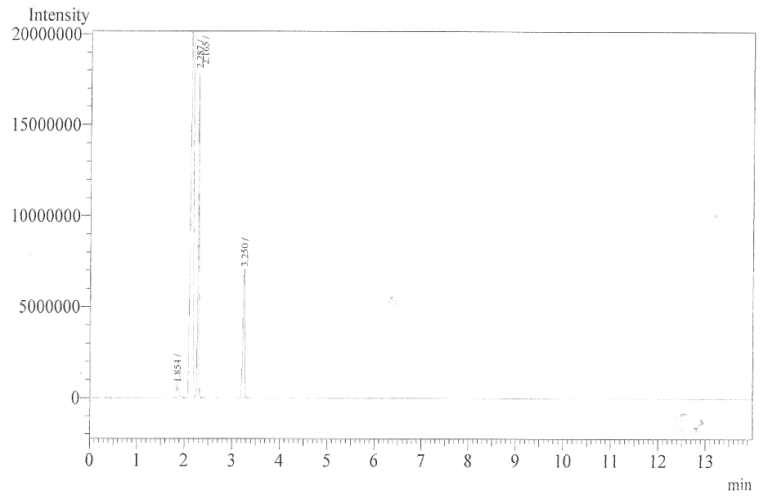


Figure 3.7: The reaction of *p*-xylene with benzyl chloride in the absence of ferrite as catalyst.

From Figure 3.7, beside the three xylene signals at the xylene rt time positions, as illustrated in Figure 3.6, an additional signal at rt of 3.3 min is also observed. This signal is assigned to BC. No other peaks were detected in the position of products i.e. at rt 13-14 min, indicating, no BC conversion occurred at the reaction conditions.

The reaction products for the reaction over Fe_3O_4 catalyst were detected by GC chromatograph and the result is illustrated in Figure 3.8.

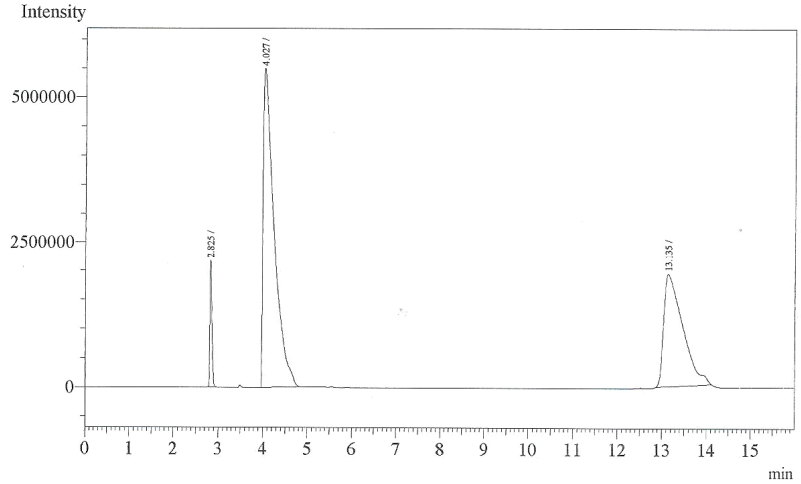


Figure 3.8: The reaction of *p*-xylene with benzyl chloride in the presence of Fe_3O_4 as catalyst.

It is obvious that the BC peak is not observed and a new broad peak appeared at rt centred at 13.1 min indicate the separation of monobenzylated products i.e. 2,5-di methyldiphenylmethane over this catalyst at the reaction conditions. The appearance of broad peak could be due to injection of sample at high concentration or the low efficiency of separating different monobenzylated isomers.

The reaction of p-xylene with benzyl chloride was studied in the presence of $NiFe_2O_4$ as catalyst at 90℃. The reaction products were detected by GC chromatograph and the result is illustrated in Figure 3.9.

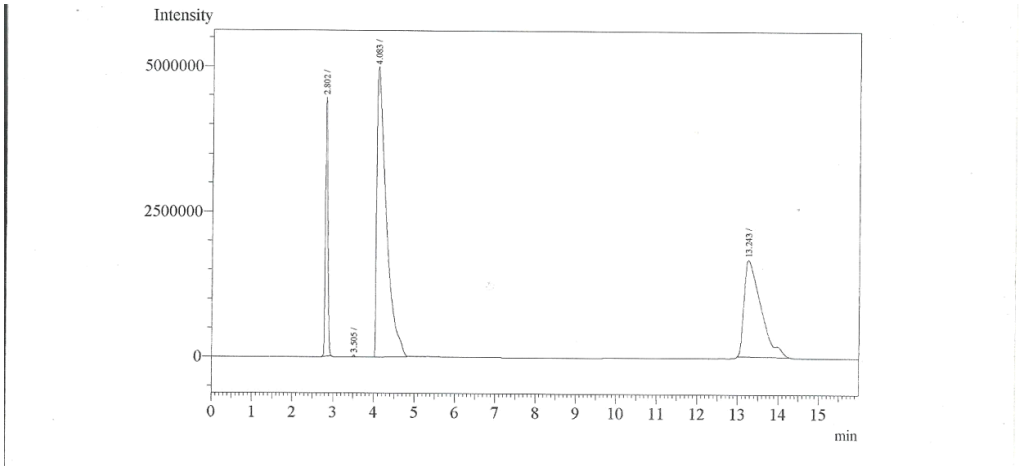


Figure 3.9: The reaction of *p*-xylene with benzyl chloride in the presence of $NiFe_2O_4$ as catalyst.

From Figure 3.9. It is obvious that the BC peak is not observed and a new broad peak appeared at rt centred at 13.3 min indicate the separation of monobenzylated products i.e. 2,5-dimethyldiphenylmethane over this catalyst at the reaction conditions.

The reaction of p-xylene with benzyl chloride was studied in the presence of $BaFe_2O_4$ as catalyst at 90℃. The reaction products were detected by GC chromatograph and the result is illustrated in Figure 3.10.

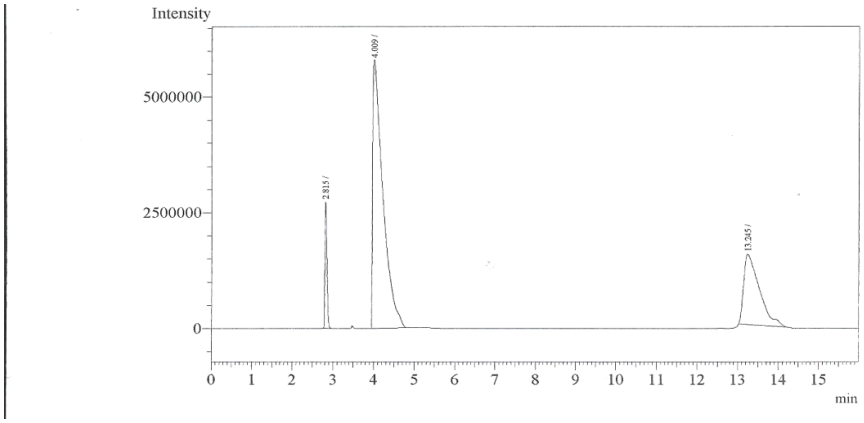


Figure 3.10: The reaction of *p*-xylene with benzyl chloride in the presence of $BaFe_2O_4$ as catalyst.

From Figure 3.10 It is obvious that the BC peak is not observed and a new broad peak appeared at rt centred at 13.2 min indicate the separation of monobenzylated products i.e. 2,5-dimethyldiphenylmethane over this catalyst at the reaction conditions.

The reaction of p-xylene with benzyl chloride was studied in the presence of $CaFe_2O_4$ as catalyst at 90℃. The reaction products were detected by GC chromatograph and the result is illustrated in Figure 3.11.

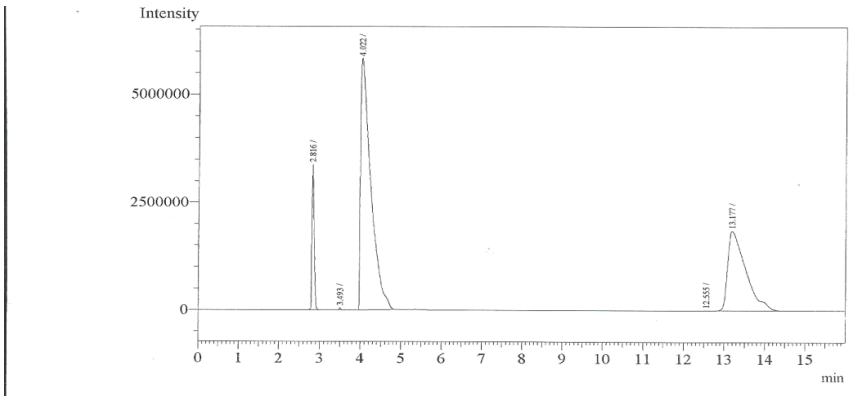


Figure 3.11: The reaction of *p*-xylene with benzyl chloride in the presence of $CaFe_2O_4$ as catalyst.

From Figure 3.11 It is obvious that the BC peak is not observed and a new broad peak appeared at rt centred at 13.2 min indicate the separation of monobenzylated products i.e. 2,5-dimethyldiphenylmethane over this catalyst at the reaction conditions.

The reaction of p-xylene with benzyl chloride was studied in the presence of $ZnFe_2O_4$ as catalyst at 90℃. The reaction products were detected by GC chromatograph and the result is illustrated in Figure 3.12.

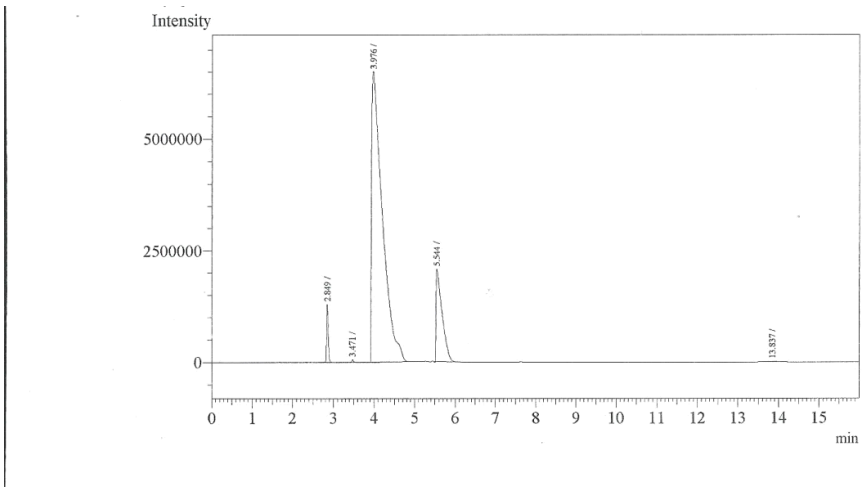


Figure 3.12: The reaction of *p*-xylene with benzyl chloride in the presence of $ZnFe_2O_4$ as catalyst.

From Figure 3.12 signal at rt of 5.5 min is observed. This signal is assigned to BC. No other peaks were detected in the position of products i.e. at rt 13-14 min, indicating, no BC conversion over this catalyst at the reaction conditions.

Chapter Four

Conclusion and Recommendations

4.1. Conclusion

Many ferrite materials were synthesized from simple salts precursors. The synthesized ferrite material included calcium ferrite (Ca-Fer), barium ferrite (Ba-Fer), nickel ferrite (NiFer), zinc ferrite (Zn-Fer) and iron ferrite (Fe-Fer). The synthesized ferrite materials were characterized by FT-IR and showed the Fe-O and M-O peaks. The catalytic activity of ferrite was tested in the benzylayion of xylene employing benzyl chloride as the alkylation agent at a reaction temperature of 90 C. In general the ferrite catalysts showed very high catalytic performance in this reaction for production of benzylated xylene except zinc ferrite (ZnFer). Only a product of 2, 5- di methyldiphenylmethane was detected, however, the broadening of the peak product could indicate the formation of some dimethyldiphenylmethane products.

4.2. Recommendation

A more systematic study of the catalytically active of ferrites is needed by considering many reaction parameters such as time, temperature, molar ratio, etc.

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