# Chapter one

## Introduction

### 1.1 Introduction

Catalysis plays a key role in the industrial production of liquid fuels and bulk chemicals. In the last decades the producers of fine chemicals have started to utilise catalytic conversions in their processes. For oil processes heterogeneous catalysts are preferred with one exception, the alkylation reaction for which liquid acids are being used. For the conversion of petrochemicals both homogeneous and heterogeneous catalysts are used. The number of homogeneously catalysed processes has been steadily growing in the eighties and nineties. For fine chemicals a variety of sophisticated homogeneous catalysts are being used and a wide range of catalytic reactions has become indispensable (Leeuwen, 2004).

The term catalysis was coined by Berzelius over 150 years ago when he had noticed changes in substances when they were brought in contact with small amounts of certain species called "ferments". Many years later in 1895 Ostwald came up with the definition that we use until today: A catalyst is a substancethat changes the rate of a chemical reaction without itself appearing into theproducts. This means that according to Ostwald a catalyst can also slow down a reaction. The definition used today reads as follows: A catalyst is a substancewhich increases the rate at which a chemical reaction approaches equilibriumwithout becoming itself permanently involved. The "catalyst" may be added to the reactants in different forms, the catalyst precursor, which has to be brought into an active form ("activated"). During the catalytic cycle the catalyst may be present in several intermediate forms when we look more closely at the molecular level. An active catalyst will pass number of times through this cycle of states; in this sense the catalyst remains unaltered. The number of times that a catalyst goes through this cycle is the turnover number (Leeuwen, 2004). The turnover number (TON) is the total number of substrate molecules that a catalyst

converts into product molecules. The turnover frequency (TOF) is the turnover number in a certain period of time. Substrates are present in larger amounts than the catalyst; in catalytic reactions the ratio of substrate to catalyst is an important figure.

An inhibitor is a substance that retards a reaction. An inhibitor is also present in "catalytic" or sub-stoichiometric amounts. In a radical chain reaction an inhibitor may be a radical scavenger that interrupts the chain. In a metal catalysed reaction an inhibitor could be a substance that adsorbs onto the metal making it less active or blocking the site for substrate co-ordination. A catalytic reaction also involves poison, a substance that stops the catalytic reaction,it may kill the catalyst. The catalyst dies, after which it has to be regenerated wherever possible. In catalytic reactions, the word co-catalystis used to describe a substance that forms part of the catalyst itself or plays another role somewhere in the catalytic cycle (Leeuwen, 2004).

Organometallic catalysts consist of a central metal surrounded by organic (and inorganic) ligands. Both the metal and the large variety of ligands determine the properties of the catalyst. The success of organometallic catalysts lies in the relative ease of catalyst modification by changing the ligand environment. Crucial properties to be influenced are the rate of the reaction and the selectivity to certain products. The following types of selectivity can be distinguished in a chemical reaction: chemoselectivity, when two chemically different functionalities are present such as an alkene and an aldehyde in the example in Figure 1.1 hydrogenation reaction of aldhyde and alkene which both can be hydrogenated.The chemoselectivity tells whether the aldehyde or the alkene is being hydrogenated; or when more than one reaction can take place for the same substrate e.g. hydrogenation or hydroformylation.Whereas, regioselectivity, describes the formation of linear or branched products. As shown in Figure 1.1, the formyl group can be attached to either the primary, terminal carbon atom or the secondary, internal carbon atom.This can lead

respectively to the linear and the branched product.The term diastereoselectivity is also used when the substrate contains a stereogenic centre and this together with the catalyst can direct the addition of dihydrogen in the example to give two diastereomers.
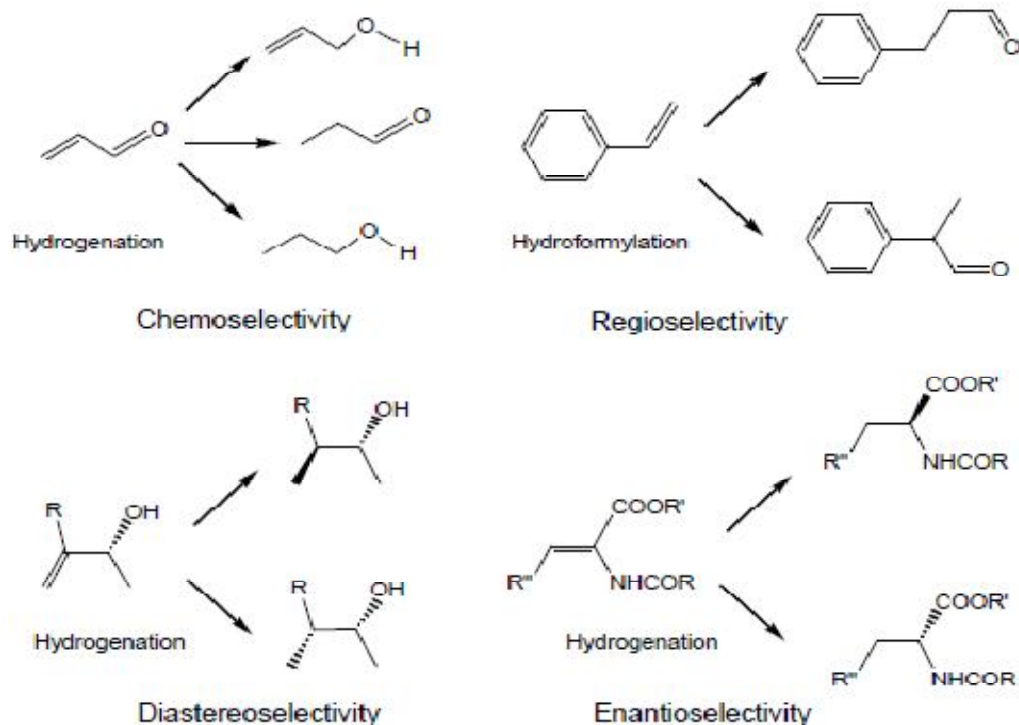


**Figure (1.1): selectivity of chemical conversions**

The term Enantio-selectivity is used when the substrate is achiral, in this instance, the enantio-pure or enantio-enriched catalyst may give rise to the formation of one specific product enantiomer (Leeuwen, 2004). High selectivity is a means to come-up with the following results:

    i. Reduce the waste,

    ii. Reduce the work-up equipment of a plant, and

    iii. Ensure a more effective use feedstocks.

Rate enhancements of many orders of magnitude can be obtained in catalysis, often by very subtle changes. Rates represent a cost factor, higher rates allowing higher space-time yields (kg of product per time and reactor volume) and hence smaller reaction vessels. Higher rates and higher overall catalyst

yields (i.e. mass of product per unit mass of catalyst) reduce the incremental contribution of catalyst costs per unit mass of product generated. In the case of metallocene catalysts for olefin polymerisation for example the higher catalyst cost contribution of these catalysts (around $0.04 per kg of polyolefin) has significantly reduced their impact and ability to displace Ziegler-Natta catalysts (where the catalyst cost contribution is only $0.006-0.011 per kg of polymer). Kinetics are an important part of catalysis, after all, catalysis is concerned with accelerating reactions. In order to describe the effectiveness of a catalyst it needs to compare a catalysed reaction with the non-catalysed reaction. Suppose there is a bimolecular reaction of species A and B with a rate of product P formation (Eq. 1.1).

$$\frac{d[P]}{dt} = k_1 [A][B] \quad 1.1$$

It is difficult to adopt conventional rate laws for the catalysed reactions, but it is reasonable that at least the catalyst concentration will also occur in it (Eq. 1.2).

$$\frac{d[P]}{dt} = k_2[Cat][A][B] \left( \text{ or } \frac{d[P]}{dt} = k_3[Cat][A], \text{etc.} \right) \qquad 1.2$$

Hence the dimension ("the order") of the reaction is different, even in the simplest case, and hence a comparison of the two rate constants is little meaning Comparisons of rates are meaningful only if the catalysts follow the same mechanism and if the product formation can be expressed by the same rate equation. In this instance,the rate enhancements of catalysts relative to another should be considered. If an uncatalysed reaction and a catalysed one occur simultaneously in a system we may determine what part of the product is made via the catalytic route and what part isn't. In enzyme catalysis and enzyme mimics one often compares the $k_1$ of the uncatalysed reaction with $k_2$ of the catalysed reaction.If the mechanisms of the two reactions are the same this may be a useful comparison. A practical yardstick of catalyst performance in industry is the "space-time-yield" mentioned above, that is to say the yield of kg of

product per reactor volume per unit of time (e.g. kg product/m3.h), assuming that other factors such as catalyst costs, including recycling, and work-up costs remain the same. In practice the rate equation may take a much more complicated form than the ones shown above. The rate equation may tell us something about the mechanism of the reaction. Before we turn to "mechanisms" let us repeat how a catalyst works. When refluxing carboxylic acids and alcohols nothing happens until the addition of traces of mineral acid that catalyse esterification. Ethylene can also be stored in cylinders for ages (until the cylinders have rusted away) without the formation of polyethylene, although the formation of the latter is exothermic by more than 80 kjoule/mol. Moreover, a mixture of methanol and carbon monoxide can be heat at 250 °C and 600 bar without acetic acid being formed. After the addition of the catalyst the desired products are obtained at a high rate. A catalyst lowers the barrier of activation of a reaction, i.e. it lowers the activation energy. When protons or Lewis acids are the catalysts this description seems accurate, as for instance in a Diels-Alder reaction (Leeuwen, 2004).

## 1.2 Homogeneous catalysis

Homogeneous catalysis, by definition, refers to a catalytic system in which the substrates for a reaction and the catalyst components are brought together in one phase, most often the liquid phase. More recently a narrower definition has become fashionable according to which homogeneous catalysis involves organometallic complexes as the catalysts. As a shorthand notation it will also be used here, but it should be borne in mind that there are many interesting and important reactions employing homogeneous catalysts that are not organometallic complexes. Examples of such systems or catalysts are:

- General acid and base catalysis (ester hydrolysis),
- Lewis acids as catalysts (Diels-Alder reactions),
- Organic catalysts (thiazolium ions in Cannizzarro reactions),
- Porphyrin complexes (epoxidations, hydroxylations),

- Enzymatic processes,
- Coordination complexes (polyester condensations).

Ligand effects are extremely important in homogeneous catalysis by metal complexes. One metal can give a variety of products from one single substrate simply by changing the ligands around the metal centre (Leeuwen, 2004).

By far the oldest homogeneous catalysts are metallo-enzymes, although one might wonder whether a metal complex built into a high-molecular weight protein, encapsulated in a compartment of a cell is truly homogeneous. If the answer is positive it means that homogeneous catalysts are millions of years old. Iron porphyrin complexes will be considered as example for homogeneous active catalysts for oxidation, zinc complexes for decarboxylation reactions and alcohol dehydrogenase, nickel complexes in hydrogenase enzymes for hydrogen activation, cobalt corrin (methylcobalamin) complexes for carbon-carbon bond formation, copper imidazole (from histidine) complexes in hemocyanin, etc (Leeuwen, 2004).

One of the oldest in vitro uses of whole-cells (in contrast with isolated enzymes) is probably yeast for the fermentation of sugars to alcohol, but one cannot exclude the use of other mechanisms for the aging of materials that we do not know about today. A very old catalytic process is the making of sulphuric acid via the so-called "lead chamber process" (~1750) in which nitrogen oxides oxidise sulfur dioxide ($SO_2$) to the trioxide ($SO_3$). Whereas,nitrogen monooxide (NO) is re-oxidised by air to nitrogen dioxide($NO_2$). Thus, $NO_x$ is reoxidised by air and $NO/NO_2$ are the catalysts and since all reside in the gas phase this should be called homogeneous catalysis. From 1870 onwards number of heterogeneous catalytic processes has been found and applied industrially (Rothenberg, 2008).

The first industrially applied catalyst working in solution and employing organometallic intermediates is most likely mercury sulfate, which was used in the nineteen twenties for the conversion of acetylene to acetaldehyde. This involves the addition of water to acetylene and no oxidation is required.

Industrially it is the predecessor of the Wacker chemistry, which uses ethylene for an oxidative conversion to acetaldehyde. This change came about when the coal based economy (coal to acetylene using electric arcs) changed to oil in the 1950's.

A second process that came on stream in the fifties is the oligomerisation of ethylene using cobalt complexes.However, the number of homogeneously catalysed processes remained low in the sixties although four more processes came on stream.These processes are the nickel catalysed hydrocyanation (Dupont), the cobalt catalysed carbonylation of methanol (BASF), cobalt catalysed hydroformylation (Shell) (discovered already in 1938 Ruhrchemie), and the molybdenum catalysed epoxidation of propene (Halcon Corporation). Since the seventies, the proportion of homogeneous catalysts has been increasing with success stories such as that of rhodium catalysed carbonylation of methanol (Monsanto), rhodium catalysed hydroformylation (Union Carbide Corporation using Wilkinson's findings). Shell has higher olefins process, asymmetric hydrogenation to L-DOPA (Monsanto), and ring-opening polymerisation of cyclooctene using tungsten metathesis catalysts (Huels). The majority of the homogeneous processes were developed for bulk chemicals as only products having a sufficiently large volume could justify the expenditure needed for the development of totally new catalysts and the engineering involved. It was only in the nineties that applications in the fine chemicals area took off, utilising the research results of the bulk chemicals area and the large academic effort that had been set up in the meantime (Leeuwen, 2004).

## 1.3 Heterogeneous Catalysis

Heterogeneous catalysis influenced our lives greatly in the 20th century. In 1908, the German chemist FritzHaber succeeded in synthesizing ammonia by feeding $N_2$ and $H_2$ at high pressures over an Osmium catalyst. This discovery was reported by Carl Bosch and Alwin Mittasch at BASF, who tested over 2500 different materials until they found an iron-based compound which was active

enough and cheap enough to serve as a commercial catalyst. The Haber–Bosch ammonia synthesis has become one of the most important chemical processes worldwide, earning Haber the 1918 Nobel Prize in chemistry (Rothenberg, 2008). Nitrogen fixation provided mankind with a much-needed fertilizer, improving crop yields for the world's growing population. Ironically, the same process also provided raw materials for making explosives, strengthening Germany's position in World War I. Mittasch's magnetite catalyst (with some modifications) is still used today on a gigantic scale – a staggering 110 million tons of ammonia was produced in 2005, accounting for 1% of the global energy consumption. The 1930s showed the development of three important types of refinery catalysts, for hydrocarbon cracking, alkylation, and dehydrogenation. Once again, heterogeneous catalysis played a major role in warfare, this time in WWII. Using new cracking and alkylation catalysts, the Allied forces produced higher-octane aviation fuel, which gave the Spitfires superior performance over the Messerschmitts in the famous Battle of Britain (Rothenberg, 2008) similarly, catalytic dehydrogenation of methylcyclohexane supplied both sides with the necessary toluene for making TNT. Another important catalytic process which emerged out of political turmoil was the Fischer–Tropsch synthesis. Germany and Japan had an abundance of coal, but no reliable source of petroleum. The Co/Fe-catalyzed Fischer–Tropsch process converted coal to syngas, further reaction of which gave a liquid mixture rich in $C_5$- $C_{11}$ olefins and paraffins. South Africa also used this process for converting coal during the apartheid period, to compensate for its shortage of petroleum supply. Interestingly, Fischer–Tropsch-type processes are now back in demand, as governments seek sulfur-free fuels and alternatives to petroleum ( (Rothenberg, 2008). Today, heterogeneous catalysis dominate  petrochemicals and the bulk chemicals industry. Not surprisingly, the biggest demand for these catalysts comes from the stricter legislation on sulfur content in diesel and gasoline. Table 4.1 gives some examples of the key processes, catalysts, and products involved.

**Table 1.1: Examples of major industrial processes using heterogeneous catalysis**

| Process | Catalyst | Reactants | Products | End usage |
|---|---|---|---|---|
| Haber–Bosch NH3 | magnetite (Fe) | $H_2$, $N_2$ | $NH_3$ | Synthesis fertilizer, gunpowder, explosives |
| Methanol synthesis | $Cu/ZnO/Al_2O_3$ | CO, $CO_2$, $H_2$ | $CH_3OH$ | bulk chemicals, fuel |
| Fischer–Tropsch | Co, Fe | coal, natural gas | $C_5$ - $C_{11}$ hydrocarbons | automotive fuel |
| Cracking | Clays | long alkanes, $C_{12+}$ | $C_7$ - $C_9$ alkanes | fuel, detergents |
| Alkylation | zeolites, clays, silicates | $C_3$ - $C_5$ alkanes | $C_7$ - $C_9$ isoalkanes | high-octane fuel |
| Dehydrogenation/reforming | $Pt/Al_2O_3$ | alkanes | alkenes | polymers, bulk chemicals |
| Hydrodesulfurization | Co/Mo sulphides | diesel fuel | sulfur-free diesel | automotive fuel |
| Hydrocracking | Pt on zeolites or aluminosilicates | aromatics mixture | saturated hydrocarbon | automotive/aviation fuel |
| Isomerization | H-ZSM-5 zeolites | xylenes, toluene | p-xylene | polymers,bulk chemicals |
| Polymerization | Ti,Ziegler–Natta | ethene | Poly (ethylene) | polymers,bulk chemicals |
| Oxidation | vanadium oxide | xylenes | phthalic acids | polymers |

In the last two decades, with the advancement of green chemistry, heterogeneous catalysis has moved into the fine-chemicals and pharmaceuticals industry as well. Solid catalysts are also used in clean energy applications such as fuel cells, solar energy conversion, and energy storage cycles (Rothenberg, 2008). At first glance, heterogeneous catalysis seems overwhelming. It is the most varied and the most complicated of the three catalysis sub-disciplines, combining physical chemistry, inorganic chemistry, organic and organometallic chemistry, surface science, and materials science. There are numerous books on various aspects of heterogeneous catalysis, several dedicated journals, and over 18000 research papers. Fortunately, these varied applications are based on few fundamental principles. This chapter explains the scientific fundamentals, illustrating them through number of industrial examples. This research will focus only on the physical chemistry and materials science issues, rather than on the engineering aspects. An excellent detailed discussion of the latter is given in the comprehensive handbook by Ertl, Knözinger, and Weitkamp (Rothenberg, 2008)It should be Noted that the distinction between heterogeneous catalysis and homogeneous catalysis or biocatalysis is subjective. A typical enzyme is so much larger than its substrate, and the reaction environment is so different from the surrounding solvent, that it qualifies as a heterogeneous catalyst. Similarly, there are soluble catalysts (e.g., surfactant-stabilized metal nanoparticles ), which are on the borderline between homogeneous and heterogeneous systems. To avoid confusion, this chapter focuses on three cases only: classic gas/solid systems, liquid/ solid systems, and liquid/liquid systems. Reactions involving immobilized organometallic complexes or immobilized enzymes are discussed in Chapters 3 and 5, respectively (Rothenberg, 2008).

Another term in the language of catalysis is texture; this general term referring to a variety of physical characteristics. A simple definition is the detailedgeometry of the void space in the catalyst particles. Essentially, it is manifested in seven measurements. These are:

i. Specific surface area (square meters per gram or square centimeters per gram): the sum of the external and the internal surface areas.

ii. Specific porosity: the accessible pore void space per unit mass.

iii. Pore shape: difficult to describe except in cases of regular structures such as zeolites.

iv. Pore size distribution: the distribution of the pore volume versus the pore size.

v. Mean pore size: either the pore size distribution or the specific porosity divided by the specific surface area. Pores are divided into three categories: macro (30–50 nm), meso (intermediate size), and micro (less than 2 nm).

vi. Shapes and sizes of agglomerates of particles: for example, pellets, granules, and extrudates.

vii. Particle size distribution: for supported metals; sometimes measured from electron micrographs and sometimes calculated from the measured number of surface atoms divided by the total number of atoms; expressed as percent dispersion (%D), percent exposed atoms, or fraction exposed (FE); perhaps the most widely cited data in the literature.

The effects of particle size on catalytic reactions are now well known and in part understood (Notheisz, 2000). Boudart has defined two classes of heterogeneous catalytic reactions: the  first classis structure sensitive, that depend on the particle size catalytic activity occurs ,  on active site  whose populations changes with  the particle size  and active site  is where the chemical action takes place . The second class is structure insensitive reaction are not influenced much  by particle size ,t seem to occur on all exposed atoms and they do not  depend on the nature of the metal atom underneath (Notheisz, 2000).

## 1.4 Ferrites

Ferrites are chemical compounds which are composed of aceramic material and iron oxide as main component (Cullity, 1972).Spinel ferrites are

represented by the formula unit $AB_2O_4$. Most of the spinel ferrites form cubic spinel structure with oxygen anions in fcc positions and cations in the tetrahedral and octahedral coordinated interstitial lattice sites , forming the A and B sublattices (Barbers, 1995).Depending upon the nature (magnetic or non-magnetic ) and distribution of cations among A and B sublattices , spinel ferrites can exhibit properties of different type magnets ,such as ferrimagent,antiferromagnet and paramagnet (Costa, 2006).Soft ferrites are most widely used magnetic materials for low-cost , high-frequency applications.Ferrites are stable and easily manufactured and possess environmental stability (Goldman, 1990).The hard ferrites have gained a great significance in the technology during the last decades .New application were found for these ceramic permanent magnets .In most small dc – motors the wire wound field was replaced by permanent field of hard ferrites ,but the permanent magnets had to meet special requirements and this means that they must have special properties .The variations or tolerances of these magnetic properties were limited partially very narrowly . There, it is necessary to know the correlation between manufacturing parameters and the magnetic properties (Bosh, 1977) .

Catalytic applications include the use of mainly cobalt, nickel, copper, and zinc ferrites, as well as their mixed-metal combinations with Cr, Cd, Mn and sometimes some lanthanides. Core–shell nanostructures with silica and titania are also used without loss of magnetic properties. The ferrite nanomaterials are obtained mainly by wet-chemical sol-gel or co-precipitation methods, more rarely by the sonochemical technique, mechanical high-energy ball milling, spark plasma sintering, microwave heating or hydrothermal route (Boris I. Kharisov, 2014). Catalytic processes with application of ferrite nanoparticles include decomposition (in particular photocatalytic), reactions of dehydrogenation, oxidation, alkylation, C–C coupling, among other processes. Ferrite nano catalysts can be easily recovered from reaction systems and reused

up to several runs almost without loss of catalytic activity (Boris I. Kharisov, 2014) .

## 1.4.1 Nickel ferrite

Nickel ferrite ($NiFe_2O_4$) nanoparticles have been widely studied for their unique magnetic properties which can be influenced by their shape, particle size and their composites with other materials. Nickel ferrite based nanomaterials also have different industrial applications in high frequency devices, power transformers, drugs delivery and gas sensors. To utilize the applications of such magnetic materials, it is important to study the magnetic properties of both bare and coated nickel ferrite nanoparticles in detail (Nadeem K, 2014)

## 1.4.2 Cobalt ferrite

The ferrite nanoparticles have aspinel structure and the general spinel structure is in the form as $AB_2O_4$. Cobalt ferrite ($CoFe_2O_4$) is a partially inverted spinel structure with cobalt atmosphere dominantly in the octahedral sites (Yinyong Sun, 2006) and it is a well-known hard magnetic material.It has been studied in detail due to its high coercivity (5400 Oe), high chemical stability, good electrical insulation, significant mechanical hardness and moderate saturation magnetization (~80 emu/g) at room temperature. However, in the case of $CoFe_2O_4$ nanoparticles, magnetic and electrical properties are much different than those in the bulk form and variation of these properties with the size and synthesis methods have been reported. Since the past decades, various synthesis methods have been used for the preparation of nano-crystalline magnetic materials. These methods include, mechanical-milling, co-precipitation, microwave assisted route, reverse and normal micelles, reflux method, oxidation–reduction method, sol–gel method, micro emulsion method, and thermal decomposition method. There are some advantages and disadvantages during the production processes because of the time consumption, cost, crystallinity and morphology of the nanoparticles. The properties of ferrite

nanoparticles are influenced by composition and microstructure. The addition of impurities induces changes in the defect structure and texture of the crystal, creating significant modifications in the magnetic and electrical properties of these materials (Yu¨ksel K¨ oseo˘ glu, 2012) .

### 1.4.3 Iron ferrite (Magentite)

Magnetite ($Fe_3 O_4$), also called loadstone, is a genuine ferrite and was the first magnetic material known  to the ancient people . Ferrites are unique class of compounds comprising lanthanides and fast transition metal in particular, iron, chromium, and manganese. the general formula is $M`M_2 O_4$ where $\acute{M}$ isadivalent metal such as $Fe^{2+}$ , $Mg^{2+}$ , $Ni^{2+}$ , $Co^{2+}$ , $Zn^{2+}$ , $Cu^{2+}$ and M is atrivalent metal ion such as $Fe^{3+}$ , $Cr^{3+}$ , $Al^{3+}$ , $Mn^{3+}$ (Richa,.2012)

### 1.5 Friedel – Crafts alkylation Reactions

Friedel-Crafts alkylation reaction is anucleophilic substitution reaction, as it involves anucleophilic attack by an aromatic ring on the alkyl group (Morrison, 1973) (Olah, 2003). The first typical Friedel-Crafts alkylation reaction was the reaction of benzene (aromatic) with amyl chloride (alkylating agent)in the presence of $AlCl_3$ to produce amyl benzene.This reaction was exclusively carried out by Charles Friedel and his American collaborator James Mason Crafts in Paris in 1877 (Roberts, 1984).  The most important alkylating agents are alkyl halides, alkenes and alcohols, but many other types of reagents have also been employed (Olah, 2003). The reactivity of Friedel – Crafts alkylation is based on these alkylation agents. For alkyl halides, the reactivity was found to decrease in the order, Allylic ~ benzylic > tertiary > secondary > primary (Smith, 2001)

Alkylation of aromatic compounds is an important area of industrial research. Benzylated aromatics, class of alkylated aromatics, are very useful intermediates in petrochemicals, cosmetics, dyes, pharmaceuticals and many other chemicals industries (Olah, 1964). They are formed by replacement of

hydrogen atom of an aromatic compound by benzyl group derived from benzylating agent by means of a catalyst .This reaction can be illustrated in scheme (1).

$(R)_n$-Ar-H $\quad + \quad C_6H_5-CH_2-X \quad \xrightarrow{\text{catalyst}} \quad (R)_n$-Ar-$CH_2C_6H_5 \quad + \quad HX$
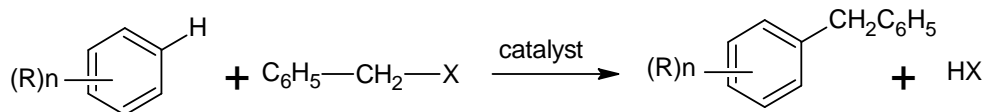
$(R_n)$-Ar-H= Aromatic, $C_6H_5$-$CH_2$-X= Benzylting agent, X= Cl, Br, I, OH

Figure (1): Friedel – Crafts alkylation

## 1.6 Literature review

Manish and Manohar carried out Liquid phase Friedel-Crafts alkylation of benzene with benzyl chloride over various ferrites viz. $CuFe_2O_4$, $NiFe_2O_4$, $CoFe_2O_4$, $ZnFe_2O_4$, and $MgFe_2O_4$. Among the various ferrites $ZnFe_2O_4$ showed the highest activity. These ferrites were prepared by co-precipitation technique. The effect of variation of catalyst, speed of agitation and reaction temperature has been studied. Benzylation of other substrates such as toluene, anisole and chlorobenzene was also studied. The catalyst $ZnFe_2O_4$ was found to be reusable. The acid base properties of the catalyst were studied by cyclohexanol dehydration reaction and the data was correlated with activity (Manish M.S., 2003).

Al, Ga and Fe catalysts supported on silica obtained from rice husk ash (RHA) were synthesized using the sol–gel technique at room temperature and were denoted as RHA–Al, RHA–Ga and RHA–Fe, respectively were studied by Adil Elhag Ahmed and Farook Adam (Adil Elhag Ahmed, 2009). The benzylation of benzene and substituted benzenes with benzyl chloride were studied over the prepared catalysts. RHA–Fe showed excellent activity for the benzylation of benzene, whereas, RHA–Ga gave good selectivity towards diphenylmethane . Almost complete benzyl chloride conversion and about 86% and 80% selectivity to diphenylmethane. However, RHA–Al was found to be

inactive under the reaction conditions studied. Catalytic activity of RHA–Ga with substituted benzenes showed a reverse trend to that of the conventional Friedel–Crafts reaction, i.e. benzene > toluene > ethyl benzene > anisole. (Adil Elhag Ahmed, 2009).

Benzylation of benzene and toluene with benzyl alcohol has been investigated over a series of zeolites and metal modified zeolites by Narender *et al.,* (Narender N., 2006). 5 wt% Ceb, 5 wt% Feb and 5 wt% Wb were found to be good catalysts for the liquid phase benzylation of benzene and toluene. The catalysts were characterized using XRD, FTIR and $NH_3$-TPD.

Highly selective synthesis of diphenylmethane was carried out by Friedel–Crafts benzylation of benzene using benzyl chloride as alkylating agent in the presence of a flow of nitrogen under liquid phase reaction conditions over novel mesoporous $SO_4^{2-}$/Al-MCM-41 catalysts with different Si/Al ratios by M. Selvaraj and T.G. Lee (Selvaraj M., 2006). For these reactions, the influences of various reaction parameters, such as different catalysts, reaction temperature, time, mmol ratios of reactants and recyclability are discussed. With increasing the Si/Al ratios of $SO_4^{2-}$/Al-MCM-41 catalysts from 21 to 83, the conversion of BC and selectivity of DPM decreased because the numbers of Lewis acid sites in $SO_4^{2-}$/Al-MCM-41 catalysts are found to decrease almost linearly with increasing ratios of Si/Al. Further the catalytic results were compared with those obtained by using 0.8N sulphuric acid, different Si/Al ratios of Al-MCM-41, HY, H_, HM and H-ZSM-5 zeolites. From the comparison of the results, $SO_4^{2-}$/Al-MCM-41(21) is found to be a highly active and recyclable heterogeneous catalyst for the highly selective synthesis of DPM. Thus, the selectivity of DPM in $SO_4^{2-}$/Al-MCM-41(21) is higher than that in other $SO_4^{2-}$/Al-MCM-41 (Si/Al = 42 and 83), Al-MCM-41 (Si/Al = 21, 42 and 83), HY, H, HM and H-ZSM-5.

Liquid phase benzylation of benzene by benzyl chloride to diphenylmethane over $FeCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$ supported

on acidic alumina (at 80 **C**) has been investigated by Salavati-Niasari*et al* (Salavati-Niasari M., 2004).The redox property of alumina-supported transition metal chloride seems to play a very important role in the benzene benzylation process. Among the catalyst, the $FeCl_3/Al_2O_3$ showed both high conversation and high selectivity for the benzylation of benzene. These catalysts can also be reused in the benzylation of benzene for several times. A plausible reaction mechanism for the benzene benzylation over the alumina-supported metal chloride catalysts is proposed.

Iron-containing aluminophosphate molecular sieves were synthesized in AEL and AFI structure types by static hydrothermal crystallization by Hentit*et al* (Hentit H., 2007). These materials have been characterized by elemental analysis, X-ray diffraction, scanning electron microscopy, $N_2$ adsorption–desorption, temperature programmed desorption of ammonia ($NH_3$-TPD), and $^{57}$FeMössbauerspectroscopy. Alkylation of benzene and other aromatics by benzyl chloride has been investigated over these solids. Indeed, the iron containing microporous alumino-phosphates showed both high activity and high selectivity for this reaction. The activity of these catalysts for the benzylation of different aromatic compounds is in the following order: benzene > toluene > p-xylene > anisole. More interesting,was the observation that this catalyst can be reused in the benzylation of benzene for several times. Kinetics of the benzene benzylation over these catalysts has also been investigated (Hentit H., 2007)

Iron oxide supported on ordered mesoporous SBA-15 was prepared by Yinyong*et al.,* (Yinyong Sun, 2006) through impregnating the as-synthesized SBA-15 with a methanolic solution of $Fe(NO_3)3.9H_2O$. The impregnated material was characterized by X-ray diffraction (XRD), $N_2$-sorption, transmission electron microscopy (TEM), and UV–vis spectroscopy. Characterization results revealed that iron oxide was present as highly dispersed nanoclusters in the well-ordered mesoporous channels of SBA-15. The supported material still maintained its ordered mesoporous structure similar to SBA-15 and

possessed high surface area, large pore volume and uniform pore size. The benzylation of benzene by benzyl chloride showed that iron oxide nanoclusters-supported SBA-15 was a very active catalyst and able to activate the reactant at relatively low temperature such as 313 K. Moreover, the catalyst could be reused. Such outstanding catalytic performance should be attributed to the presence of active sites from iron oxide nanoclusters, large surface area, open pore channels, and high pore volume. Additionally, the catalyst has found potential applications in other Friedel–Crafts alkylations, especially to large molecular reactions due to its ordered mesoporous structure.

M. Laribi*et al.,* (Laribi M., 2012) synthesized Ni-impregnated nickel over mesoporous silica with different Ni contents has been synthesized and the resulting samples were characterized by elemental analysis, N2 sorpometry at 77 K, XRD, TEM and temperature programmed reduction (TPR). The mesoporous nickel-containing materials showed both high activity and high selectivity for benzylation of benzene. More interesting is the observation that this catalyst is always active and selective for large molecules like naphthenic compounds such as methylnaphthalene and it can also be reused in the benzylation of benzene for several times.

Rice husk ash (RHA) was used to synthesize RHA-Ga, RHA-In and RHA-Fe catalysts by direct incorporation of the respective ions into rice husk ash silica at room temperature. The prepared catalysts were used to catalyze the benzylation of *p*-xylene with benzyl chloride . The catalytic activity increased with a decrease in the *p*-Xylene/benzylchloride molar ratio. However, the selectivity towards the mono-benzylated product decreased. RHA-Feshowed the highest catalytic activity whereas RHA-In and RHA-Ga gave higher selectivity to 2,5-dimethyldiphenylmethane (2,5-DMDPM). The catalytic activity followed the order: RHA-Fe > RHA-In > RHA-Ga. The activity of RHA catalyst towards Xyl isomers was found to follow the order: *o*-Xyl>*m*-Xyl>*p*-Xyl whereas the

selectivity for DMDPM products decreased in the order: *m*-Xyl>*p*-Xyl>*o*-Xyl (Farook Adam, 2008).

Tarek *et al* studied Nanocrystalline $Fe_2O_3$and NiO mesoporous $ZrO_2$supported catalysts were prepared and thermally treated at 500 **C** (Tarek T. Alia, 2014). The efficiency of the catalysts was studied for catalyzing the benzylation of benzene using benzyl chloride as benzylating agent. The pure mesoporous $ZrO_2$ showed only benzyl chloride conversion of 44% after a reaction time of 600 min at 75 **C**. An increase in the conversion of benzyl chloride to 49% was observed after loading 10 wt% of NiO on $ZrO_2$.The conversion was found to increase to 58% with the increase of NiO loading to 20 wt%. However, a drastic increase of conversion was observed after loading 10 wt% $Fe_2O_3$on$ZrO_2$, the conversion reached to 78% under similar reaction conditions. The increase of $Fe_2O_3$loading to20 wt% led to a significant increase in conversion of benzyl chloride to 91%. The study also showed that $ZrO_2$ support maintained the stability of catalytically active $Fe_2O_3$speciesafter six reaction cycles. The enhanced catalytic activity of this catalyst was attributed to the presence of a greater degree of dispersion of $Fe_2O_3$over $ZrO_2$, higher redox potential and a greater degree of accessible surface Lewis acid sites (Tarek T. Alia, 2014).

## 1.6 Objectives

The current study was conducted to fulfil the following objectives:

- To prepare Ni, Co and Fe –ferrite materials (Ni-Fer, Co-Fer and Fe-Fer).
- To characterize the synthesized ferrite materials.
- To study the catalytic activity of the synthesized materials as heterogeneous catalysts for the Friedel-Crafts benzylation reaction of toluene and benzyl chloride.

## Chapter two
## Materials and methods

### 2.1. Materials

Barium Chloride, $BaCl_2$, Min.assay 96%, Prabhat chemicals, India

Ammonium Oxalate mono hydrate, $(NH_4)_2C_2O_4.H_2O$ .Min assay 97%, Prabhat Chemicals, India

Hydrochloric acid, HCl,Assay 35-38%,LobaChemiePVT Ltd, India.

Cobalt (II) sulphate hepta hydrate, $CoSO_4.7H_2O$ ,Park scientific limited , Northampton,UK.

Toluene, $C_7H_8$, Assay >98, Alpha Chemica, India.

Ferrous sulphatehepta hydrate $FeSO_4.7H_2O$, Min. assay 98%,Prabhat chemicals, India.

Nickel (II) Sulphate hexa hydrate, $NiSO_4.6H_2O$,Min. assay 98%,Lobachemie Pvt.Ltd, India.

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

Potassium nitrate, $KNO_3$, Min. assay 85%, Scott science, UK.

Benzyl chloride, $C_7H_7Cl$, Min. assay (GC) 98.5%,KentTN  279xj,England.

n-Octane,$C_8H_{18}$, Min. assay(GC) 99.o%,sd fine-chem limited ,Mumbai .

Praffien oil, SIGMA-ALDRICH.

Hot plate stirrer, Bible sterling Ltd, UK.

Muffle furnace, CARB-OLITE .

All chemicals were of analytical grade and were used directly without further purification.

### 2.2. Methods
### 2.2.1. Synthesis of Iron ferrite, $Fe_3O_4$ (Fe–Fer)

A quantity of 13.8909g of $FeSO_4.7H_2O$ was dissolved in 100 mL of distilled water then 0.4041g of $KNO_3$ and 5.148g of KOH were mixed and dissolved in 50 mL distilled water in separate beaker. Each solution was heated about 75 **C** then the two solutions were mixed together with vigorous stirring, a

thick gelatinous green precipitate was formed. After being stirred at 90 to 100 $C$ for 10 min, the precipitate 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 through filter paper and washed with distilled water until the water gave no test for sulphate with $BaCl_2$ solution. The material was dried at 110 $C$ for more than 1 hour then weighed and labelled as Fe–Fer.

### 2.2.2. Synthesis of Nickel ferrite (Ni–Fer)

A mixture of 2.6286 g of $NiSO_4.6H_2O$ and 5.5604 g of $FeSO_4.7H_2O$ and 1 mL of 10% $H_2SO_4$ was dissolved in 100 mL of distilled water. A quantity of 4.2633 g of $(NH_4)_2C_2O_4.H_2O$ was dissolved in 150 mL of warm distilled water. The solution was heated to about 75 $C$ and while stirring vigorously, the oxalate solution was added to the metal sulfate solution. The mixture was stirred while maintaining the temperature at about 90–95 $C$ for about 5min. The yellow mixed oxalate precipitate was filtered through normal 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 2 hours at 110 $C$ then transferred to aporcelain crucible. The crucible was placed and calcined in amuffle at about 700 $C$ for 3 hours, then allowed to cool in aroom temperature then weighed and labelled as Ni-Fer.

### 2.2.3. Cobalt Ferrite (Co–Fer)

Amixture of 2.811 g of $CoSO_4.6H_2O$ , 5.563 g of $FeSO_4.6H_2O$ and 1mL of 10% $H_2SO_4$ was dissolved in 100 mL of distilled water. Aquantity of 4.2635 g of $(NH_4)_2C_2O_4.H_2O$ was dissolved in 150 mL of warm distilled water. The solution was heated to about 75 $C$ and while stirring vigorously, the oxalate solution was added to the metal sulfate solution. The mixture was stirred while maintaining the temperature at 90 - 95 $C$ for about 5 min. The yellow mixed oxalate precipitate was filtered  through normal filter paper  and washed with distilled water until sulfate was no longer detected in the wash (using $BaCl_2$ solution).The mixed precipitate was dried for two hours at 110 $C$ then transferred to a

porcelain crucible and heated in a muffle furnace at 700 **C** for 3 hours. The material was allowed to cool at room temperature then weighed and labelled as Co-Fer.

## 2.3. Catalyst characterization

The prepared catalysts were characterized by Fourier Transform Infra-Red (FT-IR) Spectrometric analysis, atomic absorption spectroscopy AAS

### 2.3.1. FT-IR Spectroscopic Analysis

Fourier Transform Infra –Red (FT- IR) data of (Co-fer ),(Ni-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 disk was prepared at weight ratio of KBr (spectral grade) to ferrite samples of about 20:1.

### 2.3.2. AAS Spectroscopic Analysis

An atomic absorption (AAS) analysis was conducted for the aqueous solutions of ferrite samples using Varian model spectra (220 FS). The aqueous solution of any ferrite sample was obtained by digesting about 1g of a solid sample in alittle quantity of concentrated hydrochloric acid and nitric acid. The resultant acidic solution was diluted to 100 mL with distilled water.

## 2.4. Catalytic Benzylation Reactions

All catalytic benzylation reactions were carried out in a magnetically stirred two necks round-bottom flask equipped with a reflux condenser. The temperature of the reaction vessel was maintained constant using an oil bath. The reactions were conducted under atmospheric pressure. Typically, 21.0 mL of toluene and 1.0 mL of n-octane (internal standard) were added to a quantity of 0.1g ferrite catalyst, which had been activated for 2 hours at 100 **C.** The reaction mixture was maintained for 30 min at the predetermined temperature. This was followed by the injection of 4.0 mL of benzyl chloride to obtain the required benzylcloride\toluene molar ratio of 5:1.Reactions with molar ratios of 10:1,

15:1 and 20:1 were also studied, keeping the total volume of the reaction mixture at 25.0 mL.

To monitor the extent of the reaction, very small portion of the reaction mixture was periodically withdrawn and analysed by a GC (Shimadzu GC 2010). The conversion of benzyl chloride and selectivity of methyl diphenyl methane were calculated. To attain the maximum conversion and selectivity, the reaction of benzyl chloride and toluene was optimized by varying the reaction time, temperature, molar ratio of benzyl chloride to toluene and the amount of catalyst.

## 2.4.1. Gas Chromatography (GC)

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 were, Injector temperature: 250 **C**; Detector temperature: 250 **C**. Column Oven program: Initial temperature 90 **C** hold 3 min (90-220 **C** at 20**C**/min, hold 5min); Carrier gas: Nitrogen; Injection volume: 0.2μL; Split ratio: 50:1.

## Chapter three

## Results and discussion

### 3.1. Catalyst characterization

### 3.1.1. FT-IR spectroscopy of synthesized ferrites

Figure 3.1 shows the FT-IR spectrum of synthesized iron ferrite in the range of 400 –4000cm$^{-1}$. The characteristic bands at 3822 cm$^{-1}$ and 3693cm$^{-1}$ are due to O-H stretching vibration of physically absorbed water. The peak at 2365 cm$^{-1}$ is due to O=C=O atmospheric $CO_2$, whereas the peak at 1641cm$^{-1}$ and 1474cm$^{-1}$ is assigned to O-H bending vibration of physically adsorbed water. Many peaks assigned to M-O bonds were observed in the range of 1000 – 400cm$^{-1}$. The peak at627cm$^{-1}$ is due to Fe-O band that matches well with the characteristic peak of iron ferrite (Ming. Ma, 2003).

Figure 3.2 shows the FT-IR spectrum of the synthesized cobalt ferrite in the range of 400 – 4000cm$^{-1}$. The characteristic bands at 3795 cm$^{-1}$are due to O-H stretching vibration of physically absorbed water, whereas the peak at 1633 cm$^{-1}$ and 1474cm$^{-1}$ are attributed to O-H bending vibration of physically adsorbed water.The peak at 582.79cm$^{-1}$ is due to  Co-O of Co-Fer sample, these results were found consistent to those reported by researchers (Pradeep, 2006) (Waldron, 1995).

Figure 3.3 shows the FT-IR spectrum of synthesized Nickel ferrite (Ni-Fer) in the range of 400 – 4000cm$^{-1}$. The characteristic band at 3495 cm$^{-1}$is due to O-H stretching vibration of physically absorbed water. Whereas the peak at 1632cm$^{-1}$ and 1405 cm$^{-1}$ are assigned to O-H bending vibration of physically adsorbed water.The peak at 593 cm$^{-1}$ is due to Ni-O bond  of   Ni-Fer, this peak was also observed by other researchers for analogous materials (Waldron, 1995).
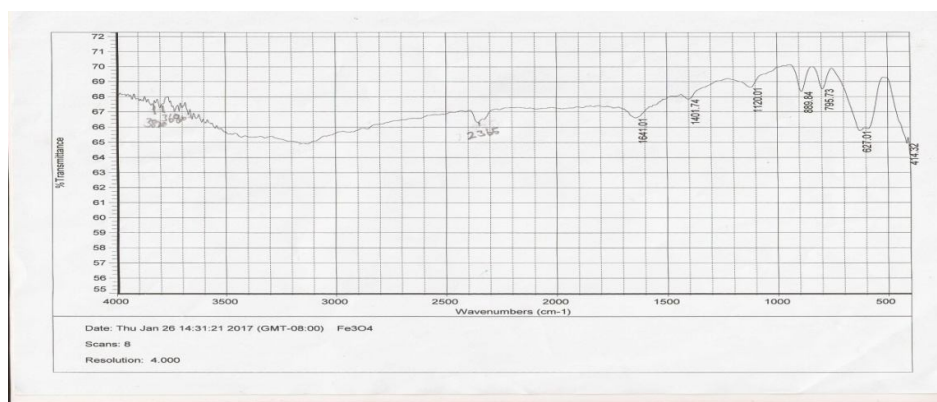
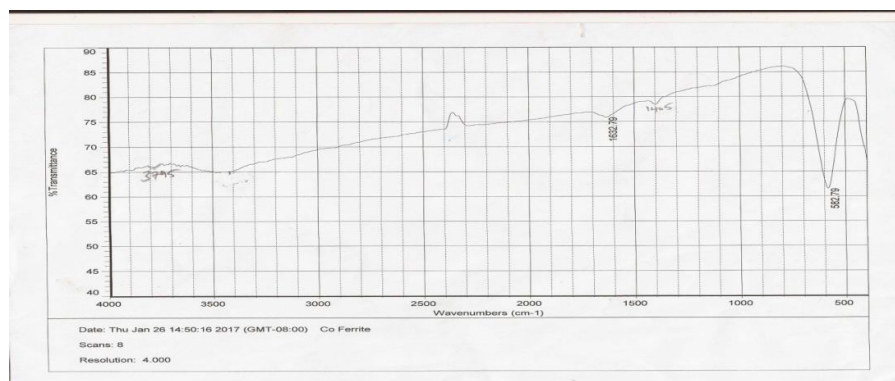**Figure (3.1): The FT-IR spectrum of synthesized iron ferrite (Fe-Fer)**



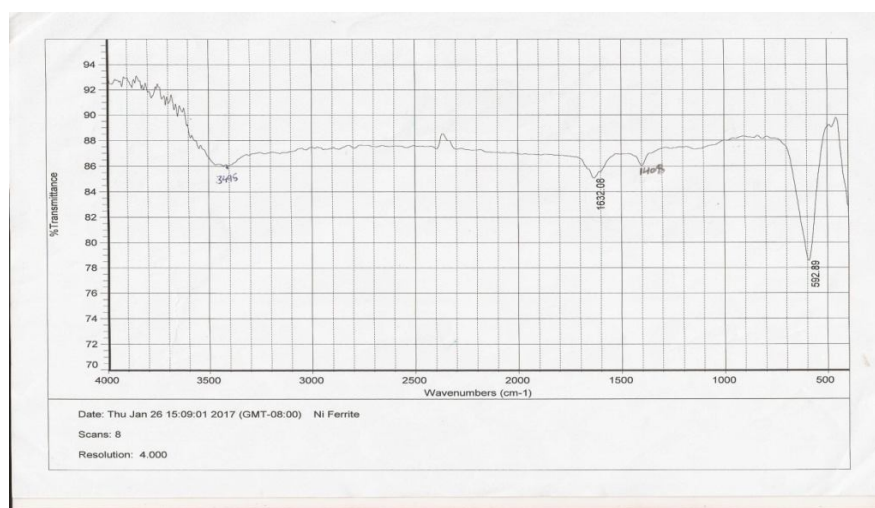**Figure (3.2): The FT-IR spectrum of cobalt ferrite (Co-Fer)**



**Figure (3.3): The FT-IR spectrum of Nickel ferrite (Ni-Fer)**

### 3.1.2. Atomic absorption spectroscopy (AAS) analysis

Table 3.1 shows the AAS analysis results of all ferrites samples. For Ni-Fer the experimental percentages of $Ni^{2+}$, $Fe^{3+}$ and $O^{2-}$ were found to be 27.21%,43.65% and 29.14%,respectively.Hence by calculating the number of moles for any element, the empirical formula of type $NiFe_{1.7}O_{3.66}$ was obtained. This formula was observed to be closed to the theoretical formula for spinel ferrite, i.e. $NiFe_2O_4$. Table 3.1 also listed the percentages of iron and oxygen for Fe-Fer sample to be 62.61% and 37.39%, respectively. However, the empirical did not resemble the formula of magnetite $Fe_3O_4$, may be caused by the flame temperature in the atomic absorption device, which has changed in the oxidation state for iron. For Co-Fer sample the experimental percentages of $Co^{2+}$, $Fe^{3+}$ and $O^{2-}$were found to be 31.98%, 43.98% and 25.04 %,respectively. Hence the empirical formula of the synthesized Co-Fer was calculated to be $CoFe_{1.6}O_{3.57}$, which is quite close to the theoretical formula "$CoFe_2O_4$"for spinel ferrite.

**Table 3.1: Atomic absorption spectrometric analysis of ferrite samples**

| Samples | Elements % | | |
|---------|------|------|------|
|         | Co   | Ni   | Fe   |
| Co - Fer | 31.98 | - | 43.98 |
| Ni - Fer | - | 27.21 | 43.65 |
| Fe - Fer | - | - | 62.61 |

### 3.2. Catalytic reactions

The liquid phase benzylation of toluene with benzyl chloride was conducted over the activity of the synthesized ferrite catalysts (M-Fer). Various reaction parameters such as reactants molar rations, temperature, catalyst type and catalyst loading were considered to study the catalytic benzylation reaction.

### 3.2.1. Effect of reactants molar ratio

In order to study the effect of molar ratios on the conversion of benzyl chloride for the benzylation of toluene, parameters like temperature and weight

of catalyst were kept constant. The molar ratio of toluene: benzylchloride was varied, i.e. 5:1, 10:1, 15:1and 20:1.The percentages of conversion and selectivity towards2-benzyltoluene are listed in table 3.2.

**Table 3.2: Effect of toluene/benzylchloride molar ratio on the catalytic performance of Ni-Fer(0.1 g) for the benzylation of toluene with benzylchloride at 100 C for 10 min**

| Tol/BC molar ratio | BC conversion (%) | Selectivity of 2- Benzyltoluene  (%) |
|---|---|---|
| 5:1 | 99.01 | 67.22 |
| 10:1 | 94.6 | 44.78 |
| 15:1 | 82.96 | 4.6 |
| 20:1 | NO conversion | - |

Figure 3.4 also depicts the effect of toluene: benzyl chloride molar ratio on the catalytic benzylation reaction at 100 **C**. It is clear that with decreasing toluene/benzyl chloride molar ratio, the catalytic activity of Ni-Fer increases. This could be attributed to the fact that more carbocations were formed due to high concentration of benzyl chloride being in contact with the metal ions on the catalyst surface. The highest conversion of benzyl chloride 99% was obtained by introducing reactants with a molar ratio of 5:1, increasing the molar ratio to 10:1 resulted in a decrease of conversion up to 94.6%. However, further increase in the molar ratio beyond that lead to a significant decrease in a conversion. Zero or no conversion was obtained from the reaction with molar ratio of 20:1 at 10 min.

Figure 3.5 shows the percent selectivity of 2-benzyl toluene product with respect to reaction time. In all cases the selectivity of 2- benzyl toluene decreases as the reaction time and reactants molar ratio are increased 4.6% was registered from the reaction of 15:1 is odd value this could attributed to decrease of volume of benzyl chloride i.e:  low concentration of benzyl chloride (few carbocations were formed which in contact with metal ions on the catalyst surface). Higher

selectivity of 67.22% was registered from the reaction of 5:1 ratio; hence this ratio was selected as an optimum molar ratio.
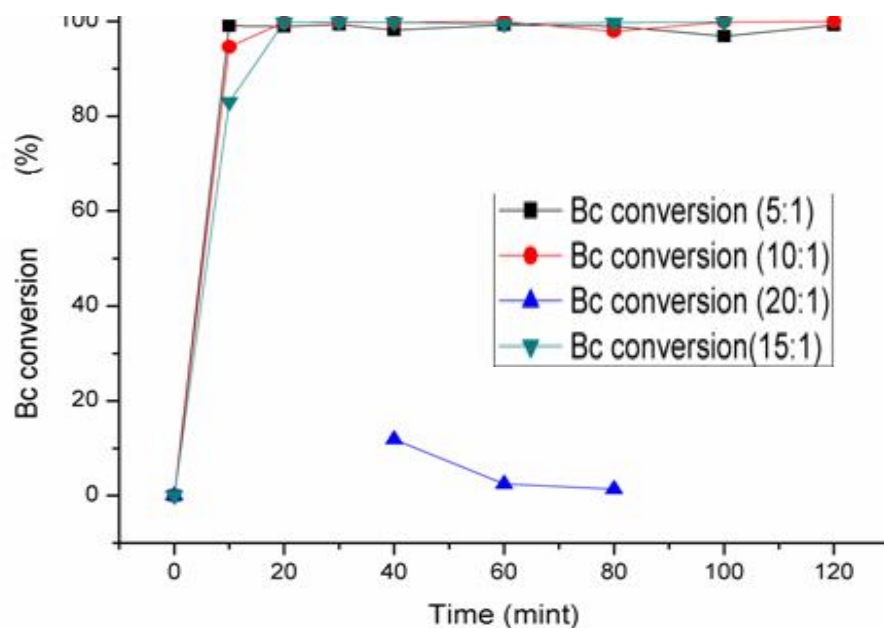


**Figure (3.4): The percentages conversions of benzylchloride for the benzylation of toluene over Ni-Fer catalyst at 100C and various toluene/benzylchloride molar ratios.**
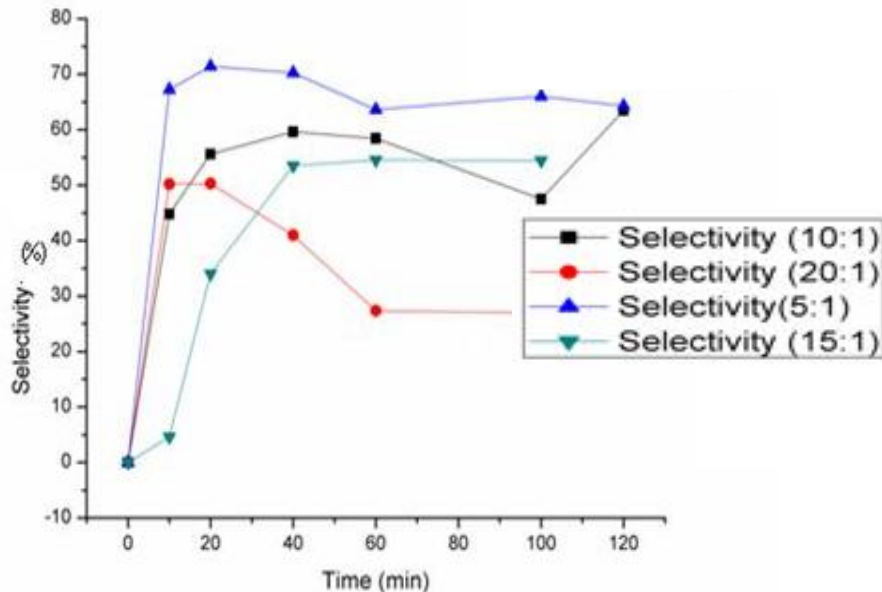
**Figure (3.5): The percentages selectivity of 2- benzyltoluene for the benzylation of toluene with benzylchloride over Ni-Fer catalyst at 100 C and various toluene/benzylchloride molar ratios.**

Figure 3.5 show the percentage selectivity of 2- benzyl toluene with respect to reaction time for the benzylation of toluene over the activity of Ni-Fer catalyst (0.1 g) at 100 **C**. In this figure the selectivity of 2- benzyl toluene decreased as the reaction time increased .For 5:1 molar ratio, the selectivity towards 2-benzyltoluene was the highest at ca.67.22%, Within 10 min. It is clear that with increasing toluene/benzyl chloride molar ratio, the percentage selectivity of 2-benzyltoluene decreases.

### 3.2.2. Effect of temperature

The effect of temperature was studied at 80, 90, 100 and 110 **C** using toluene: benzyl chloride molar ratio of 5:1 (optimum molar ratio) and catalyst weight 0.1g.It is clear from table 3.3 and figure 3.6 that 99.94 of benzyl chloride conversion was reached over 80 **C** and the decrease in conversion with increasing the temperature to 80 **C**.

**Table 3.3: Effect of reaction temperature use 5:1 ratio and (0.1 g) Ni-Fer for the benzylation of toluene for molar ratio (5:1) .**

| Temperature C | BC Conversion % | Selectivity of4-benzyltoluene% |
|---|---|---|
| 80 | 99.94 | 83.36 |
| 90 | 87.45 | 74.08 |
| 100 | 98.91 | 13.29 |
| 110 | 56.89 | 56.53 |

However, there was different in the selectivity towards 4-benzyltoluene in particularly when the temperature was increased above 80 **C**. The decrease in selectivity with increasing the temperature above 80 **C** could be due to isomerisation of 2-benzyltoluene and 4-benzyltoluene as well as the formation of higher benzylated toluene products such as dibenzyltoluene .Considering the temperature was selected as an optimum temperature to study the subsequent parameters.

Figure 3.7 shows the percent selectivity towards 4-benzyltoluene at deferent temperature. At the highest temperature of 110 **C** used in this study, the selectivity for 4-benzyltoluene was the low at ca.56.53%. At 80 **C**, the selectivity reached an optimum value of ca. 83.36%.
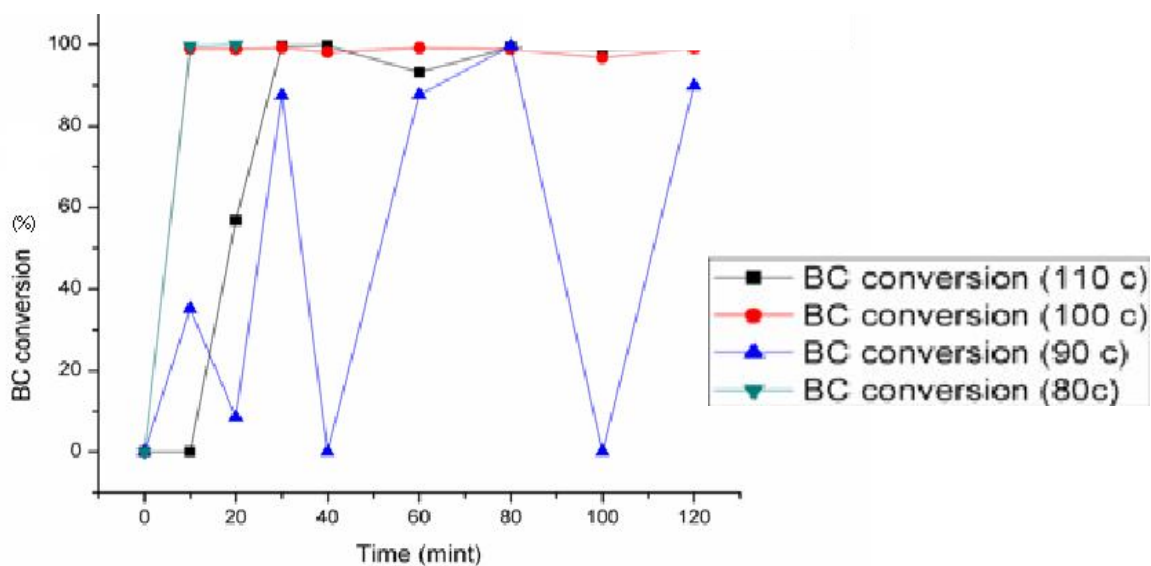
**Figure (3.6): The percentages conversions of benzylchloride for the benzylation of toluene at various temperatures and over Ni-Fer catalyst and toluene/benzylchloride molar ratio of 5:1.**
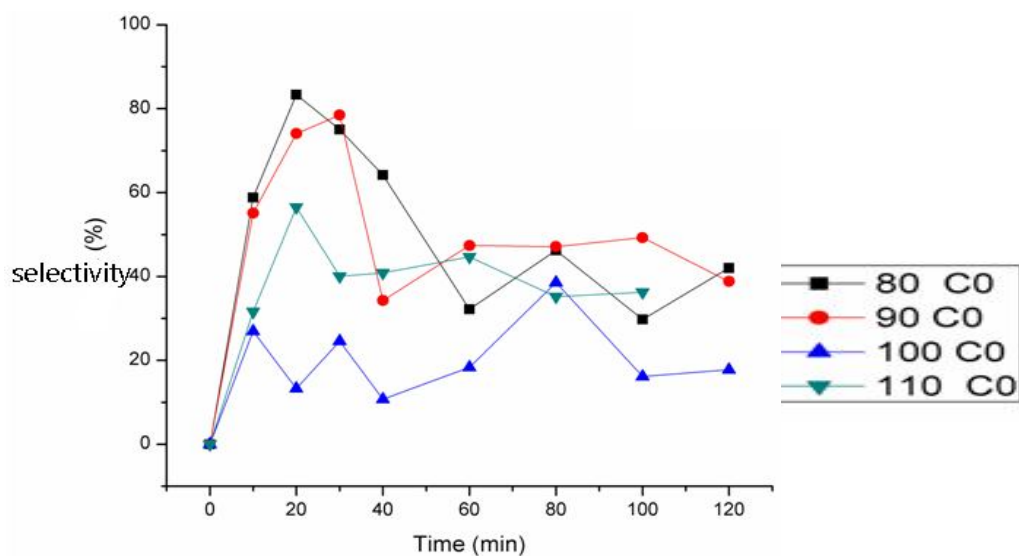


**Figure 3.7: The percentages selectivity towards 4- benzyltoluene for the benzylation of Tol at different temperature over Ni-Fer using Tol/BC reactants molar ratio of 5:1.**

**3.2.3. Effect of catalyst type**

In order to study the effect of various M-ferrite catalysts, the toluene benzylation reaction was conducted over the catalytic activity of Ni-Fer, Co-Fer and Fe-Fer catalysts. The reactions were carried out at the optimum conditions (i.e. at 80 **C** and toluene/ benzylchloride molar ratio of 5:1) using 0.1 g of the catalyst. Figure 3.8 presents the catalytic behaviour of all catalysts. It is interesting to note that the activity of Fe-ferrite was the highest, since almost complete conversion of benzylchloride was observed within 30 min ,much higher activity was observed with Ni-ferrite ,since 99.94%the percentage conversion was achieved within 20 min ,and activity of Co-ferrite was low ,since 30.11%within 20min .Fig 3.9and 3.10 shows the selectivity of 2-benzyltoluene and 4- benzyltoluene with Ni –ferrite was found to be16.6% and 83.36% respectively achieved in 20min and  with Fe-ferrite ca. 25.47 % and 74.53%which was achieved within 20 min while with Co-ferrite catalyst was 51.71 % and 48.49% within 20 min respectively .that is mean the selectivity of first product of different ferrite was increase and another product, the selectivity was decrease. The activity of the metal –ferrite catalysts on the benzyltion reaction of toluene decreases in the following order:Ni-ferrite > Fe –ferrite >Co-ferrite
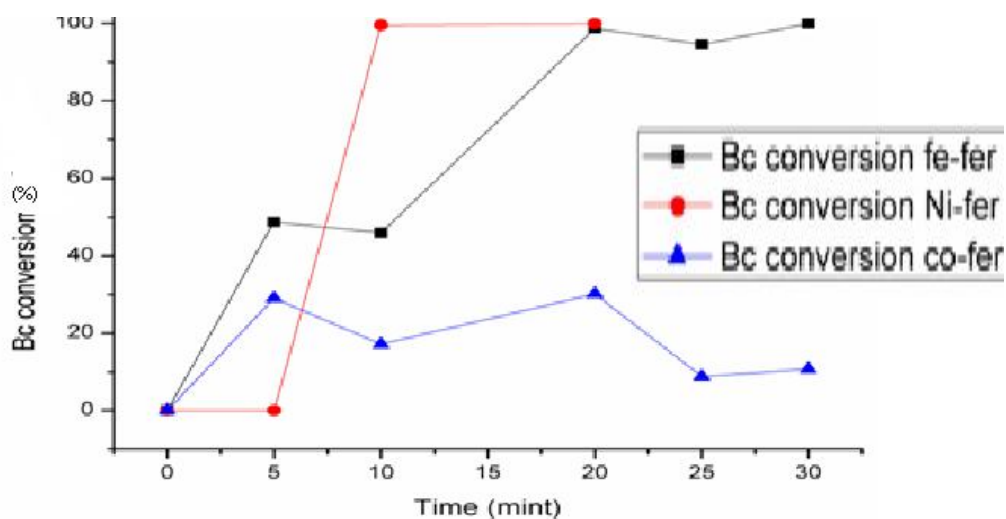
**Figure (3.8): Effect of type of catalyst on conversion % use 5:1 ratio toluene/benzylchlorideand 0.1g weight of catalyst.**
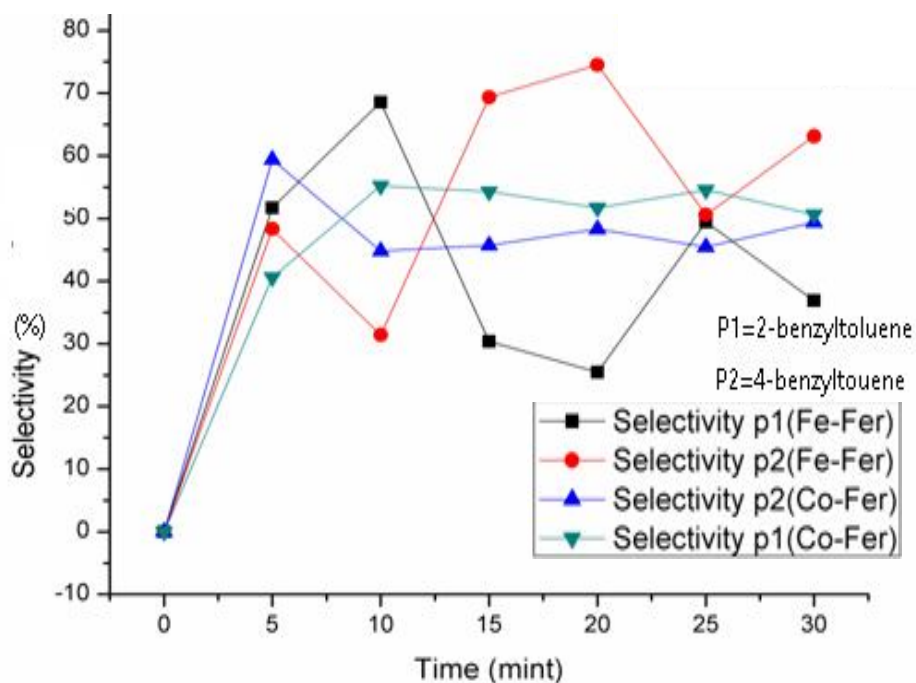


**Figure (3.9): the selectivity% of Cobalt ferrite and iron ferrite use 5:1ratiotoluene/benzylchloride and 0.1g weight of catalyst.**
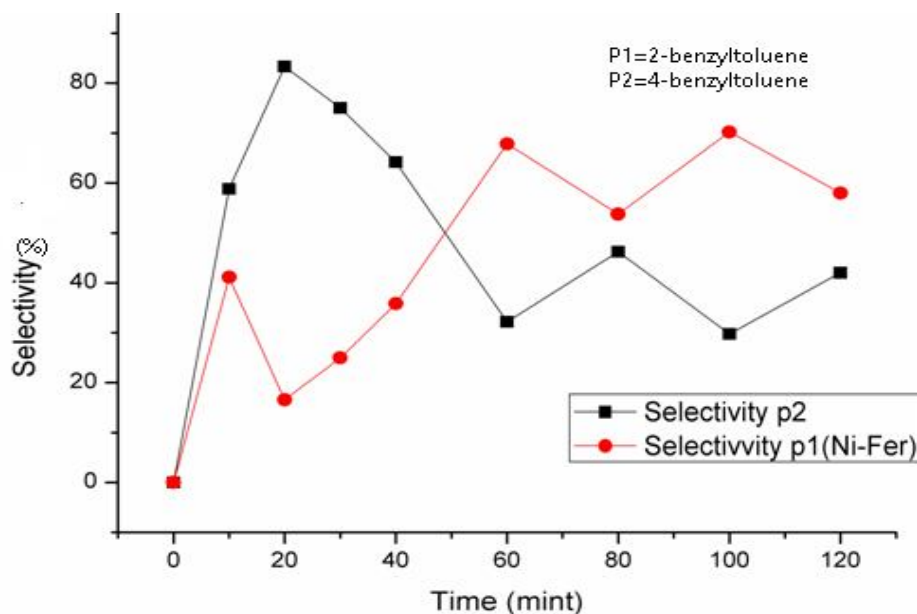
**Figure (3.10): The selectivity % of Nickel ferrite use 5:1 ratio toluene/benzylchloride and 0.1g weight of catalyst.**

### 3.2.4 .Effect of catalyst loading

The effect of the amount of catalyst in the benzylation of toluene was also investigated over Ni-Fer catalyst. Various weights of Ni-Fer were applied to catalyze the reaction between toluene and benzylchloride at 80 **C** with a molar ratio of 5:1  for 30min to produce two benzyltoluene products. The results are presented in Figure 3.11 .It could be observed from Fig. 3.11 that as the mass of the catalyst was increased the percentage conversion increased as well particularly at the beginning of the reaction. Interestingly, reaction with a catalyst mass of 0.05 g needed longer induction period before exhibiting the performance of that with higher loading (0.1 g). This could be explained to the availability of extra active species in the catalyst surface to initiate benzyl carbocations for the reaction. Availability of lower active species demanded longer periods to initiate effective and sufficient carbocation species to produce benzyltoluene products. However, catalyst masses higher than 0.1 did not show regular catalytic performances due to probably to compactness of catalyst particles of the higher masses catalyst.
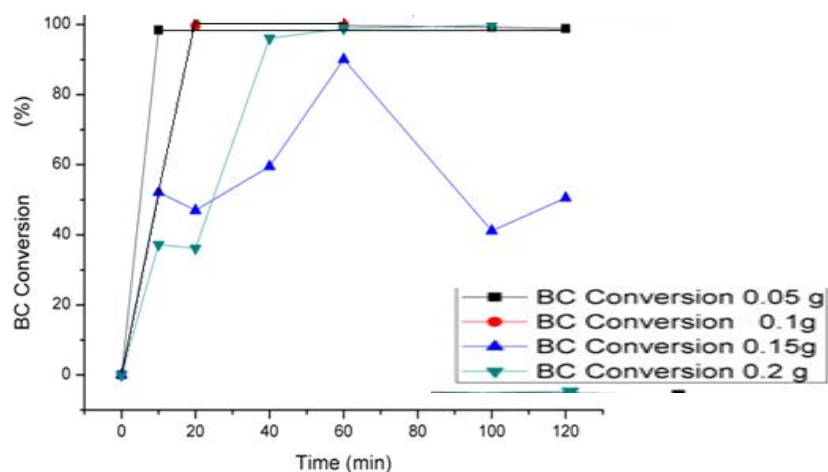
**Figure (3.11): The percentages conversions of BC for the benzylation of tolueneat 80 C over various masses of Ni-Fer catalyst using toluene/benzylchloride molar ratio of 5:1.**
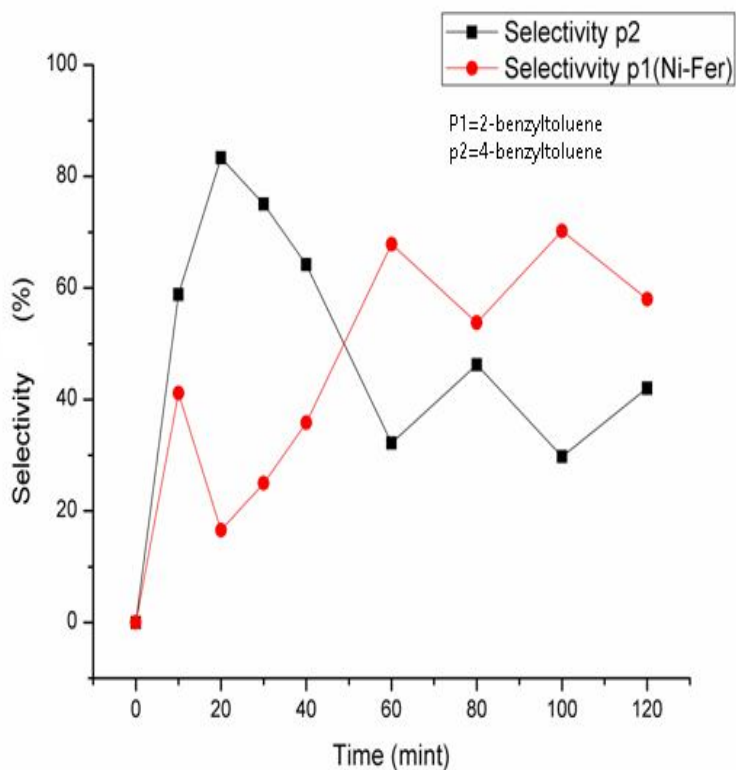


**Figure (3.12): The selectivity % of Nickel ferrite use 5:1 ratio toluene/benzylchloride and 0.1g weight of catalyst.**

The amount of catalyst used to catalyst the benzylation reaction was also varied to investigate its influence. Various weights of Ni-ferrite catalyst were applied to catalyze the reaction between toluene and benzyl chloride at 80 **C** and molar ratio 5:1 . The yields obtained by these reactions are presented in Figure.3.12. It could be observed that the selectivity yield is strongly affected by the amount of catalyst used in the reaction. The best result was obtained when the reaction was proceeded in the presence of 0.1g of Ni-ferrite catalyst ,hence highest selectivity 83.36 % for  (p2) 4-benzyltoluene and highest conversion 99.94%.

**3.3. Conclusion**

- The catalytic performance of the catalyst was found to increase with catalyst loading to certain limit. The optimum molar ratio was found to be 5:1 whereas, the optimum temperature was observed to be 80 **C** and the optimum weight of catalyst was 0.1g.All catalysts showed catalytic performance for the reaction and the catalytic performance was found to decrease in the orderNi-Fer > Fe-Fer > Co-Fer.

- The highest conversion of benzyl chloride 99% was obtained by introducing reactants with a molar ratio of 5:1, increasing the molar ratio to 10:1 resulted in a decrease of conversion up to 94.6%. However, further increase in the molar ratio beyond that lead to a significant decrease in a conversion. Zero or no conversion was obtained from the reaction with molar ratio of 20:1 at 10 min

- The percent 99.94% of benzyl chloride conversion was reached over 80 **C** and the decrease in conversion with increasing the temperature to 80 **C**.
- The best result was obtained when the reaction was proceeded in the presence of 0.1g of Ni-ferrite catalyst ,hence highest selectivity 83.36 % for (p2) 4-benzyltoluene and highest conversion 99.94% because Para-position prefer to ortho- position caused to stereo crowding of ortho – position greater than para –position.
- the empirical formula of the synthesized Co-Fer and Ni-Fer were calculated to be $CoFe_{1.6}O_{3.57}$, $NiFe_{1.7}O_{3.57}$which are quite close to the theoretical formula "$MFe_2O_4$"for spinel ferrite.

## 3.4. Recommendation

Based on results of the current study, some research gabs were detected and hence further investigations are recommended which include:

- More studies to optimize enhance the selectivity of either of the two MDPM products.
- Study the catalytic performance of many transition metal ferrites and investigate their catalytic trends.
- Study the catalytic performance of many main groups' metal ferrites and investigate their catalytic trends.
- Can be was heated precipitate (the oxalate transition metal) at temperature less than 700**C** to remove the oxalate ions and were produced transition metal oxides.

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