ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSTITUTE OF TECHNOLOGY

DEPARTMENT OF CHEMICAL ENGINEERING

Preparation and Characterization of Cu-Fe-O Bulk Catalyst

BY

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Acronyms

AI	Absolute intensities
BABA	Blaine air permeability apparatus
BET	Brunauer, Emmett and Teller
c-$CuFe_2O_4$	Cubic copper ferrite
ESE	East south of east
FCC	Face centered cubic
FWHM	Full width at half maximum
GC	Gas chromatography
HC	Hydrocarbon
JCPDS	Joint Committee on Powder Diffractions
RI	Relative intensities
SEM	Scanning electron microscope
S_{sample}	Specific surface area of the sample
$S_{standard}$	Specific surface area of the standared
t-$CuFe_2O_4$	Tetragonal copper ferrite
TEM	Transmission electron microscope
TGA	Thermo gravimeter analysis
TRA	Theoretical reference axis
XRD	X-Ray diffraction
XRF	X-Ray fluorescence

Abstract

This work is devoted to the investigation of local raw materials, its preparations processes and characterization technique of a Cu-Fe-O applied as a catalyst for hydrocarbon (HC) oxidation. Samples obtained by high temperature solid state method using copper oxide (CuO) and iron oxide (Fe_2O_3) and by wet chemical synthesis method using water as a solvent, applying iron nitrate ($Fe(NO_3).9H_2O$) and copper nitrate ($Cu(NO_3)_2.3H_2O$). In wet synthesis method the thermal treatment at 100^oC and 150^oC, water and nitrates removed from the sample, respectively. Three samples prepared at different quantitative precursor composition that is Fe/Cu = 0.5, 1 and 2 for each principal procedures. Mixing and calcinations at 850^oC for 8hours were the common unit operations for both preparation routes.

In this work it is demonstrated that, the nature of preparation ways, the structural property of precursors and the quantitative precursor composition affects the formation of desired phase, crystal property, size and strain of crystals, microstructure and specific surface area of the sample; which are among the most relevant physical and chemical properties for the catalytic activity. The phase identification, structural property and morphology analysis of samples were characterized by X-ray diffraction and Blaine air permeability apparatus and the samples prepared by solid state method on a precursor composition of Fe/Cu = 0.5 showed optimized property.

1. Introduction

1.1 Back ground of the study

In Ethiopia, the need to raise the industry particularly chemical industry has considerable advantage to build up strong economy. The chemical industry is among the most diversified industrial sector and it is crucial to sustain high growth in the long run. The series of studies on chemical industry has reveled theses industry has been substantially growing in Ethiopia [1]. Most chemical industry in this country engaged in the production of food, beverages, textile, tannery, drug, glass, tobacco, ceramics and cement [2]. Comprehensive improvement on chemical industry at all level i.e. preparation of the desired local raw material and using advanced production technology are vital for the sustainable development.

Catalyst plays decisive tasks in more than 90% of the chemical industry [3]. The role of catalyst in chemical industry has a direct effect on efficient utilization of raw material, for the development of new product, assist systems for environmental protection, aid proper use of energy sources, and serve for the development of new processes and technology [4]. So a scrutiny of catalysts offers a tremendous benefit especially for the chemical application, design and operation of most chemical industry. The chemical industry sector of Ethiopia is small and highly import dependant [5]. Specifically, Ethiopia imports transitional active metal substance which serves as catalyst within four years by more than $ 77464 to fulfill the demand of the sector [6]. Production of catalyst from local raw material has a strategic importance to create an import substituting product.

Ethiopia has a great opportunity to prepare catalyst from local raw material because of the availability of various types of metal oxides in the country. This metallic oxide are existing in the form of ore, the main type of metallic oxide and their specific area are mentioned. The Kata polymetallic deposits contain Cu-Zn-Ag ores and the south Abetselo zone has a massive Cu-Zn-Pb-Ag-Au sulfide deposits at depth [7]. The Ethiopian geology survey investigated the base metal potential (Cu-Zn-Pb-Au) in the area of Azale-Akendeyu and the geochemical exploration in Tigray at Tsehafi Emba showed the occurrence of Copper from soil sample [7]. The Ethio - Korean iron exploration project showed a huge deposit of iron around the area of Bikilal [8].

Around Melka Arba (Bale region) and Chango contain a high grade and low grade iron ore deposit [8]. In addition to the above mentioned place, in north Gonder (chilga) there is a high amount of metal oxides [7]. Generally, the Ethiopian geology survey exploration identified many iron occurrences in Wollega specifically Bikilal, Gordana, Worakalu, Chago, Yubdo, Nejo, Kata, Tsoli, Sirba, Korkandi, Kiltukara and Wobera KIltu [8].

Ethiopia is reach in metal oxide which is necessary for the preparation of bulk catalyst, specifically copper and iron ore are quite accessible in most parts of the country. From different kinds of metal oxides the synergy of iron and copper are believed to be important for high catalytic activity for complete hydrocarbon oxidation [9]. In Ethiopia, chemical industries like ceramics processing, cement manufacturing and steel mill uses various quality of hydrocarbon combustion to satisfy their energy demand [10]. Ethiopian iron and steel factory, Zuqalla steel rolling mill enterprise and Akaki metal products factory are a steel mill industries in Ethiopia which uses huge amount of combustion for their processes [10]. Mugher, Mososbo and National cement industry are also uses huge amount of hydrocarbon fuels for their kiln and pre-calciners plants [11]. As a result, catalyzed hydrocarbon combustion has tremendous advantage for Ethiopia and the extensive availability and high catalytic activity of copper and iron can serve as a raw material for the preparation of catalyst to satisfy the need of catalyzed hydrocarbon combustions. At last, doing research in this area diversify the potential of chemical industry to create a power full economy in Ethiopia.

1.2 Statement of the problem

To realize the development of Ethiopian economy, industries have vast contribution [5]. From the industry sector, a robust chemical industry is an indication of powerful economy and it has strategic benefits to the nation. Specially, applications of highly selective and active catalyst are crucial to make smooth the growth of chemical industries [4]. A non catalytic hydrocarbon oxidation in chemical industries has insufficient energy generation and emission control, also the processes is not environmental friendly [9]. Chemical industries in Ethiopia like ceramics processing, cement manufacturing and steel mill uses various quality of hydrocarbon combustion to satisfy their energy demand [10]. The proper use of Cu-Fe-O catalyst for hydrocarbon oxidation has the advantage for sustainable increase in production at lower energy consumption and radically limited generation of wastes [9]. Exploring appropriate local raw materials, knowing catalyst preparation way, discovering the exact composition of the starting materials and using the XRD and BAPA characterization technique have critical role to get a desired Cu-Fe-O catalyst which is necessary for hydrocarbon oxidation. So preparation of the mentioned bulk catalyst from local raw materials and accurate use of characterization techniques have strategic importance to get sufficient energy generation and environmental friendly process from hydrocarbon oxidation.

1.3 Objective of the study

1.3.1 General objective

The general aim of this project is to investigate the preparation and characterization of Cu-Fe-O bulk catalyst from local raw material.

1.3.2 Specific objective

In this project the following objectives will be covered specifically.

- To review raw materials available in Ethiopia for bulk catalyst preparation
- To prepare Cu-Fe-O catalyst
- To study characterization of Cu-Fe-O catalyst using XRD
- To analyze surface morphology of Cu-Fe-O catalyst using BAPA

2. Review of Literature

2.1 Catalyst

In order to achieve the demand of modern human being it was necessary to invent thousands of new material and to find out the ways of their fast and cheap production in large quantities. This was realized by the dream of alchemist which can transfer various raw materials in to a desired product, the unique possibility of fast and selective production of the desired chemicals offered by catalysis due to their diversified physicochemical nature. Therefore, the development of the science and practice of catalysis may be considered as the fulfillment of the alchemists' dream [3]. Catalysis comprises the largest scale such as cracking a billion tons of crude oil per year, and smallest scale like enzymatic reactions with micrograms. Materials produced by catalytic technology are responsible for modern medicine, new fibers for clothing and construction, a wide variety of consumer products and cleaner burning fuels. Increasingly important is not only the production of materials needed in our modern society, but also the destruction of undesired by-products of its activities, making application of catalysis is important for pollution control.

Catalysis is a phenomenon, which facilitates the transformation of reactants to products through a repeated cycle of steps using relatively small amount of foreign material, called catalyst. Very often the given reactants react along several different thermodynamically possible reaction paths and a mixture of many different products can be obtained. The catalyst may create preference for the reaction along one of these path ways, very often not thermodynamically the most convenient, by modifying the potential energy surface to make reaction along the selected reaction coordinates more facile and those along other pathways more difficult [3]. This selectivity of action is the most important and characteristic property of the catalyst, making possible the formation of products, which in the absence of catalyst would have never been formed because of the much more rapidly proceedings competitive processes. Thus by selecting the appropriate catalyst and reaction conditions it is possible to direct the reaction along only one selected pathway to obtain the desired product.

The catalyst surface is thus in dynamic interaction with the reactants. When steady state conditions of catalytic reaction are changed, structure of the catalyst surface may also change; the catalyst modifies the activity and selectivity itself. The overall activity of a catalytic system is a function of the turn over frequency of the reaction at the active center and the number of these centers easily accessible to the reacting molecules [3]. Therefore one of the main objectives of the development of a catalytic system is the generation of active centers in highest, possibly molecular dispersion. This is usually achieved by supporting the active phase on a high surface area carrier. In recent years a different approach is also being adopted, based on the application of micro emulsion. Many organic reactions are carried out in non aqueous media, but many catalysts like enzymes active only in the presence of water.

The production of most industrially important chemicals involves catalysis, especially catalyst has a prominent role on the following area, for preparation of bulk chemicals (Some of the largest-scale chemicals are produced via catalytic oxidation e.g ammonia and sulfuric acid), in energy processing industries (petroleum refining needs intensive use of catalyst, bio fuel require processing via both inorganic and bio catalyst), in food processing (One of the most obvious applications of catalysis is the hydrogenation of fats using nickel catalyst to produce margarine. Many other foodstuffs are prepared via bio catalysis). Generally, catalysis offer the possibility of fast and selective production of the desired chemical molecules and more than 90% of the production of chemical industry is based on catalysis [3].

2.2 Raw materials available in Ethiopia for bulk catalyst preparation

Solid catalysts are highly sophisticated products derived from unique raw materials by means of several different procedures. There catalytic activities are strongly affected by the quality of raw materials. Catalysts can be broadly categorized bulk, impregnated and mixed agglomerated based on their preparation procedure. Bulk catalysts are solid catalysts which comprise transitional active metal substance like copper, iron, cobalt, manganese, palladium, nickel, vanadium, zinc and tungsten oxides are just to mention a few [12]. Many bulk catalysts have highly mobile lattice oxygen and low surface oxygen binding energy, these peculiar properties makes the bulk catalyst to be strong in the catalytic activities of redox reactions [13].

Impregnated catalysts are obtained from performed supports by impregnation with the active phase [12]. The last category of mixed agglomerated catalysts comprises those catalysts obtained by mixing the active substances with a powdered support or a support precursor and then agglomerating the mixture [12]. Currently different bulk catalysts have received enormous attention due to their novel properties and potential application, fortunately Ethiopia has huge potential of local raw material to prepare bulk catalyst. This sub topic has an objective to sort out the available local raw materials in Ethiopia which are important for the preparation of bulk catalyst.

The physical and chemical property, cost and availability are the main factors which need attention to select the proper starting material for catalyst preparation. Therefore, the starting material should be properly selected and synthesized for the production of desired product. There are a great opportunity in Ethiopia to prepare a bulk catalyst from local raw material because a recent and decade before conducted geological studies showed the presence of different types of metal oxides in different parts of the country. Diverse exploration confirmed the presence of copper, iron, gold, cobalt, rhodium, platinum, manganese, tantalite and zinc oxides [7]. These metallic oxides are available in the form of ore; some of the short listed specific area and the metallic oxide are mentioned below and exquisitely ordered in table 2.1.

The Kata poly metallic deposit occur 6km ESE of Nejo town in Wollega region. Ethio – Czechoslovakia project outlined three types of mineral occurrences in Kata on the target area of $10km^2$ which are Cu-Zn-Ag ores, Au mineralization in quartz and carbonates veins and W- Mo in granitic rocks [7]. The Abetselo area 30km due SSW from Ethio – Sudanese border town of Gizen, falls into a Zone a metallogenic belt [7]. Detailed surveys outlined impressive overlap of geochemical, geophysical and geological anomalies in the south Abetselo zone, suggesting a good chance for the discovery of massive Cu-Zn-Pb-Ag-Au sulfide deposits at depth [7]. The Ethiopian geology survey investigated the base metal potential (Cu-Zn-Pb-Au) of the Azale-Akendeyu (25km of south east of Kurmuck), anomalous zone on this area are marked by quartz and lithic fragment breccias, which are cemented by iron oxide [7]. Geochemical exploration in the Tigray at Tsehafi Emba showed the occurrence of 1.6% Cu values from soil sample [7].

The Bikilal iron deposit was explored in detail by the Ethio - Korean iron exploration project [8]. In this area a total ore reserve of about 58 million tones, with average grades of 23.3% magnetic iron and 41% total iron was calculated for 27 identified ellipsoidal ore bodies [8]. The Melka Arba iron ore occurrence is in the Bale region of SSW Ethiopia, at a distance of 620km from Addis Ababa [8]. The occurrence total iron and magnetic iron values after investigation are 66% and 24.65% respectively in Melka Arba [8]. The Chango occurrences is situated 5km south of Guliso village located along the road from Ghimbi, on this region a reserve of 440000 tons of high grade ore (57%-68% iron) in 400m length and 5m width, in addition of low grade ore (33% iron content) [7]. Generally the Ethiopian geology survey exploration identified many iron occurrences in Wollega specifically Bikilal, Gordana, Worakalu, Chago, Yubdo, Nejo, Kata, Tsoli, Sirba, Korkandi, Kiltukara and Wobera KIltu [8].

In the sidamo region of southern Ethiopia, 24 nickeliferous bodies in two serpentinite belts have been identified [7]. Seven of these were explored by drilling and pitting, it is reported that 10500000 metric tons of low grade ore at 0.55% Ni, totally 17000000 tons of nickel – bearing material [7]. The nickel mineralization occurs in the form of pimelite (garnierite group) and is contained in the upper lateritic layer above serpentinite bodies [7].

A place which is located 20km south west of Dallol in the Danakil depression in the locality name of Enkafela has manganese ore [8]. About 40000 tons of manganese ore could be exported until the end of 1963 from this area [8]. Another manganese ore deposit occurs at Ashely, 7km north of Enkafela, in the form of several thin, earthy, manganese-rich layers of less than 0.3 m thickness, in a similar geological sequence to that of the Enkafela deposit [8].

Yubdo is in the Wollega region 100km south west from Ghimbi town has a large concentration of platinum which was discovered by the Russian expedition [8]. The kenticha is located from 50km south of Leg-Dembi has 25850 tons of tantalum which was first discovered by the Russian exploration program [8]. In the locality name of Lega-Dembi, Sakaro, Wollena, Kumodu, Megado, Haramsam, Hassamte, Ababa, Chamo, Dul, Oda-Godere, Bekuji, Barude, Egambo and Adola has a large deposit of Gold [8].

Table 2.1 List of local raw materials and their specific places [7]

No	Metal type	region	Locality name
1	Primary gold	Southern Ethiopia	Lega-Dembi, Sakaro, Wollena, Kumodu, Megado, Haramsam, Hassamte, Ababa, Chamo
2	Primary gold	Western Ethiopia	Dul, Oda-Godere, Bekuji, Barude, Egambo
3	Primary gold	Northern Ethiopia	Terakemti, Adi-Zeresenay, Zager, Niraque
4	Placer gold	Sothern Ethiopia	Adola
5	Platinum	Western Ethiopia	Yubdo
6	Tantalum	Southern Ethiopia	Kenticha, Meleka
7	Copper	Western Ethiopia	Kata, Abetselo, Azale
8	Copper	Northern Ethiopia	Tsehafi-Emba,
9	Copper	Eastern Ethiopia	Chercher
10	Iron	Western Ethiopia	Bikilal, Chago, Gordana, Koree
11	Iron	South Eastern Ethiopia	Melka-Arba
12	Nickel	Southern Ethiopia	Adola
13	Manganese	Dallol	Enkafela
14	Molybdenum	Western Ethiopia	Fakusho (Dondor)

The aforementioned listed data assured that Ethiopia is fully reached in metal oxide which is necessary for the preparation of bulk catalyst. Especially cupper and iron ore are extensively available in most parts of the country which is a prominent starting material to prepare a bulk catalyst that serves for a redox reaction.

2.3 Methods of catalyst synthesis

Catalysis is vital to world economy and standard of living, yet relatively little attention is paid to optimize different parameters for rational methods of catalyst preparation. The effort of catalyst preparation requires a substantially different and complementary focus from traditional methods. Currently catalyst synthesis has much excellent progress with state of the art analytical and computational methods to obtain structure function relationship. There is no single theory for catalyst preparation, but only a series of principles to interpret and predict that occur in the preparation. It is important to recognize that preparation of catalyst is not a standalone field endeavor, but rater is more of generic area that is expected to have a critical impact and overlap in much area of science and technology. The fields, discipline, and area of expertise that fall under the umbrella of catalyst preparation are many and diverse. Some of these are material science, chemistry, geophysics, e.t.c. This diversity offers both an opportunity and a challenge to the scientific, technological and educational perspectives. The target of all discipline in the preparation of catalyst focus on activity, selectivity, stability, morphology, mechanical strength, thermal properties, regeneration and cost.

Many parameter affect the preparation of bulk catalyst some of this are reagent, pH, mixing sequence, temperature, heating rate, concentrations, template, e.t.c [14]. In fact, it is rather difficult to isolate the effects of each preparation parameters up on the structural and performance changes of the resulting catalysts. Preparation methods can play as significant roles as the chemical composition in determining the structure and catalytic properties of a catalyst especially on metal oxide catalyst. Undesirable preparation methods or conditions can lead to the formation of ineffective crystal phases in the resulting catalysts, leading to poor catalytic activity or selectivity.

Preparation of catalyst need different scientific and technological path. Based on their preparation procedure catalysts are categorized bulk catalysts and supports, impregnated catalyst and mixed agglomerated catalysts [12]. Some of the main unit operations which help to prepare bulk catalysts are mentioned below.

Mixing the precursor material is one of the unit operations and it can be either dry or wet mixing [15]. While dry mixing avoids the need for solvent removal, the resulting degree of mixing is limited by the particle size of the starting materials. Wet mixing, which can go through a solution or slurry depending on the concentration of the component solutions, may appear to be intimate at the molecular level, but the low solubility of precursor materials, in certain circumstances can still cause problems. On a typical wet mixing procedure, individual starting materials are usually first dissolved to form solutions, a slurry can sometimes form, which reflects the formation of certain precipitates with their compositions determined by the variety, concentration and solubility of the metal cations and counter anions present, as well as the pH, temperature and other parameters of the resulting mixture. After a proper composition of the catalyst precursor, the water will be removed by different kind of evaporator to obtain a solid catalyst.

Irrespective of the preparation method of solid, additional steps, such as different stage of thermal treatment, are necessary after combination of components. Calcinations can be decisive for properties of catalyst; the calcinations temperature is specific for each system [16]. After calcinations shaping of catalyst are very important, shape define pressure drop in a reactor. There are different kind of catalyst shape some of this are monoliths, rings, spheres, pellets, extrudates and broken metals [17]. The methods to gate the desired shape are breaking/milling, spray drying in small particles; granulation/pelletizing, tabletting (pressing in moulds) and extrusion are some of the vast method of shaping.

Currently the industry sector drive by environmental regulation, worker safety, energy concern and the need for improved performance. These problems are being addressees by the development of active and selective catalysts. Catalyst industry used to be primarily technology driven. Surprisingly, although many new catalyst preparation procedures and technologies have been developed and published during the past decade, only very few methods have found application in commercial catalyst production as yet [4]. Temporarily, cost reduction has become the major driving force. But also in future, all new ideas have to compete cost-wise with state of the art technology. Now a day there are massive investigation on some selected area of physicochemical properties of catalyst, some of it are investigation of the mechanism in

catalytic processes, description of its physical characteristics and their dependence on the properties of the catalyst, and studies of the pathways of its transformations on the potential energy hyper surface constitute the main subject of the science of catalysis. A Varity of metal chalet are being developed as a bulk catalyst which are environmentally acceptable and meet the cure requirement of the industry. Vast amount of data on the structure and reactivity of different metal complex have been published in recent years, new area of studies on the catalyst of metal oxides have also emerged on the number and nature of the surface active sites, selectivity and turnover frequency towards the substrate [18].

2.4 Characterization of Catalyst

The catalyst selection for a certain processes is based on studies of certain peculiar properties; this is usually a very long and difficult task. Investigating the suitable catalyst characteristic is important to get the desired product at a reasonable cost. The following are some of the factors that determine the characteristic of most catalyst and different type catalyst test.

2.4.1 Factors to determine catalyst properties

The physical and chemical factors which can influence the characteristic of a catalyst are mentioned below.

- **Structure**: The structure of catalyst is defined by the distribution in space of the atoms or ions for the desired activity. Shape, size and orientation of crystallites, the extension and arrangement of different crystals faces together with macro defects can describe the surface structure. Knowing the structure of catalyst is very decessive to analyze the active site and the role of the support. The determination of structure of solid is possible using a variety of experimental method, the method chosen being dependant on the specific information required.

- **Morphology**: It include the detail of the shape of the particle of the various phases present, their arrangement in space (including the void and pores) and the shape of larger physically

separate entities (beads, pellets, extrudates, rings). In addition to the qualitative expression, the catalyst morphology quantitatively expressed by porosity and surface area. Porosity and surface area are important properties of solids in numerous technical processes. Porosity is the concept related to texture and refers to the pore space in material. It can be defined as the fraction of the bulk volume that is occupied by pore or void space. The determination of catalyst morphology is done by the type of reaction and pressure drop that is occurred on the reactant and the type of reactor that the catalyst will be applied.

- **Stability**: Catalysts which have the capacity to absorb water or carbon dioxide from the air may exhibit weight instability due to climate change. Time and variation of temperature or pressure may, in principle, give rise to losses or gains in weight due to changes in water content. Generally particular care is necessary to control the stability of catalyst during the transport and handling of the material.

- **Strength**: It is desirable for commercial catalysts to have sufficient mechanical strength so that losses during handling and use are minimized. Broken pieces and fines (fine powder) lost during handling or produced during commercial use can represent a significant expense. Various laboratory tests have been designed to provide information concerning the ability of a catalyst to maintain its physical integrity.

- **Purity**: It has its own great significance on the performance of the catalyst. There are three possibilities that the catalyst lose its purity, i.e the processes materials, the reactor construction materials and on the time of the preparation of the catalyst. Consequences of contamination are mechanical degradation of the catalyst structure, deactivation due to shadowing effects and lose of the selectivity and activity. The impact of contamination depends on surface concentration and not on bulk concentration. For fully soluble contaminants such as iron, the impact on catalytic properties depends on the balance between the rate of surface deposition and the rate of diffusion into the bulk. Special attention has to be paid preventing pollution during the start-up period. X-ray florescence and different kind of microscope is used to analyze the purity of the catalyst.

2.4.2 Tests for catalyst characterization

The progresses in understanding the structure and properties of chemical bond of different raw material combined with development of surface science made it possible to know the real characteristic of catalyst. Several characterization techniques are available to study solid surfaces and the properties of catalysts. Experimental surface characterization methods include both microscopic and spectroscopic method. The past three decades has seen a revolution in the development of spectroscopic catalyst characterization techniques and many of these instrumental advances have had significant impacts on the challenging catalysis science of mixed metal oxide catalytic materials [3]. Consequently, many of the recent advances in a catalysis science have parallel to the development of new spectroscopic instrumentation during this rapidly expanding period. Advanced characterization technique is necessary to identify the above mentioned peculiar property of bulk catalyst. The following part briefly expresses the characterization technique which is important for catalyst.

2.4.2.1 Structure test

X-Ray diffraction is the latest equipment which is necessary to examine the structure of the catalyst which is shown in fig 2.1 below. Before X-ray diffraction, the structure of crystals was studied based on their geometry. This involves measuring the angles of crystal faces relative to theoretical reference axes (TRA), and establishing the symmetry of the crystal in question. The instrument of X-ray diffraction is an easy reconfiguration of the X-ray optics for a Varity of experimental purpose. The combination of the Gobel parabolic X-ray mirror and Cu-Ka X-ray source at 40 kV produce a beam intensity in the range of 1000's of counts per second, making the instrument well suited for phase identification and trace analysis. The instrument is equipped with two detectors, a standard scintillation detector, and a LynxEye Super Speed detector. The scintillation detector is optimal for small angles near a direct beam condition and for cases where signal to background is a concern. The LynxEyx detector is 1 dimensional solid state array detector, being able to acquire a 4 degree window at 0.02 degree resolution, designed for rapid data acquisition. These characterization methods depend on the analysis of the

diffraction patterns of a sample targeted by a beam of X-ray. The necessary properties of the XRD result to characterize the samples are:

To characterize the phase and structure of a catalyst, the XRD result should contain the following data.

- The position of the peaks
- The intensity of the peak
- The shape of the XRD pattern (the shape of the graph)

From the above result we can determine the following structural properties to characterize the catalyst:

- Crystals Phase Identification: The X-Ray diffraction pattern first allows the identification of the crystal phases. The XRD pattern could be compared to a fingerprint for the sample that can thus be identified through the comparisons with the powder diffraction files. This investigation can easily be achieved either by observation of the peak position or with the help of the software DIFFRAC^{+}EVA.

- Crystalline rate estimation: The sharpness of the peaks could be related to the crystalline rate of the powder. A well crystallized powder has a XRD pattern with thin diffraction peaks whereas an amorphous substance presents a diffusion pattern. Consequently, the pattern of partially crystallized samples will present weakened broad peaks. The observed intensity of the diffraction peak is thus proportional to the crystalline rate of the powder.

- Size and strain of the crystals: providing that the peaks resolution allows it, this characterization technique also gives the possibility to access the size of the crystallites and the micro strains by analyzing the broadening of the diffraction peaks. In addition to this the broadening is important to analyze the morphology of the catalyst. At each point of the pattern, the observed intensity is considered as the sum of the intensity of the entire individual peak.

Fig 2.1 The XRD equipment

2.4.2.2 Composition test

The composition and nature of catalyst should be monitored before utilizing the catalyst. Measurement of the chemical composition and elemental analysis is important to know the quality and purity of the catalyst. X-Ray Fluorescence (XRF) and X-Ray difracto meter examines the bulk composition of catalyst samples. XRF provides an overall assessment of the elements present on a new or used catalyst, and estimate concentrations present using a re-iterative semi-quantitative calculation. If there is a requirement to check that actual concentrations present match those in a specification, then quantitative analysis by XRF and XRD is appropriate for the accurate determination of major and minor concentrations.

2.4.2.3 Size and Morphology test

Different instrument show how morphological control influence the catalyst performance. With scanning and transmission electron microscope, we can observe the shape and estimate the size of the particles and their distributions. Scanning transmission electron microscope is used to make chemical X-ray mapping of our particles (distribution of the elements considered). To analyze the morphology of the catalyst a quantitative description of porosity and specific surface area is necessary.

- Specific surface area: Total catalyst surface area is usually measured by nitrogen adsorption using the BET method. BET measurements (named after the authors of the theory Brunauer, Emmett and Teller) permit to access the specific surface area of the powder. The apparatus which measure the specific surface area injects precise volume of nitrogen at 77.3K (liquid nitrogen). The measured relative pressure P/P_0 gives an isothermal curve that is transformed to BET straight line (the software does all the transformation based on the BET theory and equation). The other option to measure the specific surface area of the catalyst is using equipment which is known as Blaine meter (homboldt mfg.co, U.S.A). The data which is measured in this instrument is time, and the time can be converted to specific surface area using a standard equation which is proposed by the manufacturer of the equipment.

- Porosity: To do porosity test there are several methods which are available currently, like mercury porosimetry and B.E.T. gas adsorption. Therefore, porosity evaluation method consisting of a combination of image analysis and gas displacement in a pycnometer. Apart from closed pores and macrospores (>50 nm), total pore volume and pore size distribution can be measured by nitrogen adsorption. This gas adsorption prosimetry is based on a known volume of gas is isothermally expanded into unknown porous volume. After the expansion, the result of the pressure is measured, and this value depends on the unknown pore volume which is obtained using the Boyles law. Then porosity will be the volume of the gas in the sample, or in other words, the volume of pore space in the sample divided by the total sample volume.

- Final shape: Shaping a catalyst is very important and the final step of the catalyst preparation, basically it needs empirical knowledge to select the desired final shape of the catalyst. Catalysts have different types of shapes depending on their specific activity. The parameter which is influenced by the shape of the catalyst is pressure drop, diffusion, specific surface area and boundary effects [12]. As much as possible the shape of the catalyst should decrease the pressure drop in the reactor and it should enhance the diffusion of the reactant by increasing specific surface area. The selection of shape and size is driven by the type of reactor [12]. Table 2.2, gives a rough survey of the different catalyst shapes and types of reactors in which they are used. For a given reactor the shape and the size of the catalytic particles will depend on the hydrodynamic and on heat and mass transfer limitations [12].

Table 2.2 Different types of catalyst shape and the recommended reactors [12]

No	shape	Type of reactor
1	Extrudate	Fixed bed reactor
2	Pellet	Fixed bed reactor
3	Granule, Bead	Fixed bed reactor
4	Sphere	Fixed bed or moving bed reactor
5	Microspheroidal	Fluid bed or slurry reactor

2.4.2.4 Thermal stability test

Thermo gravimeter is used to study chemical, physical or physcio-chemical phenomena related to temperature variation resulting in a mass variation. It is based on continuous recording of mass changes of a sample, as a function of temperature with time. To do such kind of function, the thermo gravimetric analysis equipment should be coupled with the mass spectrometry. When the TGA coupled with a mass spectrometry, precise information on the nature of those gases is obtained since the released gaseous molecules are ionized sorted by mean of weight. So from the result we can conclude how much the sample is thermally stable.

2.4.2.5 Mechanical strength test

Measurement of crush strength is intended to provide an indication of the ability of the mechanical strength. Crush strength can be measured for single pieces (pieces crush strength) and for a bulk sample (bulk crush strength). Piece crush strength is commonly measured by placing individual catalyst pieces between two flat surfaces, applying a compressive load, and measuring the force required to crush the piece. Best results are obtained for regular shapes, such as beads and tablets. Crush strength measurement of extrudates is less straightforward, and the results will vary greatly with particle geometry and with the details of the analytical procedures used. Some methods may be repeatable within a single laboratory but irreproducible between laboratories. Bulk crush strength is commonly measured by placing a representative sample in a cylinder, applying a constant force with a piston, and mesuring the amount of fines generated. Many different variants are possible and no generally accepted method is yet available. The bulk crush strength is defined empirically and the results are expressed on an arbitrary scale. This measurement may be applied to all catalyst shapes.

Table 2.3 Different types of catalyst tests which is important for characterization

No	**Catalyst test**	**Equipment**	**Property identified**
1.	Structure test	XRD	Crystalline phase, Crystalline rate, size and strain of crystals
2.	Composition test	XRF and XRD	Elemental analysis and purity of catalyst
3	Thermal stability test	TGA	Weight loses on different temperature.
4	Specific surface area test	Blaine meter	Specific surface area
5.	Porosity test	Porosimeter	Porosity
6	Morphology test	Microscope	The shape of the final catalyst

2.5 The reaction mechanism of hydrocarbon oxidation using bulk catalyst

There have been many studies on the surface science of metals and their applications to catalysis the hydrocarbon oxidation in different mechanism. A very brief discussion and investigation of the catalyst structure and a catalytic reaction mechanism play an important role to realize the diverse mechanism of hydrocarbon oxidation which has a great interest from the point view of the environment as well as the energy production. Certain metals and metal oxides have a natural propensity for enhancing the catalytic reaction. Each of the bulk catalyst partially or completely changes the way of conversion of hydrocarbons oxidation intermediate products and influence there yield.

Different research has been carried out on mixed oxides of transition metals of the types AB_2O_4 with reverse spinal structure, which are active and thermally stable. The oxide materials containing copper and iron are potentially interesting for the catalytic combustion of hydrocarbons. The spinal structure AB_2O_4 exhibit complex disordering phenomena involving the two cation sites which has important consequences both for their thermo chemical and physical properties [19]. And the presence of defects in this spinal structure has favorable condition for its catalytic properties by creating the active site. The active site helps to activate the natural oxygen and make it ready for the oxidation. The reaction occurred by the oxidation of hydrocarbon by the catalyst and the reoxidation of the catalyst by natural oxygen molecules [20]. In many practical cases this steps are not simple and elementary but consist a number of parallel or consecutive partial reaction.

2.5.1 The structure of pervoskite Cu-Fe-O catalyst

Oxide groups consisting of two or more different cations are called complex or mixed oxides which has a structure different from those of the simple oxides. Due to their theoretical and technological relevance, complex or mixed oxides have been investigated recently. A great number of methods have been successfully employed to synthesis such material with improved properties for specific application. The most typical structure of a mixed oxide consists of two or more different cations with different oxidation states, ionic radii, and coordination number.

This diversity brings the complexity of the structures, results in a large number of different properties as compared to those of simple oxides. In particular, among the mixed oxides, the perovskite oxide is well known for displaying a multitude structures and properties, which are briefly introduced in this subtopic.

A pervoskite structure is tolerant of certain difference in size or valence of foreign atoms, and it forms a various kinds of defect structure according to the kind of inserted atoms and the formation environment such as temperature. Not only single pervoskite type but also various kinds of derivatives, so called pervoskite related compounds, form different kind of lattice defects. They have also tolerance to accept foreign atoms as an impurity or to drive from their stoichiometric composition, giving rise to some kinds of lattice defects. Such an adaptable structure of the pervoskite type oxide suggests that some constituent ions in the crystal will be mobile from one site to another if the energy needed to overcome the barrier to jump from one site to the other is small.

From vast type of complex oxides, pervoskites like ABO_3 and AB_2O_4 have the most advantageous and well known structure. A pervoskite structure ABO_3, where A and B denote two different cations. The ideal structure of this pervoskite, which is illustrated in the fig 2.2, is a cubic lattice [21]. Although few compounds have this ideal cubic structure, many oxides have slightly distorted variants with a lower symmetry. Additionally in many compounds a large extent of oxygen or cation deficiency has been observed. Various types of distortion and deficiency in the pervoskite structure strongly related to their properties.

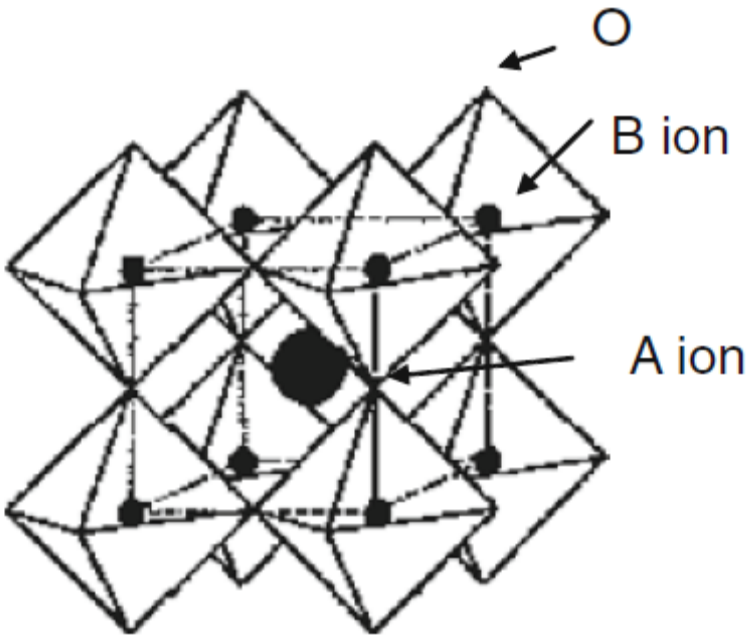


Fig 2.2 The ideal pervoskite structure of ABO_3 [20]

The next most well known and important complex oxide structures is the spinal structure AB_2O_4, which shows a most interesting complexity, where A and B are cations which are close in size and supposed to have different oxidation states, ionic radii, and coordination number [21]. The ideal structure of this pervoskite is illustrated in fig 2.3 which has a specified A and B site. However in some cases, mixing of cations in the A and B site may occur, that means a cation in the crystal will be mobile from one site to another if the energy needed to overcome the barrier to jump from one site to the other is small therefore a single cation may occupy both sites [21]. AB_2O_4 spinal has a cubic close packing (fcc) arrangement of oxide ions, with cation places in some of interstitial tetrahedral and octahedral voids.

Because of the variety structures and chemical composition, pervoskite oxides exhibit a large varity of properties. Several pervoskite oxides exhibit good electrical conductivity ($SrFeO_3$ and $LaCrO_3$), high catalytic activity ($CuFe_2O_4$, $LaCoO_3$, $LaMnO_3$ and $BaCuO_3$), ferromagnetic property ($BaTiO_3$ and $PdTiO_3$) and serve as electrode ($La0.6Sr_{0.4}CoO_3$) [16].

It is obvious that, catalysis is the phenomena that a compound shows a resultant active site, which originates from the antiparallel orientation of two or more non equivalent sub lattice structure. A compound AB_2O_4 with the spinal structure contains two cation sub lattice, the tetrahedral (A) and the octahedral (B) sites. The effective inter and intra sub lattice interactions A-B, A-A, and B-B depends on the electronic structure of the cations, as well as on the geometry of the relative configuration of the interacting cations and the intermediate ion. The structure of the crystal as well as the defect structure of the reduced dimensions is decisive for the physical properties which serve as a catalyst. In both cases the typical crystal structure of catalyst plays an important role. The unit cells contain 8 molecules of AB_2O_4, which are 32 oxygen ions, 16B ions and 8A ions. The real spinals have the closed cubic packing of the oxygen ion from their ideal position [22].

From AB_2O_4 structure there is an equivalent pervoskite that is $CuFe_2O_4$, A site is occupied by cupper ion and B site by iron ion has a promising structure for hydrocarbon oxidation. As illustrated in fig 2.3 cupper ferrite ($CuFe_2O_4$) can be described as a cubic close packing arrangement of oxygen ions with Cu^{2+} and Fe^{3+} ions at two different crystallographic sites, if the sample is slowly cooled with high temperatures, $CuFe_2O_4$ can have tetragonal unit cell symmetry. These sites have tetrahedral and octahedral oxygen coordination (A and B site respectively), the resulting local symmetries of the two sites are different. The cation distribution may be represented by $(FeCu)FeO_4$ or $CuFe_2O_4$ which is named as inverse and normal spinal structure, respectively. In inverse spinal structure, eight divalent ions are (Cu^{2+}) at the tetrahedral (A) sites and 16 trivalent (Fe^{3+}) ions are equally divided between the tetrahedral (A) and (B) sites per unit cell. The Fe^{+3} atoms are octahedrally surrounded by oxygen ion and Cu^{2+} atoms sit are tetrahedrally surrounded by the oxygen ion. For the formation of $CuFe_2O_4$ inverse spinal structure, the trivalent iron ion replaces the site of divalent copper ion. On the time of replacement an oxygen vacancies will be created because the trivalent iron ion has octahedral structure with the oxygen and the divalent copper ion has a tetrahedral structure with the oxygen. The deficiency or the vacancies of the oxygen ion on this replacement is the base to create an active site for catalytic activity. This structure is clearly described in Fig 2.3, the Fe^{+3} atoms (hidden) are octahedrally surrounded by oxygen and Cu atoms sit in tetrahedral interstices formed by the oxygen so fig 2.3 makes clear the formation of oxygen vacancies by

the replacement of cupper by iron for the formation of inverse spinal copper ferrite. Finally the inverse spinal copper ferrite structure has resultant active sites (oxygen vacancies) which facilitate or which serve as a catalyst for hydrocarbon oxidation.

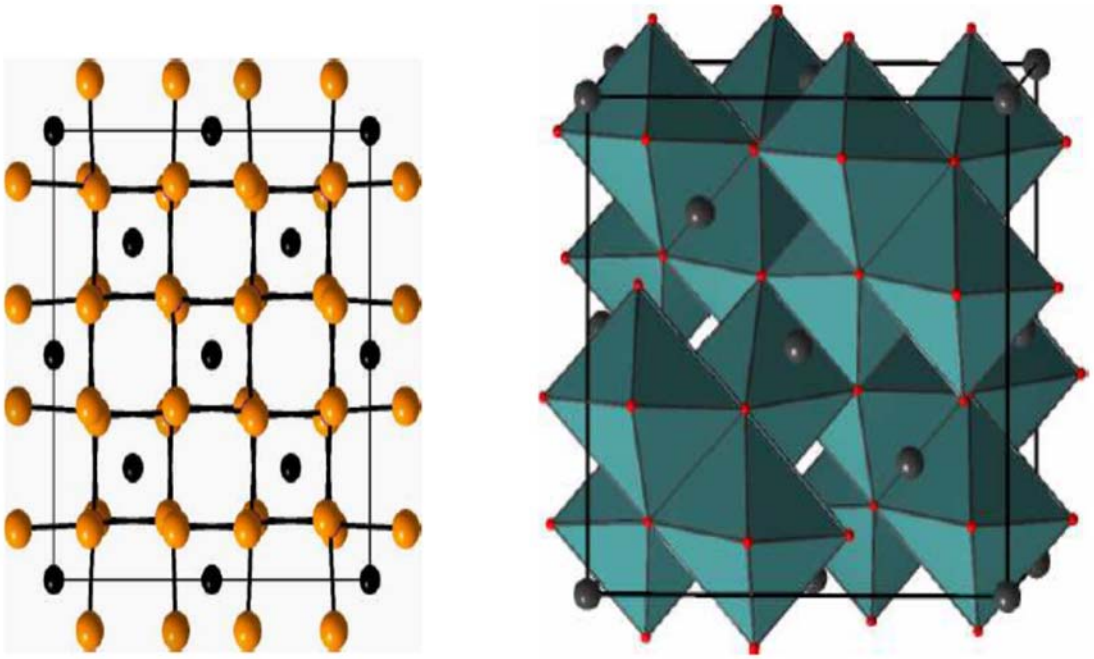


Fig 2.3 The structure of cupper ferrite ($CuFe_2O_4$)

Cupper has three oxidation state, Cu^{+}, Cu^{+2} and Cu^{+3} because of which both hole doping and electron doping are possible. Depending on the valence state of iron (Fe^{+1}, Fe^{+2} and Fe^{+3}), it has 3, 4 and 5 unpaired electrons, respectively, due to Hunds rule. A Cu^{+3} has one unpaired electron due to the $3d^9$ electronic configuration, the fraction of Fe^{+3} ions substituted at the copper site it will have extra moments which are coupled to the lattice of cupper vie super exchange. For the formation of AB_2O_4 inverse spinal structure, A is required to be a dipositive ion that is CuO (tenorite), but Cu_2O (Cuprite) is +1 oxidation state and hence formation of spinal $CuFe_2O_4$ is not favored. Due to the absence of this spinal impurity phase, mixing the iron and copper compound does not show the dominant catalytic property. The coordination number between Cupper and oxygen atoms in tenorite and cuprite is believed to play a crucial role in the

observed catalytic property difference. Generally a proper oxidation state of cupper and iron ion has critical role for the formation of oxygen vacancies in the structure of copper ferrite [23].

It is obvious that oxygen vacancies are more easily formed upon doping Fe^{+3} on CuO on the formation of cupper ferrite [20]. Most of the defects can also be present at free surface of a crystal but their energies are certainly different from those of the defects in the bulk. This means that the defect concentration at the surface also differ from those in the bulk [20]. The oxygen vacancies which are created in the cupper ferrite structure posses fast oxygen transport and high electron conductivity which has a vast application as a catalyst for hydrocarbon oxidation and attract considerable attention as electrodes for solid oxide fuel cells, membrane for oxygen separation and electrolysis [24]. These promising applications stimulate an intensive search about copper ferrite and investigation on fundamental problems related to the oxygen mobility. High catalytic activity certainly related to the high oxygen mobility, understanding of the mechanism such rapid oxygen transport in this oxide at room temperature will be useful to intensively investigate a structure which is important as a catalyst for the hydrocarbon oxidation. The next subtopic focuses how the oxygen vacancies in the copper ferrite are important for the catalytic activity of hydrocarbon oxidation.

2.5.2 The hydrocarbon oxidation mechanism using the Cu-Fe-O catalyst

In the previous subtopic it is clearly introduced the most straight foreword mode of incorporation Fe^{+3} in the CuO lattice which create an oxygen vacancy for charge compensation. In this subtopic, it will be explained how this oxygen vacancy will create an active site for the catalytic activity of hydrocarbon oxidation.

The catalytic activity of copper ferrite is correlated with its ability to (re) generate reactive oxygen hole centers (O^- and O_2^{2-}) by reaction between gaseous oxygen (natural oxygen or air) and oxygen vacancies in copper ferrite. There are a number of oxygen species like O_2 (adsorbed molecule), O (adsorbed neutral atom), O_2^-(superoxide) O_2^{2-}(peroxide), O_3^-(ozonide), etc which may present on the catalyst surface. It is obvious that the copper ferrite has an oxygen deficiency, the deficient oxygen species in this oxide are $2O^-$ because when the iron ion which

has octahedral structure replaces the cupper ion which has a tetrahedron structure, and it is fact that there will be a shortage or a deficiency of two O^- species. When the natural oxygen (O_2) interacts with the copper ferrite, the natural oxygen (O_2) will split and form two O^- to fill the vacancies of oxygen on the copper ferrite surface. The unbound O^- ion on the copper ferrite may move through the lattice to the surface and either take part in a catalytic reaction or be exchanged with gaseous oxygen molecules. The lattice oxygen of the copper ferrite is very active for the oxidation of hydrocarbon and has high recoverability [20]. The formation of surface O^- ions by insertion of oxygen molecule (O_2) in to the surface oxygen vacancies combined with the electron donation to the oxygen molecules can be written as:

$$CuFe_2O_4\,(\text{vacancies of 2 } O^-) + 1/2O_2 \longrightarrow CuFe_2O_4\,(\text{active site of 2 } O^-) \qquad (2.1)$$

There are important facts that need attention on the above mechanism (equation 2.1), the first one is the oxidation energies are more favorable on the surface than in the bulk which means that incorporation of oxygen at the surface is easier than in the bulk [20]. Also most of the defects can also present at the free surface of the crystal because of the energy difference between the bulk and the surface. Second, the relatively small value of the oxidation energy indicates that the partial pressure of oxygen may be an important factor in the relative rates of the formation of peroxides ions in the total catalytic processes. To increase the active site of the oxygen ion it is better to enhance the oxygen vacancy concentration by improving the doping of Fe^{+3}. Generally, the optimized quantity of Fe^{+3} on copper oxide enables a much faster exchange of lattice oxygen with oxygen from the gas phase.

At this stage the copper ferrite is ready to serve as a catalyst for hydrocarbon oxidation because it has an active site that can activate the oxygen molecule and make favorable for oxidation. Generally the catalytic reaction of hydrocarbon has two clear steps i.e. the oxidation of the substrate (hydrocarbon) by the catalyst and the re-oxidation of the catalyst usually by gas phase oxygen. In many practical cases these steps are not simple and elementary reaction, it consists a number of parallel or consecutive partial reactions.

One of the prominent examples of hydrocarbon and which has vast application in many areas are methane, below it will be explained the reaction mechanism of methane oxidation using the activated copper ferrite catalyst. There are strong indications that surface O^- ions are responsible for hydrogen abstraction from CH_4 by copper ferrite [20]. The oxidation of methane using the active site of copper ferrite can be written as follows on equation 2.2 and clearly shown in Fig 2.4 below.

$$2CH_4 + CuFe_2O_4(\text{active site of } 2O^-) \longrightarrow 2^-CH_3 + 2OH^- + CuFe_2O_4(\text{vacancies of } 2O^-) \qquad (2.2)$$

From the above reaction mechanism there may be a formation of methanol at 298K from $^-CH_3$ and OH^-. Desorption of the methanol or meth oxide ions at 773K leads to their decomposition in to CO and H_2 [20]. It is obvious that the target of $CuFe_2O_4$ is to activate one of the reactant using its oxygen vacancies. At this stage (on equation 2.2), the catalyst facilitate the desired reaction path to oxidized methane efficiently.

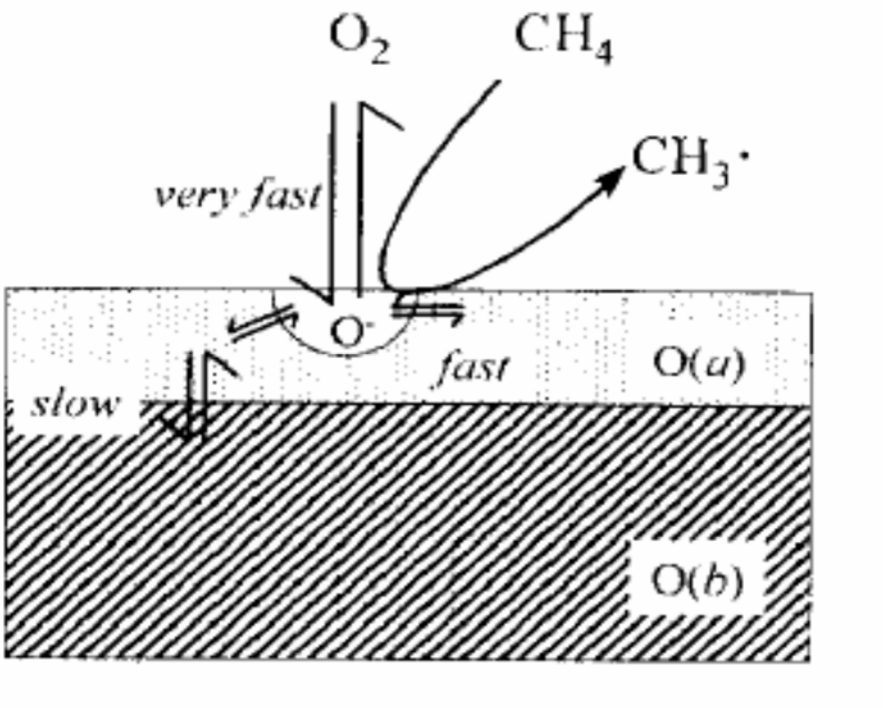


Fig 2.4 Oxygen atom flux in copper ferrite for methane oxidation [20]

The activity of oxygen transport is mainly due to the oxygen defects on catalyst and the presence of the defect play a critical role. The oxygen species are consumed faster by reaction with methane than they can recombine because the activation of oxygen is faster than that of methane [20]. There are two possible explanations if the catalyst has large accumulation of oxygen on the surface. The first one is, at a higher surface concentration of oxygen the probability of methane reacting with two or more oxygen sites leading to total oxidation is higher. Second, at a higher surface concentration of oxygen another type of oxygen species is formed which is more weakly bounded to the surface and favors the non selective oxidation of methane.

The conclusion of the hydrocarbon oxidation using the copper ferrite catalyst will be held using the following concise steps and clearly shown on fig 2.5:

- Copper ferrite should create an oxygen vacancy which paves the way for the next step.
- Basic sites associated with oxygen vacancies dissociate the natural oxygen molecule (O_2), forming active species able to activate methane molecules to enhance the methane oxidation processes. Then the oxidation of methane will go to further processes depending on the need of the oxidation.
- Finally the catalyst regenerates and repeats the first step.

Fig 2.5 General steps of catalysis

2.6 Recent research activity on catalyst

Chemical industry is developing at a steady rate worldwide [9]. Developing novel technologies, engineering solutions, methods and products, elaboration and innovation of new highly selective and active catalysts in industry, and wide application of automation and computerization may sustain the growth of the chemical industry. Recently, chemical industry which produces catalysts has to support big research teams and extensive multimillion researches and development program. All leading chemical companies, which do not produce catalysts as commercial products, have their own research programs in the field of catalysis and production of catalysts, designed for their own processes, which enable them to achieve a break-through on the market. Preservation of technological secrets on the issue of catalysis is the critical issue in businesses dealings between user and producer. As one of the chief employers and main consumer of research products, it is expected that industry will be the main initiator that will understand and define existing and future problems and find their solution. It has to be the provider of funding for research and development teams. Synthesis, characterization and

theoretical modeling of catalyst are the main categories of a latest research which runs on different university and companies.

Important specific research activities on catalyst are the following:

- Studies of catalytic reaction mechanism
- Physical chemistry of surface catalyst
- Application of quantum chemical methods in catalytic research
- Non linear phenomena in catalysis
- Nanoscale catalysis
- Catalyst selection
- Novel catalyst supports and adsorbents
- New catalyst and catalytic processes for environmental protection
- Homogeneous catalysis and catalysis by complex compounds
- Catalyst deactivation

The research in understanding the structure and properties of chemical bonds combined with development of surface science, made it possible to identify the catalytically active centers on the atomic scale and enhance the research activities which run currently especially which related with nanoscale catalyst. A key objective of nanoscale catalyst research is to produce a material with exceedingly high selectivity at high yield in the reaction product that is, chemicals or fuels by design; with the option of altering the product or product slate simply by changing the surface functionality, elemental composition, or number of atoms in the catalyst particle. Recently nanocrystalline metallic and ceramic materials have been successfully investigated for catalytic activities.

The progress of chemical industry depends on its attitude toward chemical science and interest in research work, while the good shape of science is determined by the fact how far it turns its face to the needs and prospects of developments in the industry. Even if currently most research take place on the above mentioned area in developed countries and within multinational companies, this kind of research is quite important for developing countries like Ethiopia.

3. Materials and Methods

3.1 Materials and equipment

The apparatus used in this study are; beakers (different size), measuring cylinder, pipettes, electronic balance, flasks (different size), furnace, Oven, crucibles, thermometer, magnetic plate, X-ray diffract meter, detectors (a standard scintillation detector and a LynxEye Super Speed detector) and Blaine air permeability apparatus (BAPA).

Chemicals consumed in this study are; iron nitrate, cupper nitrate, copper oxide, iron oxide and distilled water.

3.2 Methodology of the research

The methodology followed to prepare and characterize Cu-Fe-O catalyst would be conducted on the following clear steps.

3.2.1 Investigation of raw material available in Ethiopia for bulk catalyst preparation

The availability of local raw material which is necessary for bulk catalyst preparation is investigated using the data which is study by many foreign companies and the geological survey of Ethiopia. It is supposed to accomplish the following specific tasks to access data of local raw material which is important for bulk catalyst preparation;

- Raw materials explored which is available in Ethiopia from different literatures, journals and books. Mainly, it is published by Ethiopian mining ministry which is obtainable in their library. From this data, the available raw material could be figure out.

- From aforementioned data, useful raw materials which are necessary for the preparation of bulk catalyst would be sort out. For this purpose different published literatures would be applied, especially journal of catalyst is dominant source for this task. This work paves the

way to show way of bulk catalyst preparation from the mentioned local raw materials. Finally the important local raw materials which can help for the preparation of bulk catalyst would be listed.

3.2.2 Ways to prepare Cu-Fe-O catalyst

There are different route to prepare Cu-Fe-O catalyst from selected raw materials, the importance and significance of different catalyst preparation method investigated using different literature. From diverse preparation method, dry and wet methods are selected to prepare the copper ferrite at different composition.

Cu-Fe-O catalysts are supposed to be prepared in two ways at different composition, which is solid and wet chemical synthesis method. Three samples at different quantitative composition of cupper and iron are prepared in solid phase synthesis from the starting materials of CuO and Fe_2O_3. Similarly, three sample at different quantitative composition of cupper and iron are prepared in wet chemical method from the starting material $Cu(NO_3)_2.3H_2O$ and $Fe(NO_3)_3.9H_2O$.

3.2.2.1 Characteristics of raw materials

To prepare Cu-Fe-O catalyst, four different kinds of chemicals are used which is purchased from the market. The main characteristic of each chemical will be the following:

- Iron (III) nitrate: Its chemical formula is $Fe(NO_3).9H_2O$, molecular weight is 404.00g/mole. This chemical is light violet or offwhite crystals. Readily deliquescent, soluble in water, ethanol and acetone. Contact with combustible material may cause fire and it is also irritating to eye and skin. The chemical also contain trace amount of chloride, sulfate, copper and matter which is insoluble in water.

- Copper (II) oxide: Its chemical formula CuO, molecular weight is 79.55g/mole and a black powder. This chemical contain trace amount of chloride, sulphate and iron.

- Cupper nitrate: Its chemical formula is $Cu(NO_3)_2.3H_2O$, molecular weight is 241.6g/mole. It is a blue solid but it melts when it is exposed for the atmosphere.
- Iron oxide: Its chemical formula is Fe_2O_3, molecular weight is 159.66g/mole. It is a black solid powder.

3.2.2.2 Laboratory procedure to prepare samples using solid synthesis method

On this specific preparation method, three samples will be prepared at different cupper-iron ratio from CuO and Fe_2O_3 using intimate stoichiometric quantities. The following are the intimate stoichiometric quantitative expression.

- Sample A (Fe/Cu = 2); to get 20 gram of sample, 6.65gram of CuO and 13.35gram of Fe_2O_3 are mixed from its stochiometric relations.
- Sample B (Fe/Cu = 1); to get 20 gram of sample, 8.675gram of CuO and 8.703gram of Fe_2O_3 are mixed from its stochiometric relations.
- Sample C (Fe/Cu = 0.5); to get 20 gram of sample, 12.88gram of CuO and 6.459gram of Fe_2O_3 are mixed from its stochiometric relations.

The prepared samples would be calcite at 850^{o}C for 8 hours (the furnace will take 4 hours to arrive on 850^{o}C).Heating would be interrupted several times to grind the reaction mixture to facilitate the reaction progresses. Each step is clearly described in figure 3.1. Finally the prepared sample preserved for further laboratory work.

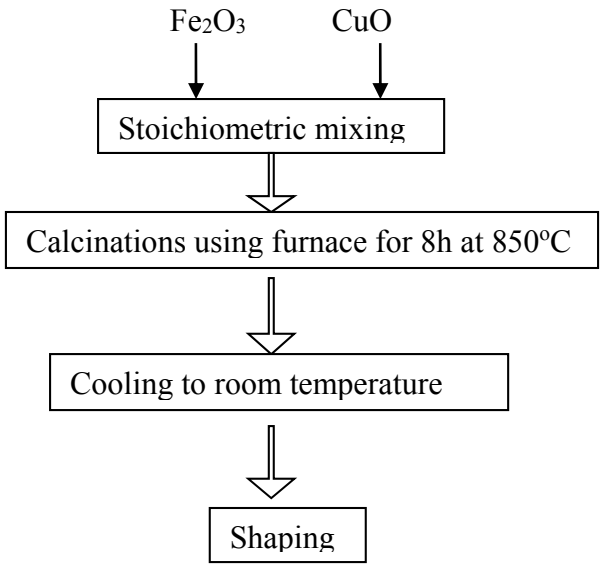


Fig 3.1 Solid state method for sample preparation

3.2.2.3 Laboratory procedure to prepare samples using wet synthesis method

This synthetic procedure was employed to prepare sample from solution residues in order to facilitate the mixing of the oxides before calcinations. On this way three samples prepared at different cupper-iron ratio from $Cu(NO_3)_2.3H_2O$ and $Fe(NO_3)_3.9H_2O$ using intimate stoichiometric quantities. The following are the intimate stoichiometric quantitative expression.

- Sample D (Fe/Cu = 2); to get 20 gram of sample, 20.193gram of $Cu(NO_3)_2.3H_2O$ and 67.523gram of $Fe(NO_3)_3.9H_2O$ are mixed from its stochiometric relations.
- Sample E (Fe/Cu = 1); to get 20 gram of sample, 26.34gram of $Cu(NO_3)_2.3H_2O$ and 44.02gram of $Fe(NO_3)_3.9H_2O$ are mixed from its stochiometric relations.
- Sample F (Fe/Cu = 0.5); to get 20 gram of sample, 39.13gram of $Cu(NO_3)_2.3H_2O$ and 32.71gram of $Fe(NO_3)_3.9H_2O$ are mixed from its stochiometric relations.

Appropriate stochiometric quantities of $Cu(NO_3)_2.3H_2O$ and $Fe(NO_3)_3.9H_2O$ are mixed to 50ml of distilled water in order to make 20gram product. The resulting solution would be heated at 100°C for 48 hours to remove the water using the oven. The resulting solid should be treated at 150°C for 36 hours to allow the complete decomposition of nitrates and then it would be fire in

a furnace at 850°C for 8 hours (the furnace took 4 hours to arrive on 850°C). Its principal procedure is seen in figure 3.2. Finally all samples become ready for characterization. All the above laboratory works are conducted at Addis Ababa Institute of Technology, Chemical Engineering Department.

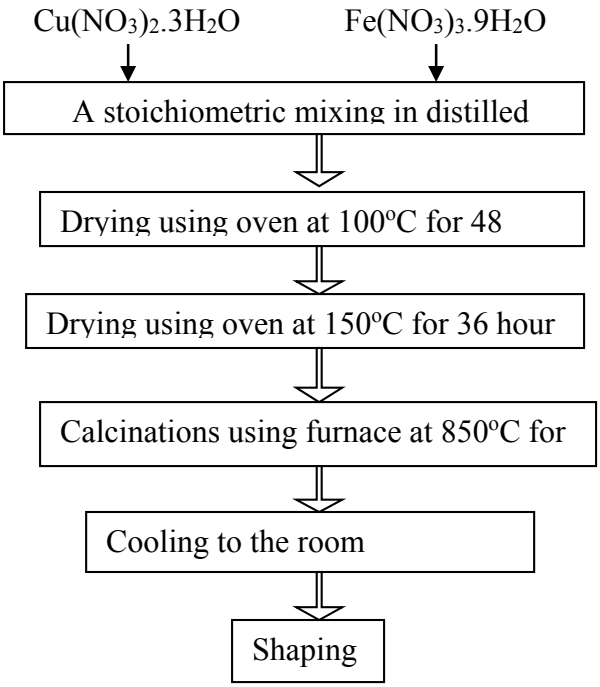


Fig 3.2 Wet-synthesis method for sample preparation

3.2.3 Characterization of Cu-Fe-O sample using XRD

The characterization of different samples which is prepared at different way and at different quantitative composition covered using the following technique. The steps to characterize the sample using XRD are categorized in two steps that is, technique of XRD measurement and way of the XRD result interpretations.

3.2.3.1 Technique of XRD measurement

The structural and phase identification of the prepared sample performed using the XRD equipment so all samples are examined systematically using this equipment. The XRD equipment which will be applied for this work uses Cu-K radiation and it uses computer software

which is known as DIFFRAC^{+}EVA. And the equipment configured with the computer easily and the test of the final result would be captured from the computer. The XRD equipment is available in the Ethiopian geology survey laboratory; this characterization held in this place. The technique to use the XRD equipment is clearly short listed below.

- Prepare the crystalline sample in different tubes.
- There are two types of assembly that make up the sample holder, detector arm and associated gearing one of it is θ: 2θ assembly, the X-Ray tube is stationary, the sample moves by the angle θ and the detector simultaneously moves by the angle 2θ. The second one is θ: θ assembly, the sample is stationary in the horizontal position, the X-Ray tube and the detector both move simultaneously over the angular range θ. In this work θ: 2θ assembly are applied which is seen in figure 3.3.
- The sample tubes placed on the sample holder properly
- The XRD equipment configured with the computer.
- The X-ray tube held stationary.
- The sample holder moves by some specified angle θ, and the detector simultaneously moves by angle 2θ.
- The final diffraction pattern result of each sample captured from the computer

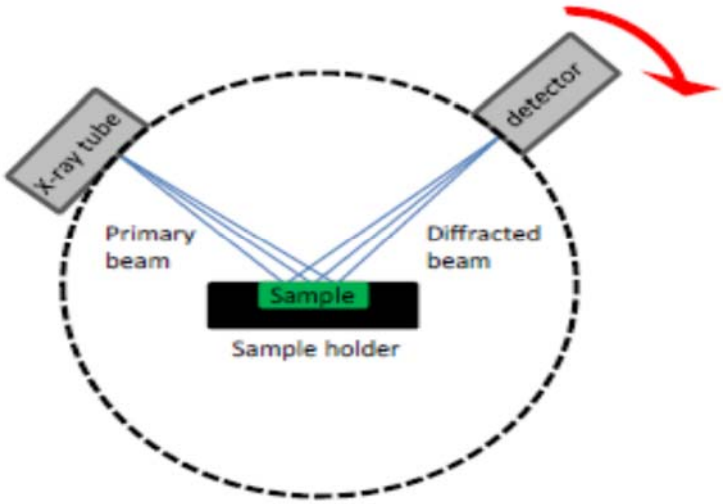


Figure 3.3 The mechanical assembly of X-ray tube, sample holder and detector

3.2.3.2 Methodology of the XRD result interpretations

When X-Rays interact with a crystalline substance (phase), one gets a diffraction pattern. Every crystalline substance gives a pattern: the same substance always gives the same pattern: and in a mixture of substances each produces its pattern independently of the others. The X-Ray diffraction pattern of a pure substance is, therefore, a fingerprint of the substance [25]. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phase. Today a lot of crystalline phase, diffraction patterns have been collected and stored on magnetic or optical media as standards. The main use of powder diffraction is to identify components in the sample by a search or mach procedure [2].

The electrons in an atom coherently scatter light. X-Rays are also reflected, scattered, absorbed, refracted, and transmitted when they interact with matter. The scattering of X-Rays from atoms produces a diffraction pattern, which occurs when light is scattered by a periodic array with a long range order, producing constructive interference at specific angle. The conditions required for constructive interference determined by Braggs' law. Braggs' law is a simplistic model to understand what conditions are required for diffraction. That means, for parallel planes of atoms, with space between the planes is d_{hkl}, constructive interference only occurs when Bragg's law is satisfied and it is stated in equation 3.1 and figure 3.4. Greater electron density in the lattice plane can bring higher scattering factor of a given phase which leads to the idea of intensity is proportional to sum of the scattering factor of a given phase in a given lattice plane. For powder samples all planes with equivalent d-spacing overlap, intensity dependant on the number of overlapping planes.

$$n\lambda = 2d\sin\theta \qquad (3.1)$$

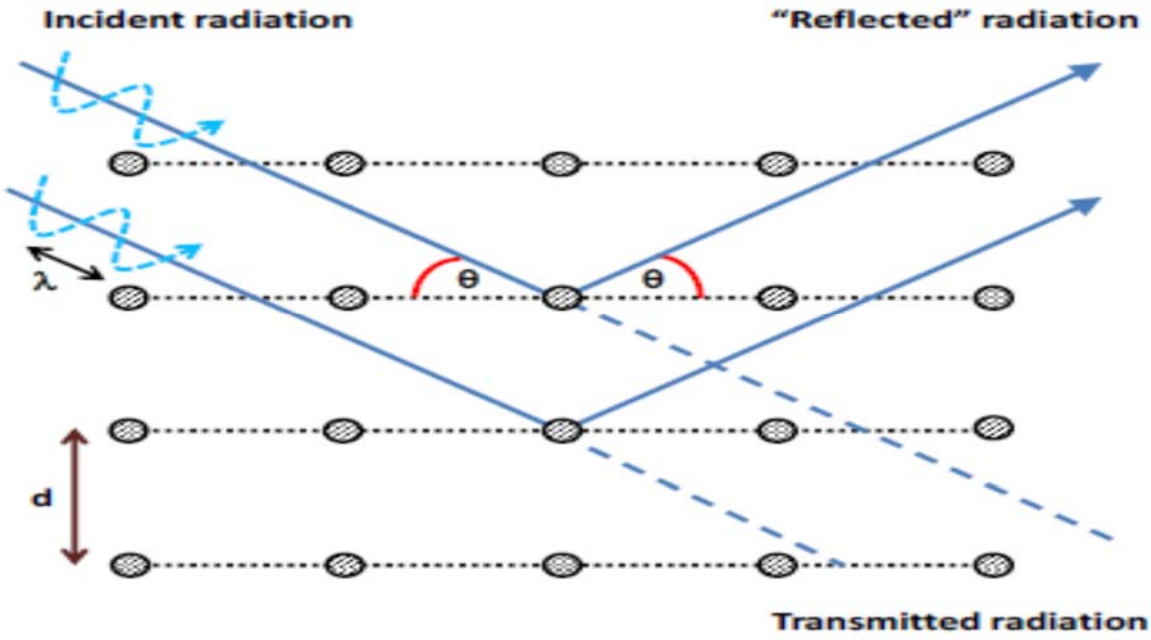


Fig 3.4 Sample of X-Ray diffraction

The diffraction patterns contain information about the atomic arrangement with in the crystal which is a product of the unique crystal structure of the material. The diffraction pattern is collected as 2theta versus absolute intensity. The X-axis, 2theta, corresponds to the angular position of the detector that rotates around the sample. The Y-axis, absolute intensity, shows the number of X-Rays observed in a given peak. Precise analysis of XRD data requires separation of the sample signal from the background and noise. Increasing intensity of incoming beam, using shorter wavelength and increasing amount of sample beam are the important strategies to improve the signal/noise ratio. Generally, the diffraction pattern has information about the position, intensity, width, and shape of a pattern from a polycrystalline sample. All information which is observed from the diffraction pattern is used to determine different characteristic of the catalyst; some of it are mentioned below and clearly shown in figure 3.5.

- Peak position: phase identification using X-Ray diffraction relies mainly on the positions of the peaks in a diffraction profile and to some extent on the relative intensities of these peaks. The types of the phases can be identified using the position and relative intensity of a series peaks. Specimen displacement error that is a misalignment of the sample will cause a small

amount of error in peak position, peaks that are close together should be shifted the same direction and by the same amount and this kind of error is quite tolerable.

- Peak intensity: the intensity of the diffraction peaks are determined by the arrangement of the atoms in the entire crystal which shows the efficiency of X-Ray scattering at any angle by the group of electron on each atom. Each peak also has an intensity which differs from other peaks in the pattern and reflects the relative strength of the atoms this depends on the electron density. The peak intensity is determined by what atoms are in a diffracting plane. The absolute intensity i.e the number of X-Rays observed in a given peak can vary due to instrumental and experimental parameters. The relative intensities of the diffraction peaks should be instrument independent. To calculate the relative intensities, divide the absolute intensities of every peak by the absolute intensities of the most intense peak, and then convert to a percentage. The most intense peak of a phase is therefore always called the 100% peak.

- Peak width: Peak widths are the result of imperfections in both the experimental set up (e.g sample size, slit width, goniometer radius) and the sample type. From the sample type, peak broadening is due to the crystallite size and strain. Strain broadening is come due to the lattice imperfection like dislocations, vacancies, faulting and grain surface relaxation. Crystalline materials composed of infinite array of identical lattice plane. However, periodicity in some sample is not infinite due to imperfection; these finite sizes bring a peak broadening due to size. If the peak broadening is consistent for each peak then it is reasonable that the broadening is due to only crystallite size. The width of the peaks increases as the size of the crystalline domains (crystallites) that diffract the X-Rays decreases. So smaller crystals produce broader XRD peak. Scherrer formula which is stated in equation 3.2 is important to calculate the crystallite size.

$$t = \frac{k\lambda}{(FWHM)\cos\theta} \qquad (3.2)$$

t = thickness or diameter of crystallite (it shows the size of the crystallite)

FWHM = full width at half maximum (the angle broadening should converted to radian)

k = constant dependant on the crystallite shape, it will be 0.89 up to 1.39

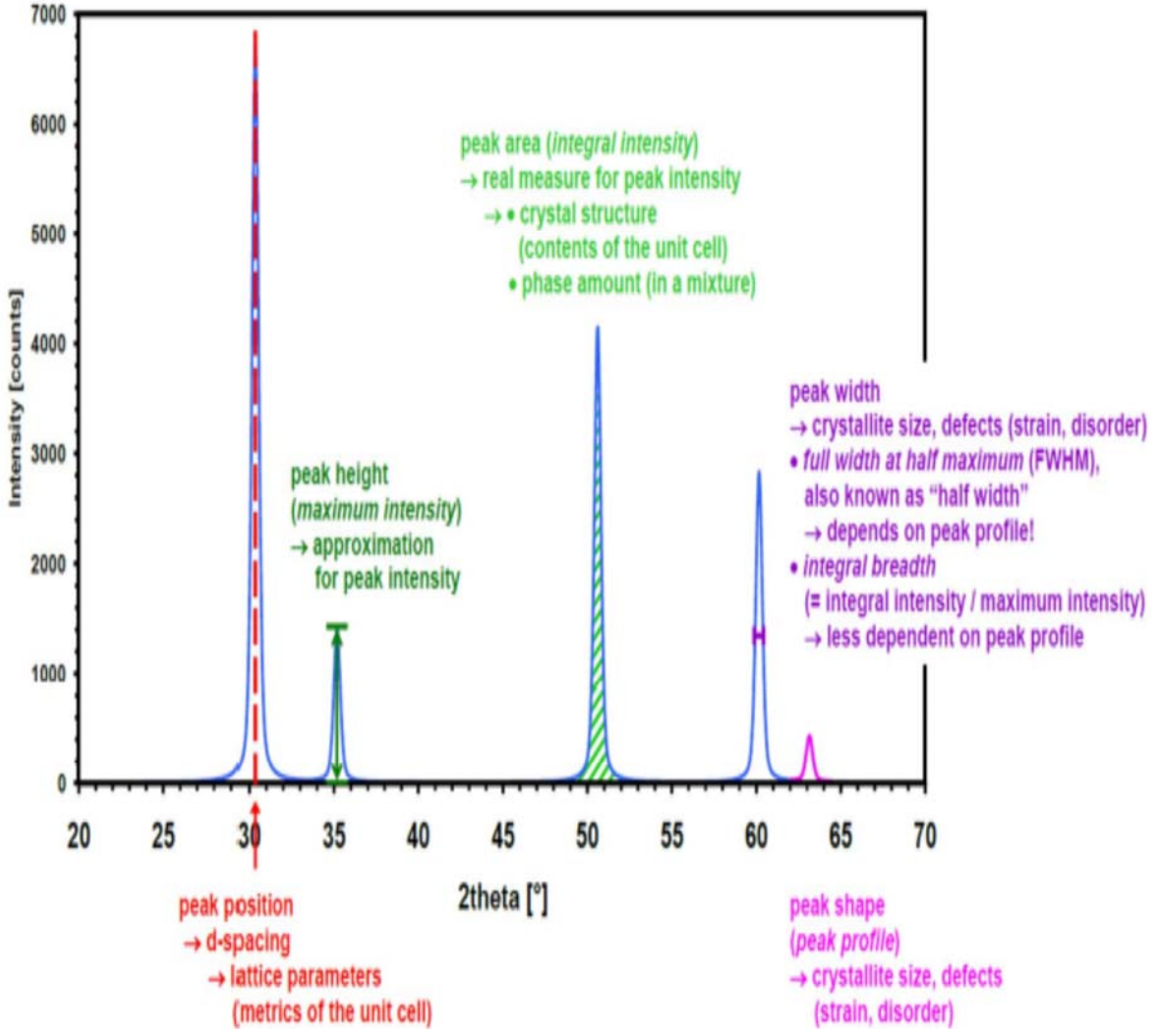


Fig 3.5 Information content of an idealized anatomy of XRD pattern

3.2.4 Analyzing the morphology of Cu-Fe-O catalyst using BAPA

The surface morphology of the catalyst analyzed using different equipment by measuring the specific surface area, porosity and optimum shape of the catalyst. The available equipment in Addis Ababa institute of technology to measure specific surface area is the Blaine air permeability apparatus and all the samples which are prepared at different precursor composition and preparation route are measured using this latest equipment.

Blaine air permeability apparatus (homboldt mfg.co, U.S.A, H-3810) which is illustrated in fig 3.6 below can determine the fineness of the catalyst in terms of specific surface area expressed as total surface area in square centimeters per gram of the catalyst. The set up of the equipment which showed in fig 3.6, consists of calibrated U-tube manometer, ground glass joint, stainless steel test cell, rubber aspirator bulb, perforated disc, wood block for holding test cells, filter paper and red manometer fluid. To measure the specific surface area of the samples using BAPA the following consecutive principal procedure should be conducted.

- Put the sample using the stainless steel at the top of the apparatus
- Close the valve which connect the sample and the manometer
- Creating vacuum on the manometer using a rubber aspirator
- Open the valve
- Measure the time that the red fluid in the manometer arrive on the specified line
- Convert the measured time to the specific surface area using the equation which is found on the manual of the apparatus.
- Repeat all this processes for all samples

Fig 3.6 Set-up of Blaine air permeability apparatus

4. Results and Discussions

4.1 Review of raw materials available in Ethiopia for bulk catalyst preparation

Wide verities of mineral resources are available in Ethiopia, according to recently conducted geological studies. Among various minerals such as metallic, industrial, construction and gemstones, occurrences and deposits have been discovered in different parts of the country [26]. The industrial sector of Ethiopia is small and highly import dependent, using these identified local raw materials is best and along run solution to diversify it.

There are a great opportunity in Ethiopia to prepare a bulk catalyst from local raw material because a recent and decade before conducted geological studies showed the presence of different types of metal oxides. Diverse exploration confirmed the presence of gold, platinum, copper, iron, lead, zinc, tantalite-colombite, manganese and molybdenum. All the mentioned raw materials can serve as a starting material for the preparation of specific bulk catalyst to the intended reaction. The physical and chemical property, cost and availability are main factors which need attention to select the proper starting material for catalyst preparation.

From the aforementioned local metal oxides, there is a great abundance of copper and iron. Kata, Abetselo, Azale-Akendeyu, Tsehafi Emba are specific places which have huge quantity of copper ore [7]. Bikilal, Melka Arba, Chango, Gordana, Worakalu, Yubdo, Kata, Sirba, Korkandi, Kiltukara and Wobera Kiltu are the distinct local places which showed the occurrence of iron ore [7]. From different kinds of metal oxides the composition of iron and copper are believed to be important for high activity in complete hydrocarbon oxidation [9]. Standing from these two concrete ideas i.e. availability and high activity are factors to select cupper and iron as local raw materials to prepare bulk catalyst for hydrocarbon oxidation.

4.2 Characterization of Cu-Fe-O catalyst

Effective catalyst development sciences need an optimization of various properties on catalyst synthesis and using advanced characterization technique. In this project two principal routes applied to get copper ferrite catalyst i.e. solid state and wet-chemical synthesis method. Each route has its own principal procedures to yield an active and selective catalyst. Three samples prepared by conventional solid state method, firing intimate stoichiometric mixture of copper oxide and iron oxide at different composition to realize the desired structure. The remaining three samples prepared by a wet-synthesis method which is an appropriate stoichiometric quantities of copper nitrate and iron nitrate added to distilled water and the resulting solutions had treated thermally.

Solid state mixing avoids the need for solvent removal; the resulting degree of mixing is limited by the particle size of the starting materials. Wet mixing, which can go through a solution or slurry has a better mixing but the removal of water can result in a certain collapse of the structure. To select the best preparation route and the optimum precursor composition, all samples are characterized by XRD and their specific area is measured using Blaine air permeability apparatus.

In the literature review part, the correlation between the catalytic behaviors with the structure of cupper ferrite briefly discussed which shows the catalytic importance of the cupper ferrite structure for the hydrocarbon oxidation. The XRD characterization technique can reveal the types of phase which exists in each sample, the intensity of crystalline for each phases and their periodicity. The general structure characterization was performed for the samples without any size sorting. Generally, the XRD data interpretation of the sample accomplished using the following concise steps:

- Plot the data (2θ vs counts)
- Determine the Bragg angle and the relative intensities for each peak which helps to identify phase. The phase identification can do by matching the samples peak position with the peak position of Joint Committee on Power Diffraction (JCPDS). The JCPDS peak position and their relative intensities is given in table 4.1 and table 4.2 for different types of species.

- Calculate the d-spacing, the lattice parameter and the Miller index (hkl) for each peak using the Bragg law to analyze the atomic structure and microstructure of the atoms.
- Find the broadening of each peak and the thickness of the crystallite using Scherrer's formula.

Table 4.1 Peak position and relative intensities of the Joint Committee on Power Diffraction (α - Fe_2O_3 (JCPDS 034-1266), γ - Fe_2O_3 (JCPDS 39-1346), Fe_3O_4 (JCPDS 19-629))

α - Fe_2O_3 (hematite) JCPDS 034-1266		γ - Fe_2O_3 (maghemite) JCPDS 39-1346		Fe_3O_4 (magnetite) JCPDS 19-629	
2θ	Relative Intensity	2θ	Relative Intensity	2θ	Relative Intensity
24.128	31	18.384	4	18.269	8
33.118	100	30.241	35	30.095	30
35.612	70	35.630	100	35.422	100
40.829	19	37.249	3	37.052	8
49.419	34	43.284	16	43.052	20
54.004	41	53.733	10	53.391	10
57.505	8	57.271	24	56.942	30
62.386	25	62.925	34	62.515	40
63.964	24	71.376	3	70.924	4
71.821	9	74.471	5	73.948	10

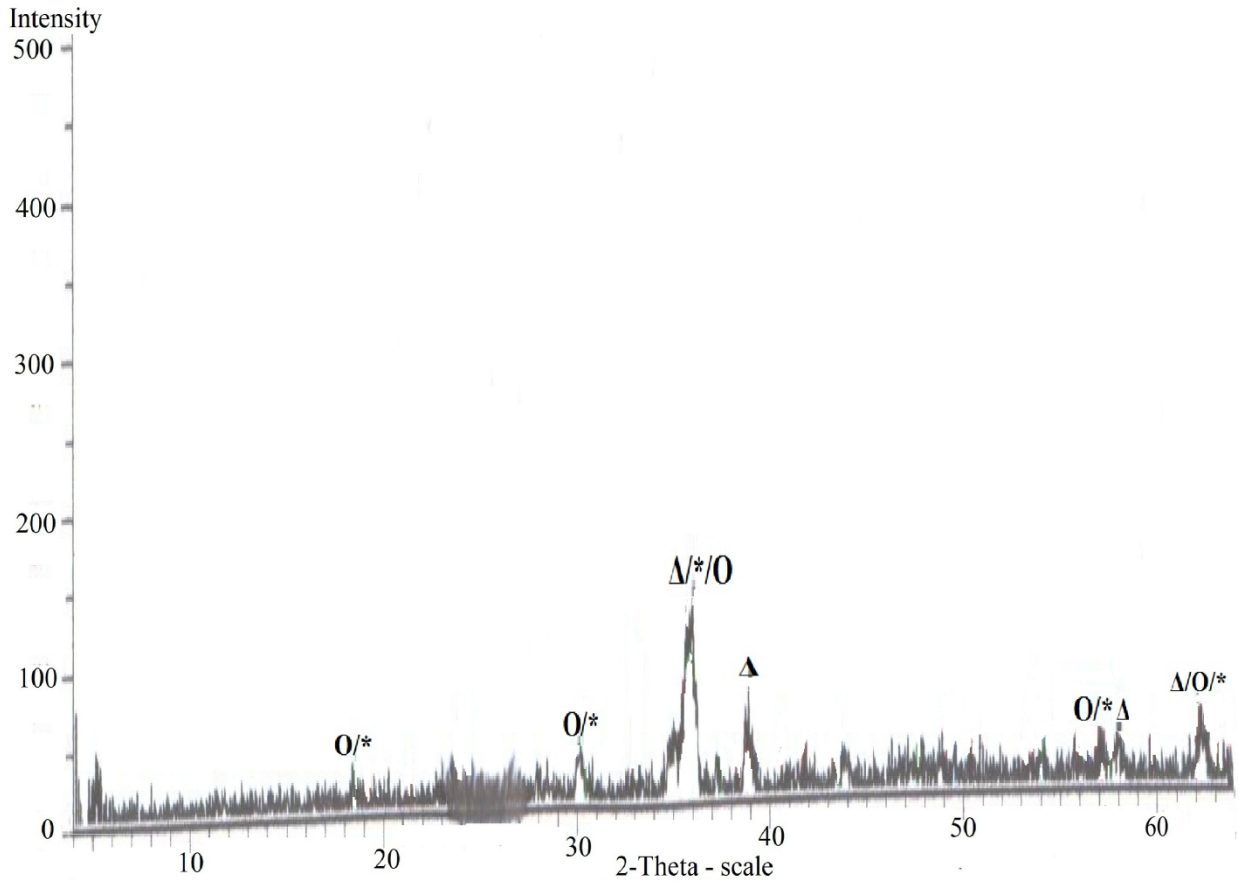
Table 4.2 Peak position and relative intensities of the Joint Committee on Power Diffraction (Cu_2O (JCPDS 05-0667), Cu_2O (JCPDS 05-0667), t-$CuFe_2O_4$ (JCPDS 34-0425), c-$CuFe_2O_4$ (JCPDS 25-0283))

Cu_2O (cuprite) JCPDS 05-0667		CuO (tenorite) JCPDS 05-0661		t-$CuFe_2O_4$ JCPDS 34-0425		c-$CuFe_2O_4$ JCPDS 25-0283	
2θ	Relative Intensity	2θ	Relative Intensity	2θ	Relative Intensity	2θ	Relative Intensity
29.579	9	32.4	8	18.2	17	18.5	30
36.450	100	35.4	100	29.8	32	30.2	50
42.334	37	38.6	92	30.5	13	35.6	100
52.501	1	48.7	21	34.5	53	37.2	10
61.400	27	58.1	11	35.9	100	43.0	30
69.635	1	61.4	16	37.0	14	57.1	40
73.597	17	66.3	13	41.5	11	62.8	60
77.400	4	68.1	13	43.8	22		
92.480	2	75.1	7	53.9	10		
				55.5	12		
				57.9	24		
				62.1	40		
				63.7	16		

Sample A (prepared by a solid state method on the precursor composition of Fe/Cu = 2)

Three types of phases clearly identified in the XRD result of sample A by matching the peak positions with the Joint Committee on Power Diffraction standard that is maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4) and tenorite (CuO). The major peak position at 30.2°, 35.6°, 57.2° and 62.9° are the major peaks which indicate the presence of maghemite (γ-Fe_2O_3). 30.1°, 35.4°, 56.9° and 62.5° are the major peaks which can justify the presence of magnetite (Fe_3O_4). Also there is a low intensity peak at 37.1° indicates the presence of magnetite. The existence of tenorite confirmed by the major peaks at 35.4°, 38.6°, 58.1° and 61.4°. The peak position of this sample don't show the presence of the desired phase which serves as a catalyst for hydrocarbon oxidation.

Even if the sample don't give the desired catalyst, the identified phase also don't have intense peak that means the existing phase don't have a dense electron density. The poor intensity indicates that, the released X-Ray doesn't well scattered and diffracted due to a small density of electron. The identified peak has a very small peak broadening that means all phases have good crystallites which are large crystallites size. Generally, the result of this sample (fig 4.1) has very low peak intensities, small beak broadening and lacks enough peak positions which indicate the presence of copper ferrite so the sample preparation ways and its precursor's composition is not recommended.



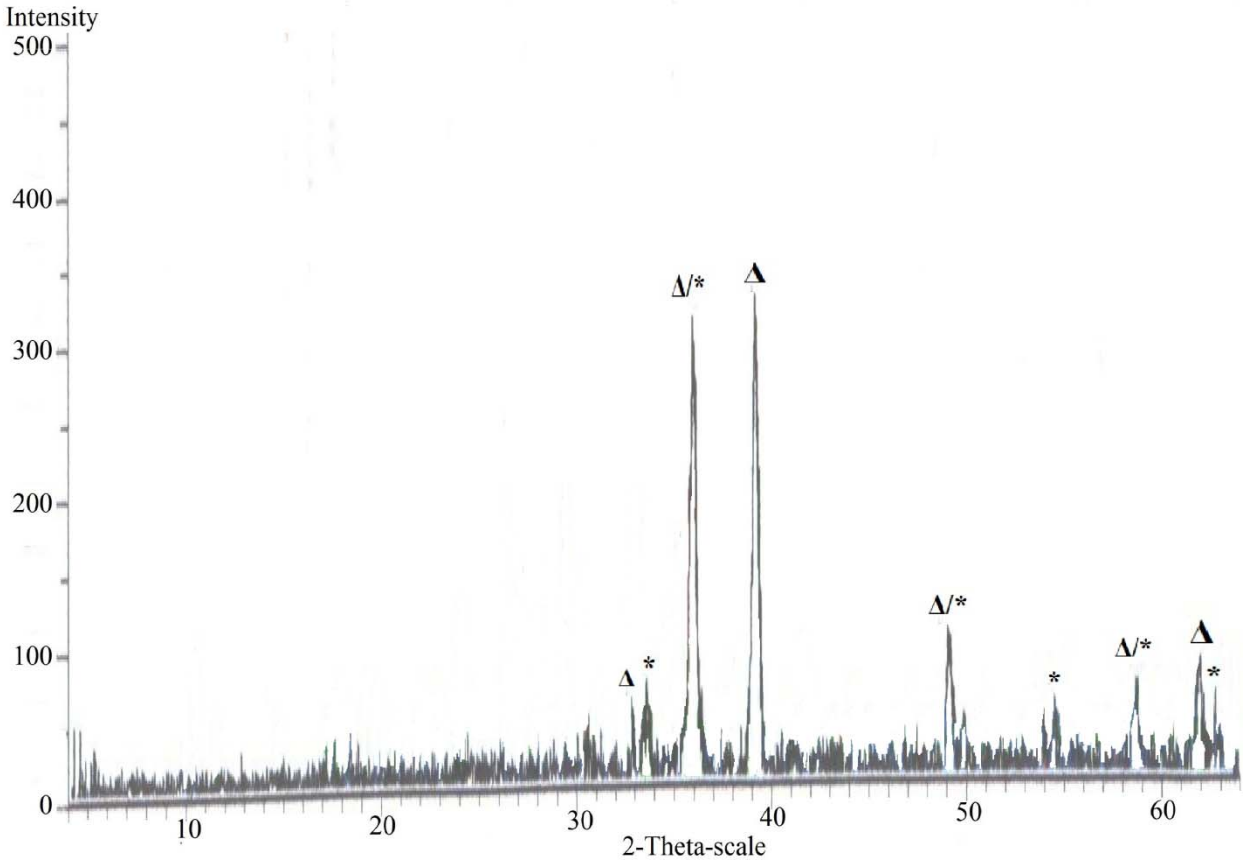
γ – Fe_2O_3 (*), CuO (Δ), Fe_3O_4 (O)

Fig 4.1 The XRD result of sample A

Sample B (prepared by a solid state method on the precursor composition of Fe/Cu = 1)

In the case of sample B, two types of phases clearly identified in accordance with the standard JCPDS peak positions data, the phases are α-Fe_2O_3 (hematite) and CuO (tenorite). The major peak positions at 33.2°, 35.6°, 49.5°, 54° and 62.4° are matched with the peak positions of JCPDS number of 034-1266; it confirms the presence of α-Fe_2O_3 (hematite). The XRD pattern on fig 4.2 showed a peak position at 35.4°, 38.6°, 48.7° and 61.4° which are justifications for the identifications for CuO (tenorite) phase. Even if there are a peak position at 2θ value of 35.9° and 62.1° which mach with the standard peak position of tetragonal cupper ferrite that is stated in table 4.2, but the quantity of peak positions are not enough to make sure the presence of the desired phase.

Even if the samples don't give the desired catalyst, the identified phase has relatively intense peak that means the existing phase have a dense electron density. Their highest intensity showed that, the released X-Ray is well scattered and diffracted due to large density of electron. The highest peak has a positive contribution for the catalytic activity if the desired phase is present. The identified peak has a very small peak broadening that means all phases have good crystallites which are large crystallites size. Generally, the XRD pattern has large peak intensities and very small peak broadening which is a desired structural characteristics for a catalytic activity but the sample don't form the copper ferrite phase so its preparation way and their starting material composition is not optimized.



α-Fe_2O_3 (*), CuO (Δ)

Fig 4.2 The XRD result of sample B

Sample C (prepared by a solid state method on the precursor composition of Fe/Cu = 0.5)

In the case of sample C, the diffraction pattern shown in fig 4.4 clearly confirms the presence of tetragonal $CuFe_2O_4$ structure with a mixture of tenorite (CuO) and γ - Fe_2O_3 (maghemite) in accordance with the JCPDS standard peak position which is given in table 4.1 and table 4.2. There are major peaks on sample C diffraction pattern at 18.2º, 30.5º, 34.5º, 35.9º, 43.8º, 53.9º and 62.1º which match with the JCPDS 34-0425 peak positions that is clearly seen on fig 4.3 and table 4.2; this justification showed the existence of tetragonal copper ferrite on the prepared sample. The presence of tenorite is come true due to a peak position at 35.4º, 38.6º, 48.7º, 58.1º and 61.4º. Peak position at 30.2º, 35.6º, 43.2º, 53.7º and 62.9º are enough values to assure the presence of maghemite. There are small peaks position shift in the same direction and almost by the same amount for all identified phases, it is occurred due to a tiny specimen misalignment of

the sample on the time of XRD measurement and the result is tolerable. Generally, it is quite reasonable to decide the presence of the three phases that is tenorite, maghemite and tetragonal structure cupper ferrite.

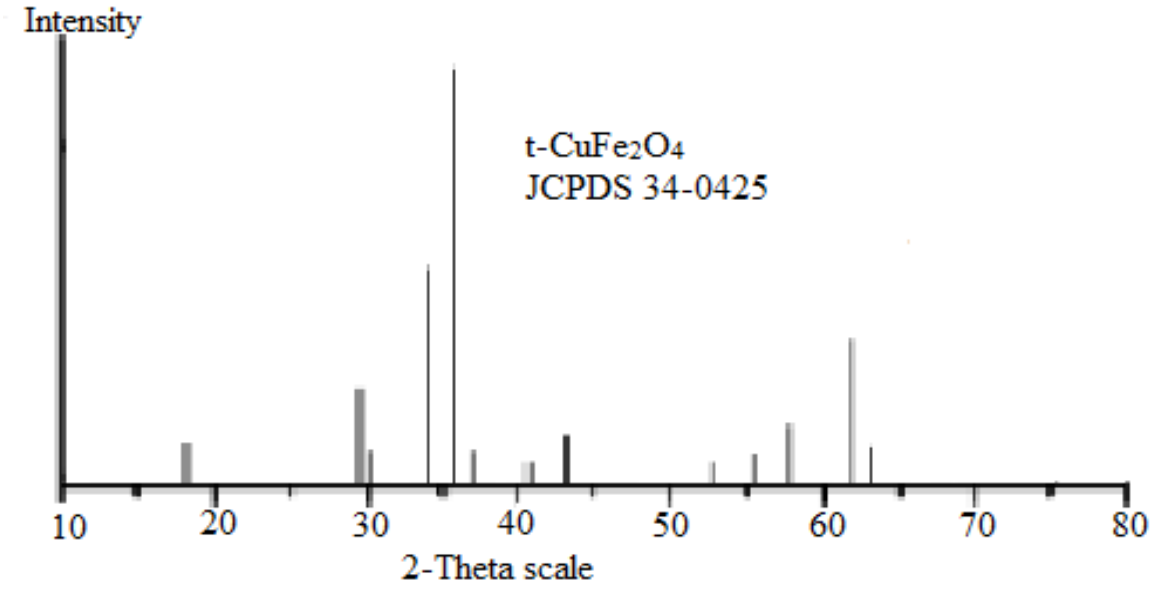
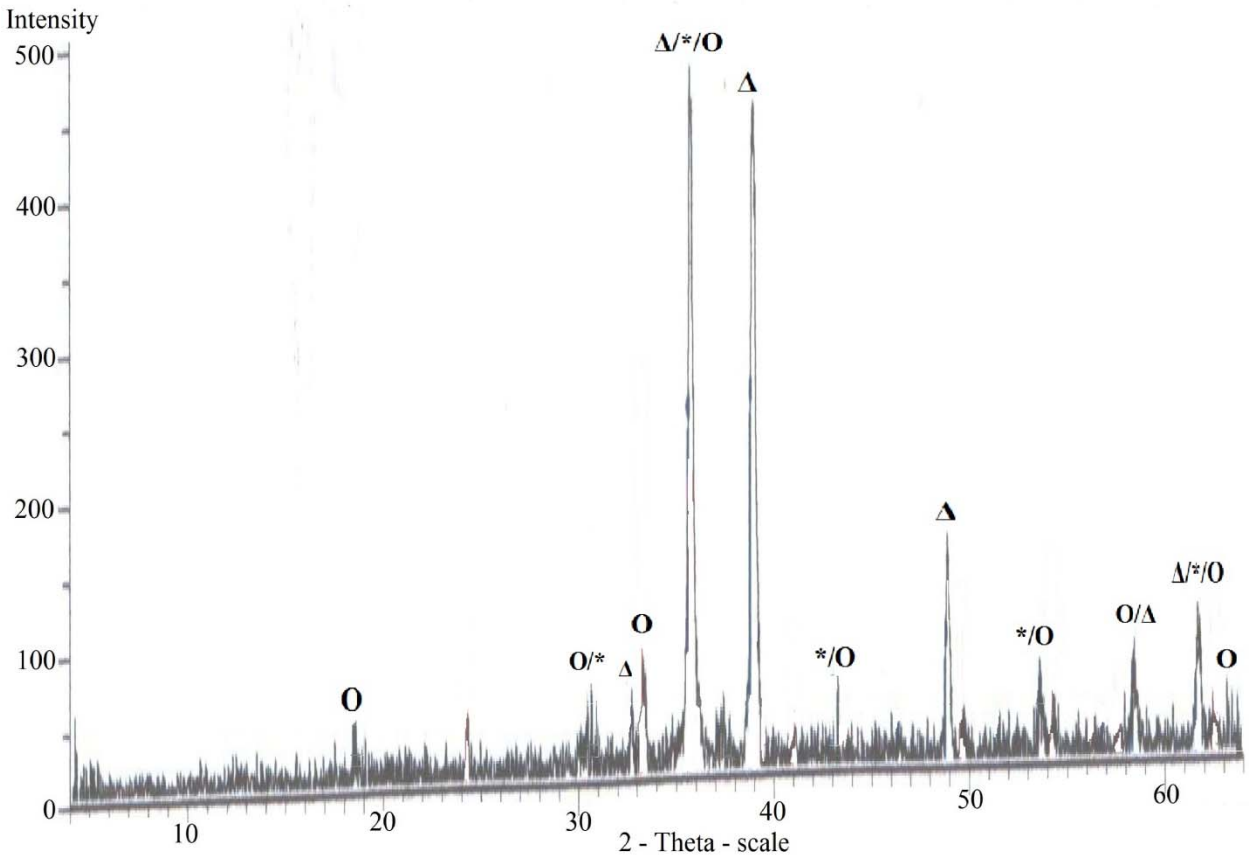


Figure 4.3, The XRD pattern of t-$CuFe_2O_4$ on JCPDS 34-0425

This sample contains the desired catalyst that has a pervoskite structure of AB_2O_4 which plays a critical role as a catalyst. Tetragonal $CuFe_2O_4$ is an inverse spinal in which Cu (II) cations occupy mainly A-sites, where as Fe (III) cations are found on B-sites and A-sites with a proximate equal occupancy. The mentioned property of cupper ferrite creates an oxygen vacancy which makes quite important as catalyst for hydrocarbon oxidation. Each peak positions of copper ferrite on XRD result will be analyzed and interpreted briefly.



γ-Fe_2O_3 (*), CuO (Δ), $CuFe_2O_4$ (O)

Fig 4.4 The XRD result of sample C

The XRD pattern of $CuFe_2O_4$ which is identified in sample C is indexed and the d-spacing is clearly stated in table 4.3 using the knowledge that is explained at the methodology part. The values of absolute intensities don't show certainly the desired result because it is instrument dependant, so calculation of relative intensities of each peak is very necessary using equation 4.1 below.

$$\text{Relative intensities of each peak} = \frac{\text{absolute intensities of each peak}}{\text{absolute intensities of highest peak}} * 100 \qquad (4.1)$$

In this case the absolute intensity of highest peak is 490 which are observed at 2θ value of 36º. The relative intensities of each peak is tabulated in table 4.3 using equation 4.1. Calculation of d_{hkl} value is performed using Bragg's law, quantitatively it can be calculated using equation 4.2.

Unit of the wave length (0.154nm) and d-spacing is similar and each value is tabulated in table 4.3 below.

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \tag{4.2}$$

Each peak is indexed using the knowledge of geometry and d-spacing. The identified phase of cupper ferrite is tetragonal, for this structure the indexed is executed either manually or using a computer programme, in these part it is solved manually. The relation between lattice parameter and d-spacing stated using equation 4.3 from geometry relation.

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \tag{4.3}$$

The lattice parameter of the tetragonal copper ferrite are a = 0.8234nm and c = 0.8646nm [6]. hkl value is parallel if all the value is multiplied by integer, that is (hkl) is parallel to (n*h n*k n*l). Some result in the table 4.3 is displayed by multiplying integer number.

Table 4.3 Structural properties of copper ferrite in sample C

2θ	Absolute intensities (AI)	Relative intensities (RI)	d-spacing (nm)	Miller index (hkl)	FWHM (radian)	Crystallite size (nm)
18.2	70	14.3	0.47	2 0 3	-	
30.5	80	16.3	0.29	9 4 6	-	
33.9	110	22.4	0.26	3 1 0	-	
35.9	490	100	0.25	3 1 1	0.0087	17.49
43.8	90	18.4	0.21	2 5 6	-	
53.9	100	20.4	0.17	1 2 1	0.0069	23.53
58.5	115	23.5	0.16	1 1 1	0.0052	31.90
62.1	145	29.6	0.15	1 0 1	0.0087	19.411
63.7	90	18.4	0.14	2 1 2	-	

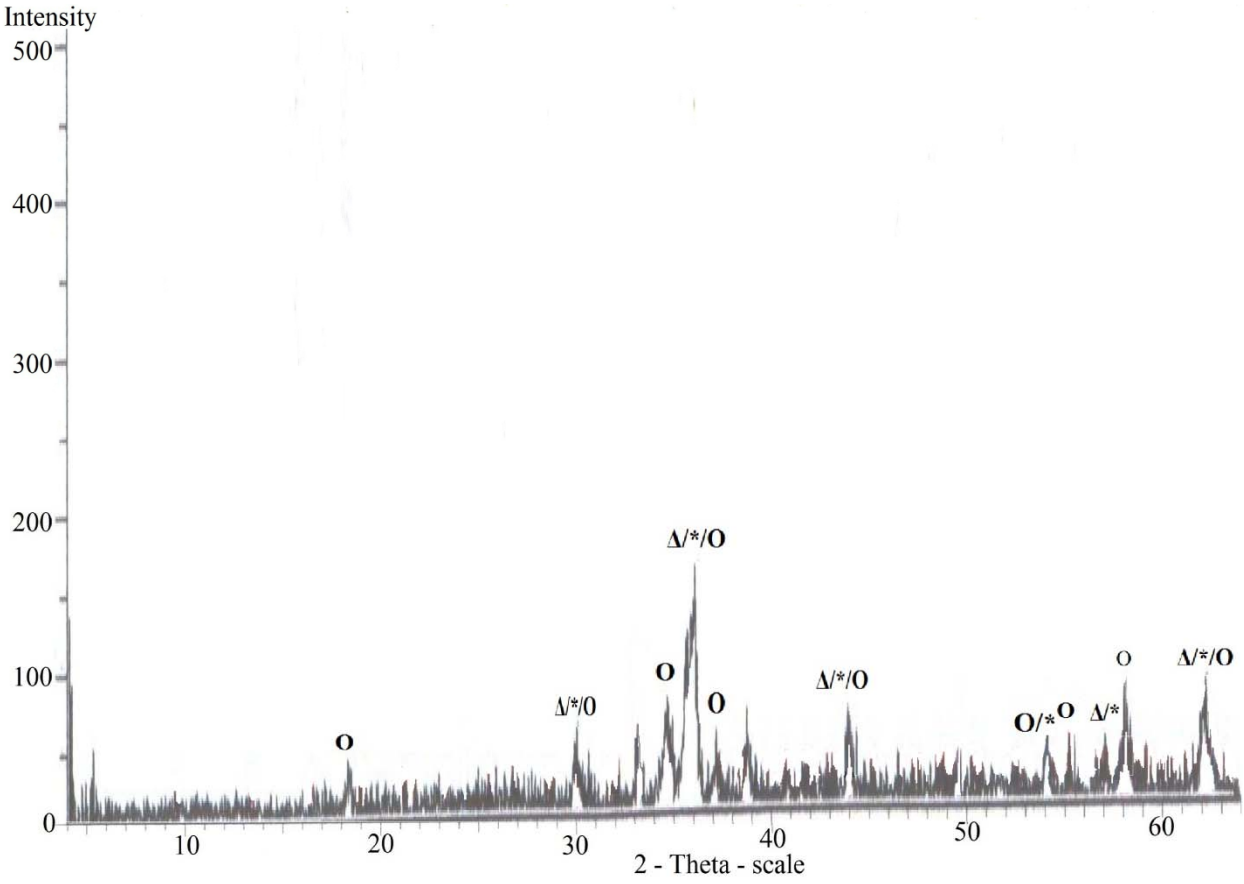
The intensities of most peak is poor except which is observed on at a peak position of 36º. The intensities indicate about the electron density inside the unit cell. Most peaks that showed the presence of copper ferrite have low intensities so on each lattice plane the electron is not densely populated. But in the peak position at 36º, there is a strong density of electron on the lattice plane of (3 1 1) therefore the catalytic activity of the copper ferrite is very active in this lattice plane.

The Bragg's law assume that ideal conditions are maintained during diffraction, one of this condition is the crystal is perfect that means the crystallite size is infinite and there is no dislocation, vacancies, faulting and grain surface relaxation. In practice this condition never exists. The implication of these imperfections is reveled on the peak broadening on sample C at a peak position of 36º, 53.9º, 58.5º, 62º on a 2θ value; it is supposed that these peaks broadening is occurred due to smaller crystallite size as well as strain. If the peak broadening is consistent for each peak then it is reasonable that the broadening is due to only crystallite size. On this sample peak broadenings are consistent, so all the peak broadening is due to the imperfection of the crystallite size not related with strain. Using Scherrer formula, the crystallite size is calculated in each peak and tabulated in table 4.3. On the 36º peak position, there is large peak broadening and the calculated crystallite size also smallest. From the table 4.3 and fig 4.4, the peak position which is observed at 18.2º, 30.5º, 33.9º, 43.8º, 63.7º at 2θ value don't have observable peak broadening so the crystallite size will approach to the ideal condition of the Bragg's law that is, on these peak position the crystallite size is close to infinite. Physically the lattice planes of the mentioned peak positions have an infinite periodicity of their crystal structure. Therefore, these peak positions are much desired in the case of catalytic activity because of the periodicity of crystallite size.

Generally, this sample shows the presence of a desired phase that is copper ferrite which serves as a catalyst for hydrocarbon oxidation. Also the identified copper ferrite has almost infinite periodicity of the crystallite size which has a positive contribution for catalytic activity and their low intensities is come due to low densities of electron on each plane except at a peak position of 36º.

Sample D (prepared by a wet-synthesis method on the precursor composition of Fe/Cu = 2)

In sample D, the diffraction pattern shown in Fig 4.5 and table 4.4 clearly confirms the presence of tetragonal structure $CuFe_2O_4$ phase with a mixture of Fe_3O_4 (magnetite) and γ - Fe_2O_3 (maghemite) in accordance with the JCPDS standard peak position which is given in the above figure 4.3, table 4.1 and table 4.2. The XRD result on this sample show a major diffraction peak at 18.2°, 30.5°, 34.5°, 35.9°, 37.0°, 43.8°, 53.9°, 55.5° and 62.1° which match with the JCPDS 34-0425 peak positions that is clearly seen on fig 4.3 and table 4.2; this justification showed the existence of tetragonal copper ferrite on the prepared sample. The presence of Fe_3O_4 (magnetite) is come true due to peak position at 30.0°, 35.4°, 43.0° and 62.5°. Peak position at 30.2°, 35.6°, 43.2°, 53.7° and 62.9° are enough values to assure the presence of maghemite. There are small peaks position shift in the same direction and almost by the same amount for all identified phases, it is occurred due to a tiny specimen misalignment of the sample on the time of XRD measurement like which is seen in sample C and the result is tolerable. Generally, it is quite reasonable to decide the presence of the three phases that is Fe_3O_4 (magnetite), γ-Fe_2O_3 (maghemite) and tetragonal cupper ferrite. But there is no clear phase identified on peak position which is observed at 32.2°. This sample contains the desired catalyst that has a pervoskite structure of AB_2O_4 which plays a critical role for hydrocarbon oxidation so each peak position of copper ferrite on XRD result will be analyzed and interpreted below.



Fe_3O_4 (Δ), γ-Fe_2O_3 (*), $CuFe_2O_4$ (O)

Fig 4.5 The XRD result of sample D

The peak position, absolute intensities, relative intensities, d-spacing, miller index, full width at half maximum and the crystallite size is clearly calculated and tabulated in table 4.4. The intensities can tell about the electron density inside the unit cell. The diffraction pattern has very low intensities so on each lattice plane the electron is not densely populated. But in the peak position of 35.9^o and 34.5^o at 2θ value the XRD pattern has very good intensities that means there is a strong density of electron on the lattice plane of (3 1 1) and (3 1 0) so the catalytic activity of the copper ferrite is very active in these plane.

Table 4.4 Structural properties of copper ferrite which exist in sample D

2θ	Absolute intensities	Relative intensities	d-spacing	Miller index (hkl)	FWHM (radian)	Crystallite size (nm)
18.2	50	27.8	0.48	6 3 1	0.0052	28.20
30.5	75	41.7	0.30	1 0 1	0.0069	21.74
34.5	90	50	0.26	3 1 0	0.0087	17.42
35.9	180	100	0.25	3 1 1	0.0122	12.48
37.0	75	41.7	0.24	3 6 1	0.0052	29.38
43.8	85	47.2	0.20	4 1 0	0.0052	30.01
57.9	100	55.6	0.16	1 1 1	0.0052	31.86
62.1	100	55.6	0.15	1 0 1	0.0087	19.44

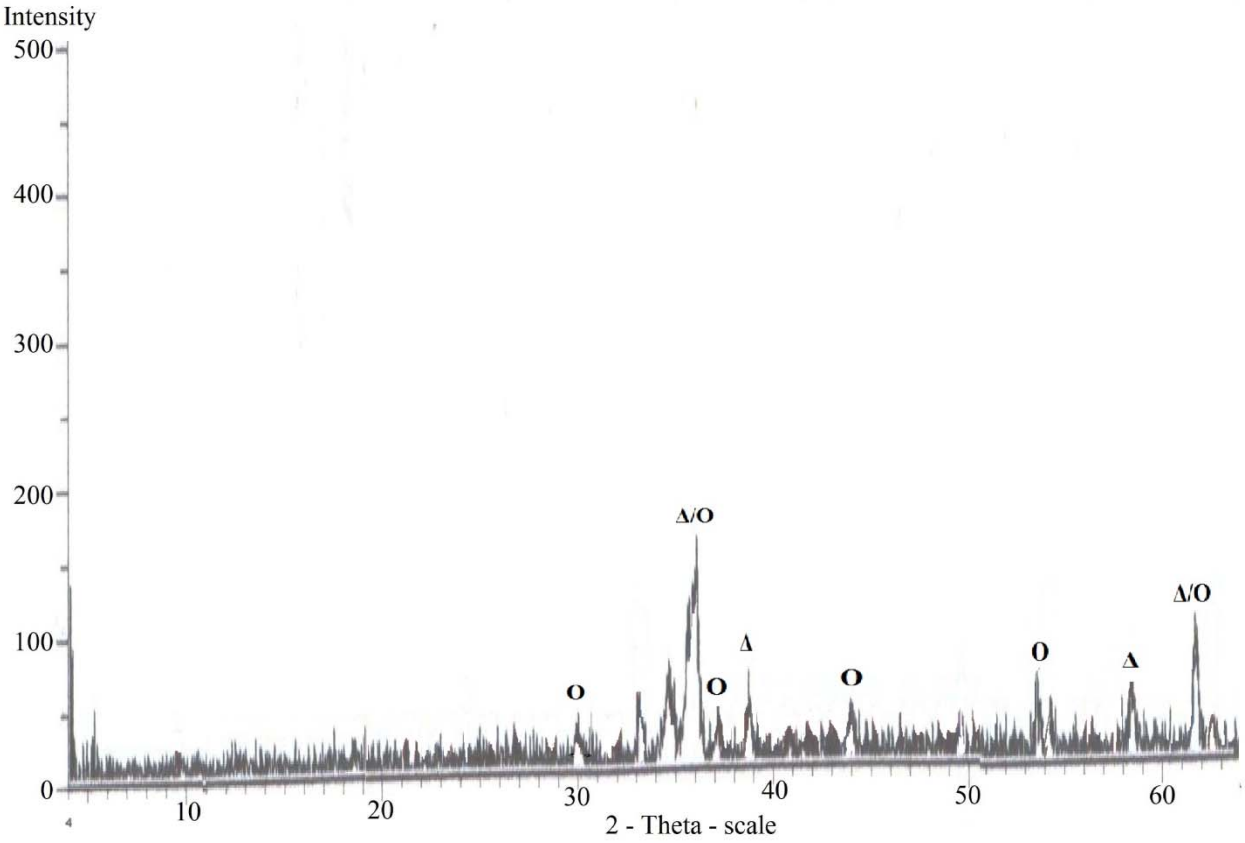
The crystallites of the catalyst should be perfect as much as possible that means the crystallite size is infinite and there is no dislocation, faulting and grain surface relaxation. But on this sample this condition is not observed. The implication of these imperfections is reveled on the peak broadening on sample D on all peak positions. The characteristics of the peak broadening are consistent, so all the peak broadening is developed due to the imperfection of the crystallite size. Using Scherrer formula, the crystallite size is calculated in each peak and tabulated in table 4.4. On the 35.9^{o} peak position, there is a large peak broadening and the calculated crystallite size also smallest: the periodicity of this lattice plane (3 1 1) will be very poor and this is not a good character for catalytic activity. Relatively the peak position which is observed at 57.9^{o} has good periodicity on the lattice plane of (1 1 1) and it will have a good contribution for the catalyst activity. Generally on this sample it has a desired phase which serves as a catalyst for hydrocarbon oxidation but the phase has poor periodicity that means it has low crystallite size also the electron is not densely populated on each lattice plane.

Sample E (prepared by wet-synthesis method on the precursor composition of Fe/Cu = 1)

In sample E, tenorite (CuO) and γ - Fe_2O_3 (maghemite) phases are clearly identified in accordance with the JCPDS standard XRD peak position. The result in this sample don't engender craved phase which serves as a catalyst, the peak positions are not enough to assure

the presence of copper ferrite. The major peak positions at 30.2°, 35.6°, 43.2°, 53.7° and 62.9° are matched with the peak positions of JCPDS number of 39-1346; it confirms the presence of γ-Fe_2O_3 (maghemite). The XRD pattern on fig 4.6 showed a peak position at 35.4°, 38.6°, 58.1° and 61.4° which are justifications for the identifications for CuO (tenorite) phase.

Except a peak position at 35.5°, all the remaining peak position is not intense that means the existing phases don't have a dense electron density. The poor intensity showed that the released X-Ray doesn't well scattered and diffracted due to small density of electron. The identified peak has a very small peak broadening that means all phases have good crystallites which are large crystallites size and very small lattice imperfection. Generally, the preparation route and the precursor composition which applied on this sample are not recommended to get a copper ferrite catalyst.



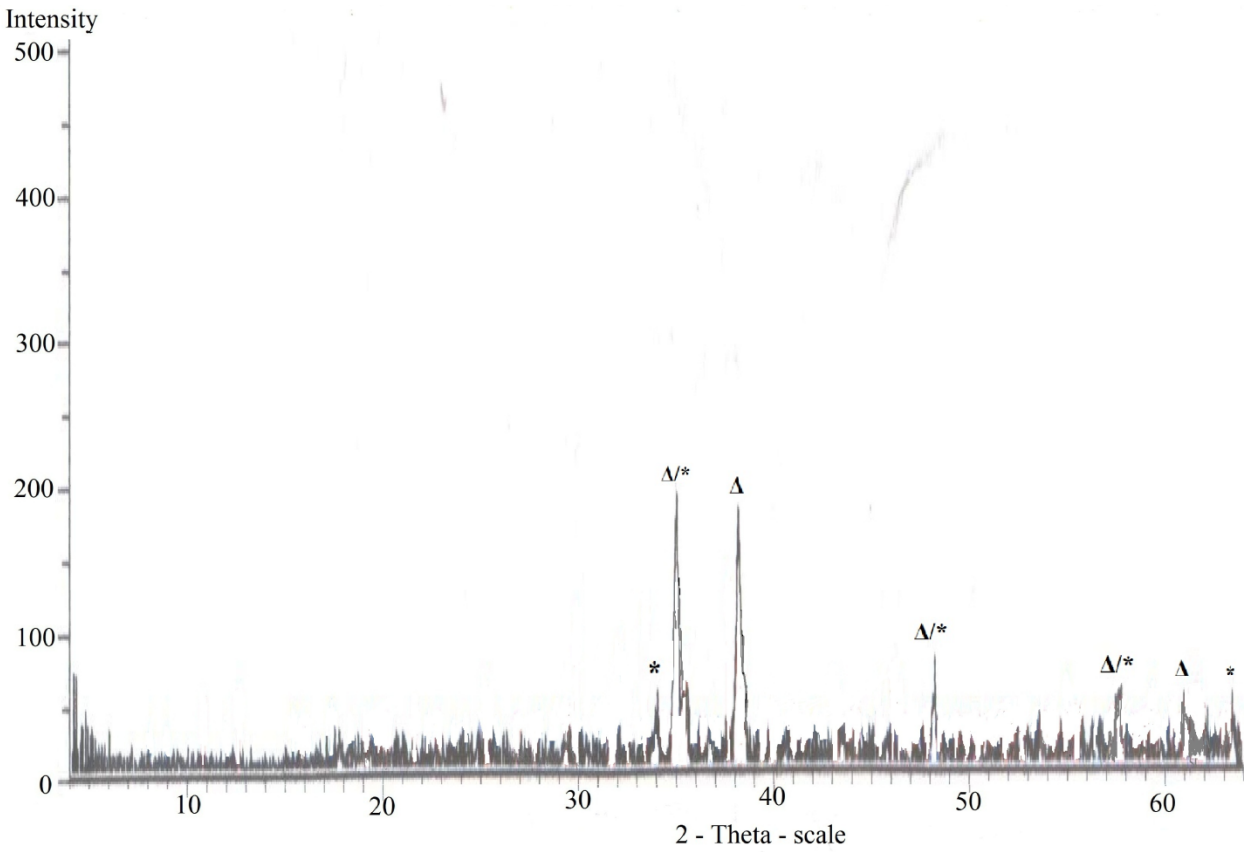
CuO (Δ), γ-Fe_2O_3 (O)

Fig, 4.6 The XRD result of sample E

Sample F (prepared by a wet-synthesis method on the precursor composition of Fe/Cu = 0.5)

In sample F, α-Fe_2O_3 (hematite) and CuO (tenorite) phases are clearly identified by matching the diffraction pattern on figure 4.7 and the JCPDS standard XRD peak position. The major peak position at 33.1º, 35.6º, 49.4º and 62.3º are the major peaks which indicate the presence of α-Fe_2O_3 (hematite). Also, 35.4º, 38.6º, 48.7º and 61.4º are the major peaks which can justify the presence of CuO (tenorite). The result in this sample don't engender craved phase which serves as a catalyst, the number of peak positions are not enough to assure the presence of copper ferrite.

Except a peak position at 35.9º and 38.5º all the remaining peak position is not intense that means the existing phases don't have a dense electron density. The poor intensity showed that the released X-Ray doesn't well scattered and diffracted due to small density of electron. The identified peak has small peak broadening that means all phases have good crystallites which are large crystallites size and very small lattice imperfection. Generally, the preparation route and the precursor composition which applied on this sample are not recommended to get a copper ferrite catalyst.



CuO (Δ), α-Fe_2O_3 (*)

Fig 4.7 The XRD result of sample F

In this work six samples are developed at different preparation route and precursor compositions and it is characterized by XRD techniques to declare the presence of Cu-Fe-O catalyst and to investigate different structural property. The result showed that only sample C and sample D shows the presence of this most wanted catalyst and the remaining samples don't provide the expected phase. All samples have good peak intensity at a peak position of 36^o and the rest peak positions have very poor intensity. The poor intensity of all peaks in each sample indicates that the presence of a poor electron density on each lattice plane. All sample shares the same characteristic regarding on the peak broadening that is it has very small broadening and this is considered to be one of a positive factor for the catalyst activity.

4.3 Surface morphology analysis for Cu-Fe-O catalyst

To find Cu-F-O catalyst which serves for hydrocarbon oxidation, the concentration and surface distribution of metal oxide alone, without considering the surface morphology is not sufficient. Getting a desired specific surface area is vital on catalyst preparation, yet relatively little attention is paid to optimize the catalytic activity through the rational method of surface morphology. Design and synthesis of materials with well defined particle size, morphology and ordered porosity is burgeoning area of current research in catalyst preparation. The specific size and morphological structure of the catalyst can have significant influence on the processing of raw materials and on the effectiveness of their catalytic activity to get the desired product [27].

There are different types of equipment which works in different principle to determine porosity and specific surface area. Blaine air permeability apparatus is one of the well known equipment which can determine fineness of a catalyst in terms of specific surface area properties. It is obvious that, all experimental method and equipment don't engender the absolute value of parameters such as porosity, surface area, pore size, and surface roughness. Each gives a characteristic values that depend on the principle involved and the nature of the probe used (atom or molecule, radiation wavelength etc). Similarly, Blaine air permeability apparatus works based on specific physical principles and theory to determine specific surface area.

The specific surface area is defined as the area of solid surface per unit mass of material. In practice, what is actually determined is the accessible or detectable area of solid surface per unit mass of material. This distinction is important because the value determined in a measurement is dependent on the method, the experimental condition employed, and the size of the probe (example the molecular size of the adsorbate or the wavelength of the radiation probe). More significantly, specific surface area measurement using Blaine air permeability apparatus is deduced from measured quantities that must be interpreted using simplified equation which can connect the measured quantities with specific surface area.

It is obvious that the six samples are prepared at different composition and catalyst preparation ways. A sample which will have a high specific surface area has advantageous for hydrocarbon

oxidation by giving large access for the reactant rather than a sample which has small specific surface area. The Blaine air permeability apparatus which serve for this purpose operates on explicit theories and it has specific equation (equation 4.4) which helps to find the specific surface area of each sample. The equation will change the amount of time which is measured from the equipment for each sample to the specific surface area. To make sure on the final results, each samples measured four times and all the result and the average value is tabulated in table 4.5.

Table 4.5 The measured time from the experiment for all samples

sample	Trial 1 (time in second)	Trial 2 (time in second)	Trial 3 (time in second)	Trial 4 (time in second)	Average value (second)
A	15.12	17.03	17.50	16.59	16.56
B	3.90	4.42	4.98	5.57	4.71
C	5.22	5.30	5.05	5.35	5.23
D	4.50	4.89	5.05	4.99	4.85
E	1.19	0.98	1.00	1.05	1.05
F	4.36	4.38	4.42	4.54	4.42

There is an equation (equation 4.4) from the manual of Blaine air permeability apparatus and the measured data from table 4.5. The above table is converted using equation 4.6 to find the specific surface area of each sample, average value of time is used for the calculation of specific surface area. And the specific surface area of each sample is tabulated in table 4.6.

$$S_{sample} = S_{standard} \frac{\sqrt{\text{Time of sample}}}{\sqrt{\text{Time of standared}}} \quad (4.4)$$

- S_{sample} = specific surface area of the sample
- $S_{standard}$ = specific surface area of the standard = 3774 cm^2/g
- Time of standard = 58.3sec

- Time of sample = a time which is measured on the experiment.

Table 4.6 Specific surface area of each sample

Sample	**Average time value (sec)**	**Specific surface area (cm^2/g)**
A	16.56	2 012.7
B	4.71	1 073.4
C	5.23	1132.69
D	4.85	1090.14
E	1.05	506.81
F	4.42	1 039.83

From the result, sample A has large specific surface area but XRD result showed that it lacks the desired phase that is copper ferrite, so this largest surface area by itself doesn't show a promising catalytic activity for the intended reaction. The second largest specific surface area is observed in sample C which shows the presence of copper ferrite in the XRD measurement, so it has proper composition of precursor and follows the right preparation technique. Sample E has the lowest specific surface area; this sample didn't show the presence of copper ferrite, so it has the improper composition and inaccurate preparation technique.

Finally, shaping a catalyst is quite important and the final step of catalyst preparation, basically it needs empirical knowledge to select the desired final shape of a catalyst. The parameters which are influenced by the shape of the catalyst are pressure drop, diffusion, specific surface area and boundary effects. As much as possible, the shape of catalyst should decrease the pressure drop in the reactor and it should enhance the diffusion of the reactant by increasing the specific surface area. Therefore, the final selection of shape and size is driven by the specific type of reactor which optimized the pressure drop and specific surface area [12].

5. Conclusion and Recommendation

5.1 Conclusion

In this project, catalyst is prepared and characterized from local raw materials which have the capacity to increase the efficiency of hydrocarbon oxidation. The final conclusion after persistent and unreserved effort is mentioned below.

Diverse mineral exploration project (Ethio-Korean, Ethio-Czechoslovakia, UN-Ethiopia, Ethio-Malaysia and Ethiopia geology survey) witnessed that, Ethiopia is blessed with abundance of natural minerals and resources. Detailed surveys of the aforementioned exploration projects outlined the presence of copper, iron, gold, cobalt, potassium, silicon, rhodium, tantalite, soda ash, and phosphate rock. As a matter of fact, the composition of iron and copper are believed to be important for high catalytic activity for hydrocarbon oxidation. Standing from these two concrete ideas that is, availability and high catalytic activity forced me to choose copper and iron as local raw materials for the preparation of bulk catalyst. Mixing, calcinations and shaping are the main unit operations that are necessary to get the most wanted result.

The phase identification and structural property of all samples characterized by XRD. Only sample C and sample D shows the presence of a desired catalyst (copper ferrite) but the remaining samples don't offer the expected phase. The XRD result of the entire sample share common structural property that is poor peak intensity which indicates the presence of poor electron density in each lattice plane. A very small peak broadening is observed in each sample which is a justification of good periodicity of crystallite size and small lattice imperfection.

The surface morphology analysis is done by Blaine air permeability apparatus and hand crew pelletizer. The result of Blaine air permeability confirms that, sample A and sample C has a highest specific surface area which is a desired property for catalyst activity. The selection of final shape and size is driven by the type of reactor to reduce a pressure drop which is supposed to occur in the reactor.

Generally, Ethiopia is reach on iron and copper ore in most parts of the country in a massive quantity that would serve as a raw material for bulk catalyst preparation. A solid state mixing of iron oxide and copper oxide on a stochiometric quantitative composition of Fe/Cu = 0.5 is needed, a properly mixed sample should calcined at 850^{o}C for 8 hour and the final shape is determined depending on the type of reactor that we used.

5.2 Recommendation

The following recommendation has made to bolster the chemical industry in Ethiopia, especially to enhance the "black art" of catalyst synthesis.

The past three decades has seen a revolution in the development of catalyst characterization techniques in most parts of the world. Some of the characterization techniques which bring dramatic paradigm changes are; X-ray diffraction (XRD), transmission electron microscopy (TEM), specific surface area analysis (BET), X-ray absorption spectroscopy and thermo gravimetric analysis (TGA). It is fact that, Addis Ababa institute of technology is the oldest and foremost institute in the country but it lacks the aforementioned characterization technique. I strongly suggest the institute to set up, organize, direct and lead the catalyst characterization laboratory which embraces the mentioned equipment.

It is no hesitation that, the progress of chemical industry depends on its attitude towards intensive and valid research especially on innovation and application of highly selective and active catalysts. Even if currently chemical industry is developing at steady rate in Ethiopia, there is no research which is harmonized by a companies and researchers in this area. An industry which is supposed to be build in the near future likes fertilizer plant need a cutting edge research in the area of catalyst. To substitute the imported catalyst and to foster the development of chemical industry, it is critically recommend industries and researchers to work jointly.

It is fact that the university community should play the leading role on a research of catalysis science, It is strongly recommend to tap the following burgeon areas.

- Catalyst selection for different reaction and modeling of a catalytic reaction mechanism
- Innovation of new catalyst and catalytic processes for environmental protection
- Regeneration of the deactivated catalysts
- Analysis a catalyst surface using physical chemistry
- Substitution of the novel catalysts by mixed oxide catalyst

Here in Ethiopia there are no chemical companies which produce catalyst as a commercial product. If the chemical industry boost up in the near future, there will be a huge demand of bulk catalysts. Finally, the investors recommend to setting up a catalyst producing companies in this raw material reached country.

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