

Chapter One

Introduction and Literature review

1 Introduction and Literature review

1.1 Background

1.1.1 copper

Copper is a chemical element with symbol Cu (from Latin: cuprum) and atomic number 29. It is a soft, malleable and ductile metal with very high thermal and electrical conductivity. A freshly exposed surface of pure copper has a reddish-orange color. It is used as a conductor of heat and electricity, as a building material and as a constituent of various metal alloys, such as sterling silver used in jewelry, cupronickel used to make marine hardware and coins and constantan used in strain gauges and thermocouples for temperature measurement. Copper is found as a pure metal in nature, and this was the first source of the metal to be used by humans, ca. 8000 BC. It was the first metal to be smelted from its ore, ca. 5000 BC, the first metal to be cast into a shape in a mold, ca. 4000 BC and the first metal to be purposefully alloyed with another metal, tin, to create bronze, ca. 3,500 BC. In the Roman era, copper was principally mined on Cyprus, the origin of the name of the metal, from aes cyprium (metal of Cyprus), later corrupted to cuprum, from which the words copper (English), cuivre (French), Koper (Dutch) and Kupfer (German) are all derived (McHenry, 1992).

The commonly encountered compounds are copper (II) salts, which often impart blue or green colors to such minerals as azurite, malachite, and turquoise, and have been used widely and historically as pigments. Architectural structures built with copper (usually roofing elements) corrode to give green verdigris (or patina). Decorative art prominently features copper, both in the elemental metal and in compounds as pigments. Copper compounds are also used as bacteriostatic agents, fungicides, and wood preservatives. Copper is essential to all living organisms as a trace dietary mineral because it is a key constituent of the respiratory enzyme complex cytochrome c oxidase. In molluscs and crustaceans copper is a constituent of the blood pigment hemocyanin, replaced by the iron-complexed hemoglobin in fish and other vertebrates. In humans, copper is found mainly in the liver, muscle, and bone (Johnson, 2008). The adult body contains between 1.4 and 2.1 mg of copper per kilogram of body weight. Hence a healthy human weighing 60 kilograms contains approximately 0.1 g of copper. However, this small amount is essential to the overall human well-being.

Copper occurs naturally as native metallic copper and was known to some of the oldest civilizations on record. The history of copper use is at least 11,000 years old, estimated to have begun in 9000 BC in the Middle East (**Csa.com-2008**) a copper pendant was found in northern Iraq that dates to 8700 BC.

(**Rayner,2007**) Evidence suggests that gold and meteoric iron (but not iron smelting) were the only metals used by humans before copper. (**vanderkrogt.net, 2008**) The history of copper metallurgy is thought to follow this sequence: 1) cold working of native copper, 2) annealing, 3) smelting, and 4) the lost wax casting. In southeastern Anatolia, all four of these techniques appear more or less simultaneously at the beginning of the Neolithic c. 7500 BC (**Renfrew, 1990**) . Just as agriculture was independently invented in several parts of the world, copper smelting was independently invented in different places. It was probably discovered in China before 2800 BC, in Central America perhaps around 600 AD, and in West Africa about the 9th or 10th century AD. (**Cowen, 2009**) Investment casting was invented in 4500–4000 BC in Southeast Asia and carbon dating has established mining at Alderley Edge in Cheshire, UK at 2280 to 1890 BC. (**Timberlake, 2005**) Ötzi the Iceman, a male dated from 3300–3200 BC, was found with an axe with a copper head 99.7% pure; high levels of arsenic in his hair suggest his involvement in copper smelting. Experience with copper has assisted the development of other metals; in particular, copper smelting led to the discovery of iron smelting. Production in the Old Copper Complex in Michigan and Wisconsin is dated between 6000 and 3000 BC (**Pleger,2002**) (**Emerson,2009**) Natural bronze, a type of copper made from ores rich in silicon, arsenic, and (rarely) tin, came into general use in the Balkans around 5500 BC. Copper does not react with water but it does slowly react with atmospheric oxygen to form a layer of brown-black copper oxide which, unlike the rust that forms on iron in moist air, protects the underlying metal from further corrosion (passivation). A green layer of verdigris (copper carbonate) can often be seen on old copper structures, such as the roofing of many older buildings (**Grieken et al, 2005**) and the Statue of Liberty. Copper tarnishes when exposed to some sulfur compounds, with which it reacts to form various copper sulfides.

The major applications of copper are electrical wire (60%), roofing and plumbing (20%), and industrial machinery (15%). Copper is used mostly as a pure metal, but when greater hardness is required, it is put into such alloys as brass and bronze (5% of total use). (**Emsley ,2003**) For more than two centuries,

copper paint has been used on boat hulls to control the growth of plants and shellfish.

A small part of the copper supply is used for nutritional supplements and fungicides in agriculture (Wiley et al, 2007) Machining of copper is possible, although alloys are preferred for good machinability in creating intricate parts.

1.1.2 Sol-Gel Method

The sol-gel process may be described as: "Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid."

A sol is a stable dispersion of colloidal particles or polymers in a solvent.

The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid. (Brinker, 1990)

A gel consists of a three dimensional continuous network, which encloses a liquid phase, in a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by van der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. (Brinke, 1981)

The gelation process may be reversible if other interactions are involved.

The idea behind sol-gel synthesis is to "dissolve" the compound in a liquid in order to bring it back as a solid in a controlled manner.

Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds. The sol-gel method prevents the problems with co-precipitation, which may be inhomogeneous, be a gelation reaction. Enables mixing at an atomic level. Results in small particles, which are easily sinterable. The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. A method was needed where dust was reduced (compared to the ceramic method) and which needed a lower sintering temperature. In addition, it should be possible to do the synthesis by remote control. One of the examples of a sol-gel system often cited is quick clay. Clay may form a sol (quick clay) if it is washed sufficiently to remove the counter ions. Quick clay may be gelled if enough counter ions are added, so that the colloidal particles aggregate. Sol-gel synthesis may be used to

prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films. **(Hench, 1990)**

A sol consists of a liquid with colloidal particles which are not dissolved, but do not agglomerate or sediment. Agglomerations of small particles are due to van der Waals forces and a tendency to decrease the total surface energy. Van der Waals forces are weak, and extend only for a few nanometers. In order to counter the van der Waals interactions, repulsive forces must be established.

May be accomplished by:

Electrostatic repulsion. By adsorption of charged species onto the surface of the particles, repulsion between the particles will increase and agglomeration will be prevented. Most important for colloidal systems.

Steric hindrance. By adsorbing a thick layer of organic molecules, the particles are prevented from approaching each other reducing the role of the van der Waals forces. This works best in concentrated dispersions. Branched adsorbates work best. Usual for nanomaterials.

Metals may be used for formation of gels, almost as silicon. However, many metals will form oxides with increasing pH. The water molecules of the hydrated metal ions are more acidic than for Si, and hydrolysis will occur. The reactions are moved toward lower pH. Metals may be used for formation of gels, almost as silicon. However, many metals will form oxides when increasing pH. **(Klein, 1980)**

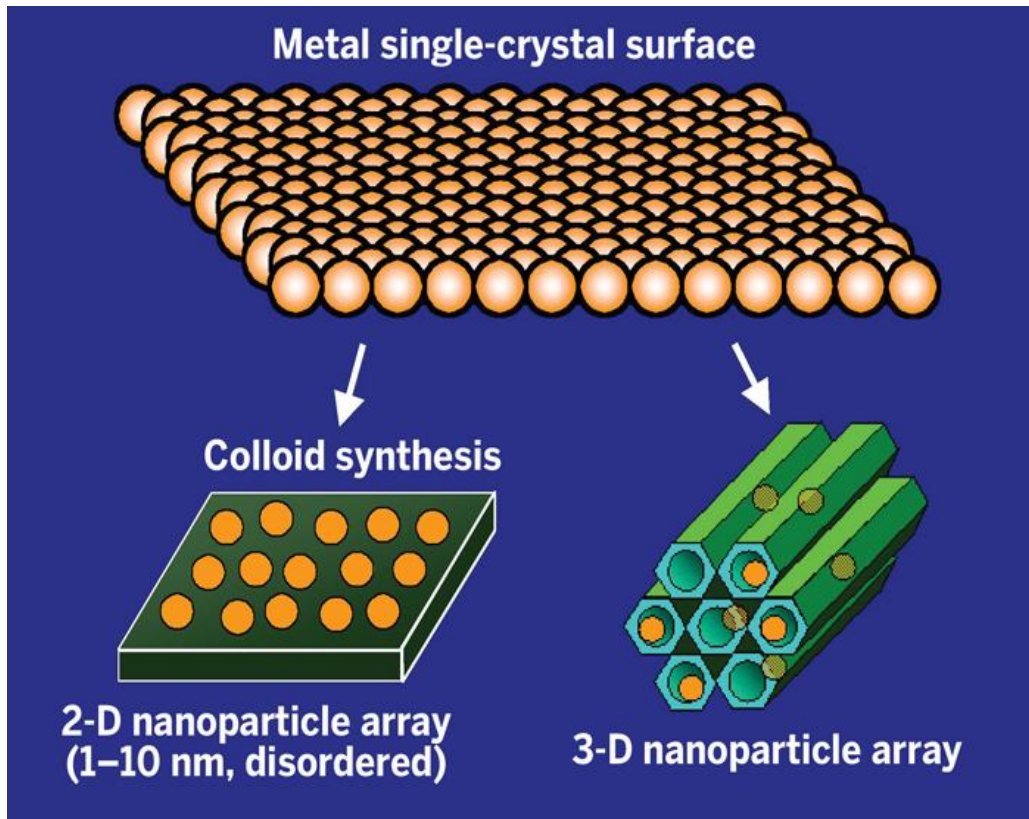


Figure 1.1 :crystal distribution in gel process

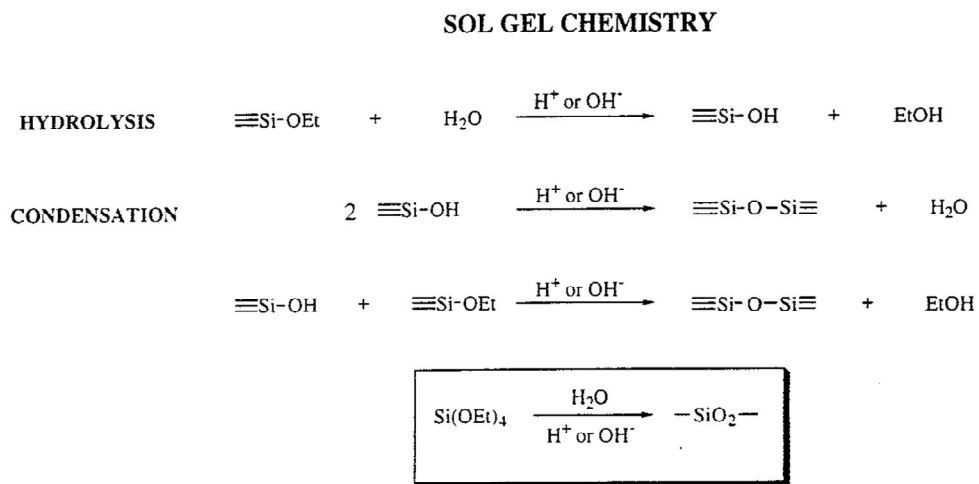


Figure 1. Summary of the key steps in sol-gel polymerization of ethoxysilanes.

Figure 1.2: chemistry of sol-gel

1.1.3 Copper Oxide

The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis (**Wolhfarth, 1980**)

Among the oxides of transition metals, copper oxide nanoparticles are of special interest it is a semiconductor material and has a natural abundance of starting material.

Copper oxide is non-toxic and easily obtained by the oxidation of Cu; it is one of the important metal oxide which has attracted recent research because of its low cost, abundant available as well as its peculiar properties.

It is used in the fields like catalysis, superconductors, ceramics as a kind of important inorganic materials etc. CuO has been used as a basic material in cuprate High-Tc superconductors as the superconductivity in these classes of systems is associated with Cu-O bondings. (**Mallick et al, 2012**)

Among all metal oxide nanoparticles, copper oxide has gained the most interest because of its wide applications, such as in solar cell technology, field emission, magnetic storage media, lithium ion batteries, gas sensing, and drug delivery, magnetic resonance imaging, and field emission devices.

Varieties of physical and chemical methods have been proposed to synthesize CuO nanoparticles (CuO-NPs). (**Shahmiri et al, 2013**)

CuO-NPs belong to monoclinic structure system with the brownish-black appearance (**El-Nahhal et al, 2012**). They find their significant role in antibacterial agents to fabrics (**Chang et al, 2012**)

CuO NP treatment is known to induce a Disruption of the blood–brain barrier in vivo in mice and rats. Under in vitro conditions, CuO NPs were also found to induce toxic effects in different types of neuronal cells such as the human SH-SY5Y neuroblastoma and H4 neuroglioma cells (**Zhanhu et al, 2007**)

Efficiency of CuO as Nano fluids in heat transfer application. For example it has been reported that 4 % addition of CuO improves the thermal conductivity of water by 20 % (**Lee et al, 1999**)

CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photothermal applications (**Rakhshni, 1986**)

However, the reports on the preparation and characterization of Nano crystalline CuO are relatively few to some other transition metal oxides such as zinc oxide, titanium dioxide, tin dioxide and iron oxide. Some methods for the preparation of Nano crystalline CuO have been reported recently such as the sonochemical method (**Kumar et al, 2000**) sol–gel technique (**Eliseev et al, 2000**) and one-step

solid state reaction method at room temperature (Shen et al, 2000). electrochemical method (Borgohain et al,2000) .thermal decomposition of precursors (J.Q. Yu ,1999)and co-implantation of metal and oxygen ions (Nakao et al ,2000) and so on.

1.1.3.1 - The general physical properties of CuO

| | |
|---------------------|---|
| Molecular formula | Cu-O |
| Molar mass | 79.545 g/mol |
| Appearance | black to brown powder |
| Melting point | 1,326 °C (2,419 °F; 1,599 K) |
| Density | 6.315 g/cm ³ |
| Solubility in water | Insoluble |
| Solubility | soluble in ammonium chloride, potassium cyanide insoluble in alcohol, ammonium hydroxide, ammonium carbonate |

Table 1.1:some physical properties of Copper oxide

1.1.3.2 The Crystal Structure of CuO

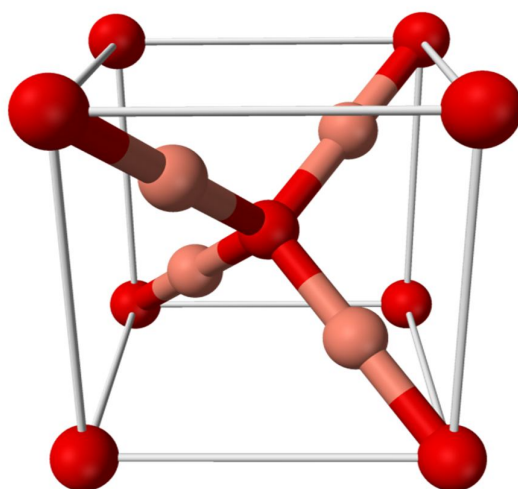


Figure 1.3:the crystal structure of CuO

Copper (II) oxide belongs to the monoclinic crystal system, with a crystallographic point group of $2/m$ or $C2h$. The space group of its unit cell is $C2/c$, and its lattice parameters are $a = 4.6837(5)$, $b = 3.4226(5)$, $c = 5.1288(6)$, $\alpha = 90^\circ$, $\beta = 99.54(1)^\circ$, $\gamma = 90^\circ$. The copper atom is coordinated by 4 oxygen atoms in an approximately square planar configuration.

1.1.4 Alumina

Aluminum oxide is a chemical compound of aluminum and oxygen with the chemical formula Al_2O_3 . It is the most commonly occurring of several aluminum oxides, and specifically identified as aluminum (III) oxide. It is commonly called alumina, and may also be called aloxide, aloxite, or alundum depending on particular forms or applications. It occurs naturally in its crystalline polymorphic phase $\alpha-Al_2O_3$ as the mineral corundum, varieties of which form the precious gemstones ruby and sapphire. Al_2O_3 is significant in its use to produce aluminum metal, as an abrasive owing to its hardness, and as a refractory material owing to its high melting point. (Zumdahl, 2009)

Corundum is the most common naturally occurring crystalline form of aluminum oxide. Rubies and sapphires are gem-quality forms of corundum, which owe their characteristic colors to trace impurities. Rubies are given their characteristic deep red color and their laser qualities by traces of chromium. Sapphires come in different colors given by various other impurities, such as iron and titanium. Al_2O_3 is an electrical insulator but has a relatively high thermal conductivity ($30 \text{ W m}^{-1} \text{ K}^{-1}$) (Makeitfrom.com, 2013) for a ceramic material. Aluminum oxide is insoluble in water. In its most commonly occurring crystalline form, called corundum or α -aluminum oxide, its hardness makes it suitable for use as an abrasive and as a component in cutting tools. Aluminum oxide is responsible for the resistance of metallic aluminum to weathering. Metallic aluminum is very reactive with atmospheric oxygen, and a thin passivation layer of aluminum oxide (4 nm thickness) forms on any exposed aluminum surface (Campbell et al, 1999) This layer protects the metal from further oxidation. The thickness and properties of this oxide layer can be enhanced using a process called anodizing. A number of alloys, such as aluminum bronzes, exploit this property by including a proportion of aluminum in the alloy to enhance corrosion resistance. The aluminum oxide generated by anodizing is typically amorphous, but discharge assisted oxidation processes

such as plasma electrolytic oxidation result in a significant proportion of crystalline aluminum oxide in the coating, enhancing its hardness. Aluminum oxide was taken off the United States Environmental Protection Agency's chemicals lists in 1988. Aluminum oxide is on EPA's Toxics Release Inventory list if it is a fibrous form. The most common form of crystalline aluminum oxide is known as corundum, which is the thermodynamically stable form. **(Levin et al, 1998)** The oxygen ions nearly form a hexagonal close-packed structure with aluminum ions filling two-thirds of the octahedral interstices. Each Al^{3+} center is octahedral. In terms of its crystallography, corundum adopts a trigonal Bravais lattice with a space group of R-3c (number 167 in the International Tables). The primitive cell contains two formula units of aluminum oxide. Aluminum oxide also exists in other phases, including the cubic γ and η phases, the monoclinic θ phase, the hexagonal χ phase, the orthorhombic κ phase and the δ phase that can be tetragonal or orthorhombic. **(Paglia, 2004)** Each has a unique crystal structure and properties. Cubic $\gamma\text{-Al}_2\text{O}_3$ has important technical applications. The so-called $\beta\text{-Al}_2\text{O}_3$ proved to be $\text{NaAl}_{11}\text{O}_{17}$. **(Wiberg et al, 2001)** Molten aluminum oxide near the melting temperature is roughly 2/3 tetrahedral (i.e. 2/3 of the Al are surrounded by 4 oxygen neighbors), and 1/3 5-coordinated, very little (<5%) octahedral Al-O is present. Around 80% of the oxygen atoms are shared among three or more Al-O polyhedral, and the majority of inter-polyhedral connections are corner-sharing, with the remaining 10–20% being edge-sharing. **(Skinner, 2013)** The breakdown of octahedral upon melting is accompanied by a relatively large volume increase (~20%); the density of the liquid close to its melting point is 2.93 g/cm^3 . **(Paradis, 2004)**

1.1.4.1 General physical Properties of Alumina

| | |
|---------------------|---|
| Molecular formula | Al_2O_3 |
| Molar mass | $101.96 \text{ g}\cdot\text{mol}^{-1}$ |
| Appearance | white solid |
| Melting point | $2,072 \text{ }^\circ\text{C}$ ($3,762 \text{ }^\circ\text{F}$; $2,345 \text{ K}$) |
| Density | $3.95\text{--}4.1 \text{ g/cm}^3$ |
| Solubility in water | Insoluble |
| Solubility | insoluble in diethyl ether practically insoluble in ethanol |

Table 1.2: some physical Properties of Alumina

1.1.5 Catalysis

There are two kinds of catalysis Homogenous and Heterogeneous Catalysts

1.1.5.1 Homogeneous Catalysts

When the catalyst and reactant are in the same phase, the process of catalysis known as homogeneous catalysis. (Leeuwen et al, 2011) The system may consist entirely of gases, or both the catalyst and reactant are in the solution phase. For instance, Nitric oxide gas catalysis the combination of moist sulphure dioxide and oxygen in the lead chamber process for the manufacture of sulphuric acid. Homogenous catalysis in solutions is more common. The most importance class of such reaction is those catalyzed by the presence of acids and base, i.e. acid-base catalysis. However parts from this class fridel-craft reaction provide another example of homogeneous catalysis in solution. The whole reaction is supposed to occur in the presence of AlCl_3 catalyst. Some other Lewis acid catalysts are also involved in this reaction i.e AlBr_3 , BF_3 , the acidic strength of the most common Lewis acids decreases in the following order $\text{BX}_3 > \text{AlX}_3 > \text{FeX}_3 > \text{GaX}_3$ etc. However the reactivity decreases in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$. (March, 1992)

An excess of aromatic or solvent i.e. carbon disulphide CS_2 dichloromethane ,olefins alcohols can also be employed in place of alky halides with protic acids i.e. H_2SO_4 , HPO_3 , HF , however these catalyst suffer from several problems such as corrosion handing ,toxicity, requirement of stoichiometric amounts , and separation disposal of spent catalyst .(Bell, 1973) products isolation and recovery of the catalyst in order to overcome these problem ,many efforts have been done to heterogenize these catalysts by supporting them with many solid porous materials such as zeolites ,alumina , clay

Mesoporous molecular sieves are very costly since they were synthesized by critically controlled process using fine chemicals as templates.

Although alumina is cheap and easy to handle, but metal supported alumina catalysts were found to be very active. (**Erdôhelyi et al, 2012**)

1.1.5.2 Heterogeneous catalysts

Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place (Langmuir-Hinshelwood, Eley-Rideal, and Mars-van Krevelen). (**Knözinger et al, 2002**)The total surface area of solid has an important effect on the reaction rate. The smaller the catalyst particle size, the larger the surface area for a given mass of particles.

A heterogeneous catalyst has active sites, which are the atoms or crystal faces where the reaction actually occurs. Depending on the mechanism, the active site may be either a planar exposed metal surface, a crystal edge with imperfect metal valence or a complicated combination of the two. Thus, not only most of the volume, but also most of the surface of a heterogeneous catalyst may be catalytically inactive. Finding out the nature of the active site requires technically challenging research. Thus, empirical research for finding out new metal combinations for catalysis continues(**Spessard et al, 1997**)

For example, in the Haber process, finely divided iron serves as a catalyst for the synthesis of ammonia from nitrogen and hydrogen. The reacting gases adsorb onto active sites on the iron particles. Once physically adsorbed, the reagents undergo chemisorption that results in dissociation into adsorbed atomic species, and new bonds between the resulting fragments form in part due to their close proximity. In this way the particularly strong triple bond in nitrogen is broken, which would be extremely uncommon in the gas phase due to its high activation energy. Thus, the activation energy of the overall reaction is lowered, and the rate of reaction increases. Another place where a heterogeneous catalyst is applied is in the oxidation of sulfur dioxide on vanadium (V) oxide for the production of sulfuric acid.(**Wiberg et al, 2011**).

Heterogeneous catalysts are typically "supported," which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Supports prevent or reduce agglomeration and sintering of the small catalyst particles, exposing more surface area, thus catalysts have a higher specific activity (per gram) on a support. Sometimes the support is merely a surface on which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction. Supports are porous materials with a high surface area, most commonly alumina, zeolites or various kinds of activated carbon. Specialized supports include silicon dioxide, titanium dioxide, calcium carbonate, and barium sulfate.(Sufang et al ,2016).

1.1.5.2.1 Example of Heterogeneous Catalytic Reaction Process

- The long journey for reactant molecules to
 - travel within gas phase
 - cross gas-liquid phase boundary
 - travel within liquid phase/stagnant layer
 - cross liquid-solid phase boundary
 - reach outer surface of solid
 - diffuse within pore
 - arrive at reaction site
 - be adsorbed on the site and activated
 - react with other reactant molecules, either being adsorbed on the same/neighbour sites or approaching from surface above
- Product molecules must follow the same track in the reverse direction to return to gas phase
- Heat transfer follows similar track
-

1.1.5.2.2 Some common solid support / carrier materials

- Alumina
 - Inexpensive
 - Surface area: 1 ~ 700 m²/g
 - Acidic
- Silica
 - Inexpensive
 - Surface area: 100 ~ 800 m²/g

- Acidic
- Zeolite
 - mixture of alumina and silica,
 - often exchanged metal ion present
 - shape selective
 - acidic

1.1.5.3 Uses of copper oxide nanoparticles as a catalyst

The activity of nano materials as a catalyst depends mostly on the nano powder material size, morphology and specific surface area of the prepared materials. Due to the potentiality of CuO, it acts as a catalyst; whereas all metal oxides are not useful for the catalytic activity. as like Fenton's reagent CuO combined with another metal oxide like CeO₂.

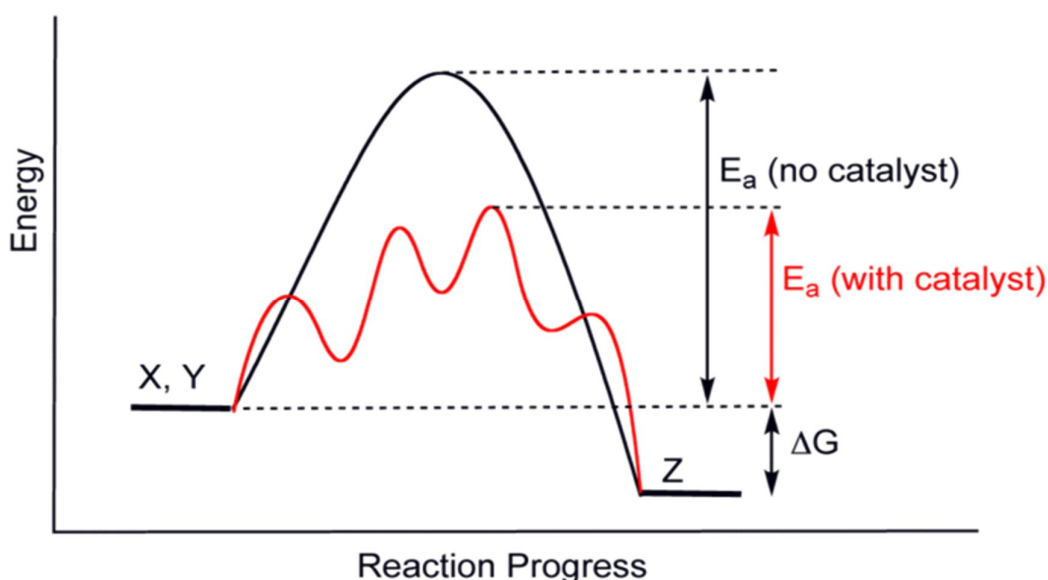


Figure 1.4 : Effect of a Catalyst on Equilibrium

1.1.6 Understanding the Synthesis of Alumina Supported Metal Catalysts at an Atomic Level

Despite the important role of supported metal catalysts in industrial processes there are significant gaps in our understanding of the atomic level transformations during their synthesis, in particular calcination. However, insight at this level is necessary to fully optimize the specificity of synthesis techniques. The proposed work will provide this insight by using a suite of analytical techniques including NMR, x-ray absorption, and IR spectroscopy, ETEM, STEM, helium ion microscopy and TGA-DSC-MS. Complementary modeling studies will be performed to rationalize the observations during these experiments. (**Crouch et al,2007**).

Alumina supported Pt, Ni, Co, Cu, and Ru catalysts will be prepared using dry impregnation and controlled adsorption. There is different impregnation or adsorption methods provide a different spatial distribution of metal precursors on the surface and this translates to differences in the size distribution of metal particles on the catalyst. In addition to mapping the distribution of metal precursors on the surface, it could determine the temperature at which the precursors decompose and the metal particles become mobile. It could also elucidate when and where metal particles bind to specific sites on the alumina surface. It is important to point out that the preferred binding sites may only be formed during calcination. Due to the complex interplay of transformations of the metal precursors and the support a comprehensive, fundamental study on the preparation supported metal catalysts is overdue.

Recently Nickel (II) oxide aerogels with an amorphous alumina support were synthesized by the epoxide addition method.(**Gill et al,2010**)the monoliths were obtained by adding propylene oxide to an alcoholic solution of hydrated metal nitrate salts. The wet gels were dried by supercritical extraction to produce porous monolithic aerogels. The as-synthesized aerogels were amorphous containing aluminum and nickel hydroxides. Annealing of the as-synthesized aerogels at 400 °C yields crystalline nickel oxide materials which retain the high surface areas (>160 m²/g) and porosities of the original aerogels. The resultant aerogel materials were characterized using powder X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray analysis, and nitrogen adsorption/desorption analysis.(**Kistle ,1932**).

1.2 Objectives of the research

The aim of this work can be summarized in the following points:

1. To prepare copper oxide nanoparticles by sol-gel method, and copper oxide supported by alumina as a catalyst.
2. To characterize copper oxide nanoparticles and the catalyst.
3. To study the catalytic activity for synthesis of Tetraethyl orthosilicate.

Chapter Two

Materials and Methods

2 Materials and Methods

CuO Nanoparticles are prepared by using economical Sol-Gel method and characterization is done to establish the size and purity of prepared nanoparticles.

2.1 Materials and equipment

2.1.1 Materials

All chemicals used in this research were of analytical grade type

- Copper chloride di hydrate .CuCl₂.2H₂O
- Glacial acetic acid.CH₃COOH
- Sodium hydroxide.NaOH
- Neutral alumina. Al₂O₃
- Distilled water .H₂O

2.2.2 Apparatus and glassware

- Round bottom flasks ,500 and 50 ml
- Dropper
- Hot plate with magnetic stirrer (405 USA)
- Thermometer
- pH paper
- Glass rod
- Filter paper(Whatman 42)
- Funnels
- Volumetric flasks 500 and 50 ml
- Beakers 500, 250 and 50 mL
- watch Glass
- Erlenmeyer flask 250 mL

2.3 Methods

2.3.1 Preparation of CuO Nanoparticles by sol-gel Method

Aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 M) was prepared in cleaned round bottom flask. 1 ml of glacial acetic acid was added to the above aqueous solution and was heated to 100 °C with constant stirring. 8 M NaOH was added to above heated solution till the pH reached 7. The color of the solution turned from green to black immediately and a large amount of black precipitate was formed immediately.

The precipitate was centrifuged and washed 3-4 times with distilled water. The obtained precipitate was dried in air for 24 hours. This powder was further used for the characterization of CuO nanoparticles.

2.3.2 Preparation of (CuO supported by alumina) catalyst ($\text{CuO} / \text{Al}_2\text{O}_3$)

Aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 M) was prepared in cleaned round bottom flask. 1 ml of glacial acetic acid was added to above aqueous solution and heated to 100 °C with constant stirring. 8 M NaOH was added to above heated solution till pH reaches to 7. The color of the solution turned from green to black immediately and the large amount of black precipitate was formed immediately

While the black precipitate was formed about 10 g of neutral alumina was added with constant stirring for one hour the precipitate was centrifuged and washed 3-4 times with distilled water. The obtained precipitate was dried in air for 24 hours.

2.3.3 application of Copper Oxide Supported on Alumina Catalyst in preparation of Tetraethyl orthosilicate

1g of ultra-pure silicon dioxide was weighted, tiny amount of copper oxide supported on alumina catalyst was added, 20 ml of diethyl ether and 25 ml of hydrochloric acid were added, and the solution was left until the precipitation was completed, the precipitate was filtered and weighted, and finally the

percentage yield of obtained product was calculated using the following equation:

$$\text{Yield \%} = (W_{\text{prac}}/W_{\text{theo}}) \times 100$$

Where:

W_{prac} practical weight

W_{theo} theoretical weight

2.4 Characterization methods

2.4.1 X-ray Diffraction (XRD)

- The powder sample was characterized by X-ray diffraction (XRD) (Mimiflex, Rigaku diffractometer) using CuK α ($\lambda = 1.5405 \text{ \AA}$) radiation. The average crystallite size (t) has been calculated from the line broadening using Scherrer's relation: $D = 0.9\lambda/\beta \cos \theta$

Where

λ is the wavelength of X-ray

β is full width of half maximum (FWHM)

θ is peak obtained angle

2.4.2 Scanning Electron Microscope (SEM)

- The morphological and microstructure aspect of CuO nanoparticles were investigated by using scanning electron microscope (FESEM) dual beam field emission scanning electron microscope (LYRA3 Tescan) equipped with energy dispersive X-Ray spectrometer (EDX, oxford instruments) and transmission electron microscope (JEM-2100F).

2.4.3 Iodometric titration to determine copper percentage

- Iodometric titration (oxidation of iodide)

1g of copper oxide was dissolved in 0.2M of HCl to prepare the sample.

2.0 g of KI was added to the sample, and titrated immediately with Na₂S₂O₃ until the solution becomes pale yellow. Starch indicator was added, and the titration was continued until the blue color became faint. The titration was completed; the disappearance of the blue starch/I₂ color was used as the end point.

2.4.4 Rate of Reaction for the formation of Tetraethyl orthosilicate

- Rate of Reaction of tetraethyl orthosilicate

The time of initially precipitate crystals was recorded, and then the rate of reaction was calculated, using following equation:

(Wt/time) g/sec.

The same procedure was applied in determine the rate of reaction of silicon alkoxide by using catalyst.

Chapter Three

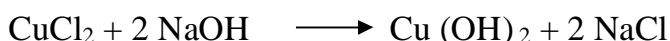
Results and discussion

3 Results and discussion

3.1 Preparation of Copper Oxide NPs by sol –gel method

There are various techniques to prepare Nano crystals *e.g.* sputtering, laser ablation, cluster deposition, sol-gel method *etc.* In the present work the synthesis of CuO is done by sol-gel route because this method is easy and economical [3, 4]. The sol-gel process involves the formation of colloidal suspension (sol) and gelation of the sol to form a network in continuous liquid phase (gel). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands

The chemical reaction is as follows:



And copper hydroxide decomposes into copper oxide on heating as follows,



The obtained CuO powder was finely black soft powder obtained in high yield .

3.2 Preparation of copper oxide supported on Alumina

The black CuO precipitate was change to gray brown precipitate with homogenously distribution of the powder supported metal oxide .

3.3 Rate of Reaction (synthesis of Tetraethyl orthosilicate)

A catalyst is a substance which speeds up a reaction, but is chemically unchanged at its end. When the reaction has finished, the mass of catalyst is the same as at the beginning.

To reiterate, catalysts do not affect the equilibrium state of a reaction. In the presence of a catalyst, the same amounts of reactants and products will be present at equilibrium as there would be in the uncatalyzed reaction. To state this in chemical terms, catalysts affect the kinetics, but not the thermodynamics, of a reaction. If the addition of catalysts could possibly alter the equilibrium state of the reaction, this would violate the second rule of thermodynamics; we would be getting "something for nothing," which is physically impossible.

Reactions can be sped up by the addition of a catalyst, including reversible reactions involving a final equilibrium state. Recalling that for a reversible reaction, the equilibrium state is one in which the forward and reverse reaction

rates are equal. In the presence of a catalyst, both the forward and reverse reaction rates will speed up equally, thereby allowing the system to reach equilibrium faster. However, it is very important to keep in mind that the addition of a catalyst has *no* effect whatsoever on the final equilibrium *position* of the reaction. It simply gets it there faster.

Elemental silicon can't react directly with reagent but it reacts in presence of catalyst or at elevated temperature. Because Silicon atom is covered by an oxide layer that prevents its attack by chemicals. Therefore, it requires a catalyst to break down this oxide layer and activate silicon to react. Accordingly, variable catalysts have been used in this work for activation of silicon in direct synthesis of tetraethoxysilane. The reaction between elemental silicon and ethanol does not take place without using any catalyst. However, the direct synthesis of tetraethoxysilane by a direct reaction of silicon with alcohol has many advantages compared to the previous method.

From this results for any 30sec was formed 0.82g from tetraethyl orthosilicate at using catalyst(0.0273g per sec), but without catalyst formed 0.72g for 90sec (0.008g per sec), this indicating that, the tetraethyl orthosilicate which prepared by using catalyst is better than the prepared without catalyst.

3.4 Characterization of Copper Oxide and Copper Oxide supported by alumina

3.4.1 XRD Results of Copper Oxide and Copper Oxide supported by alumina

X-ray diffraction is an easy and one of the most important characterization tools used in nanomaterial research field. Here, an important nanomaterial - copper nanoparticles has been successfully prepared by sol-Gel method in normal room temperature and its structural characterizations have been studied by important tool - X-ray diffraction.

In figure (3.1) the results confirm nanoparticles, uniformed size less than 10nm.

Values of $2\theta = (32.4; 35.6 \text{ And } 39.8)$ deg Have a high intensity

Planes of copper have been observed and in agreement with data obtained from the other studies from the literature review.

The 3 main peaks give a single-phase with a monoclinic structure No characteristic peaks of any other impurities such as $\text{Cu}(\text{OH})_2$, Cu_2O was observed.

In other hand we observed in figure (3.2) that the copper oxide with alumina have a similar peaks of figure (3.1) with a clear distortion make the peaks have a low intensity

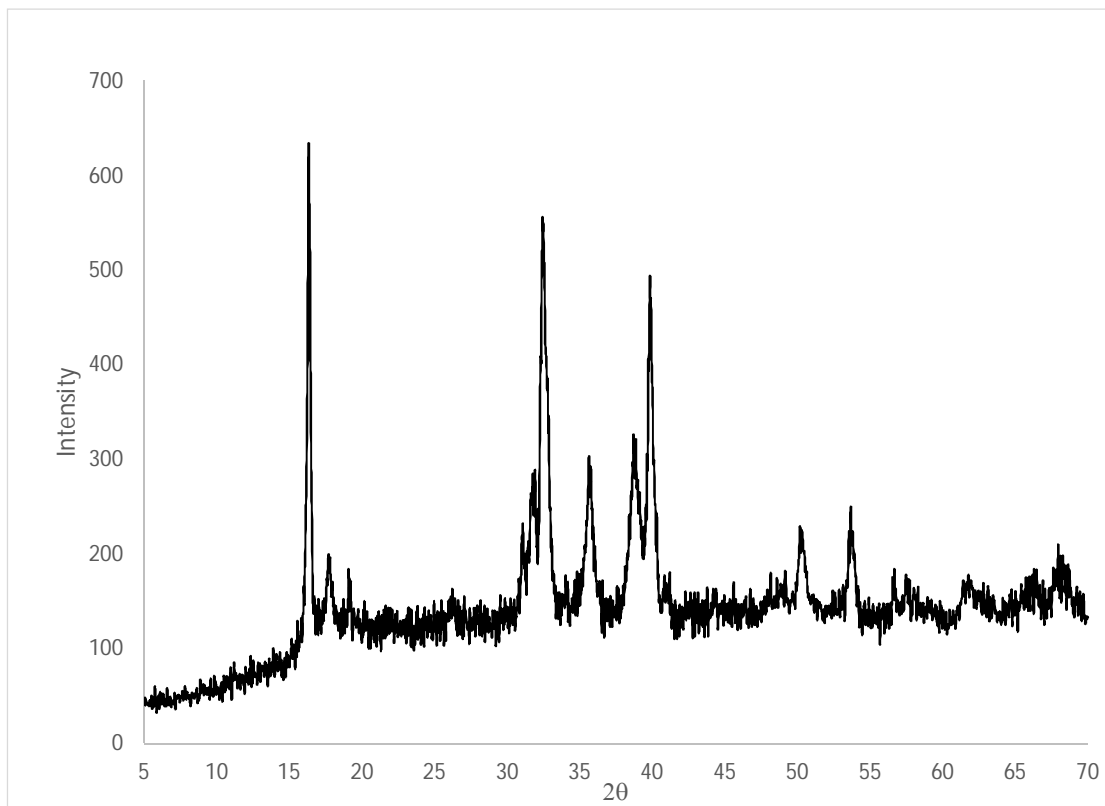


Figure 3.1: XRD of copper oxide

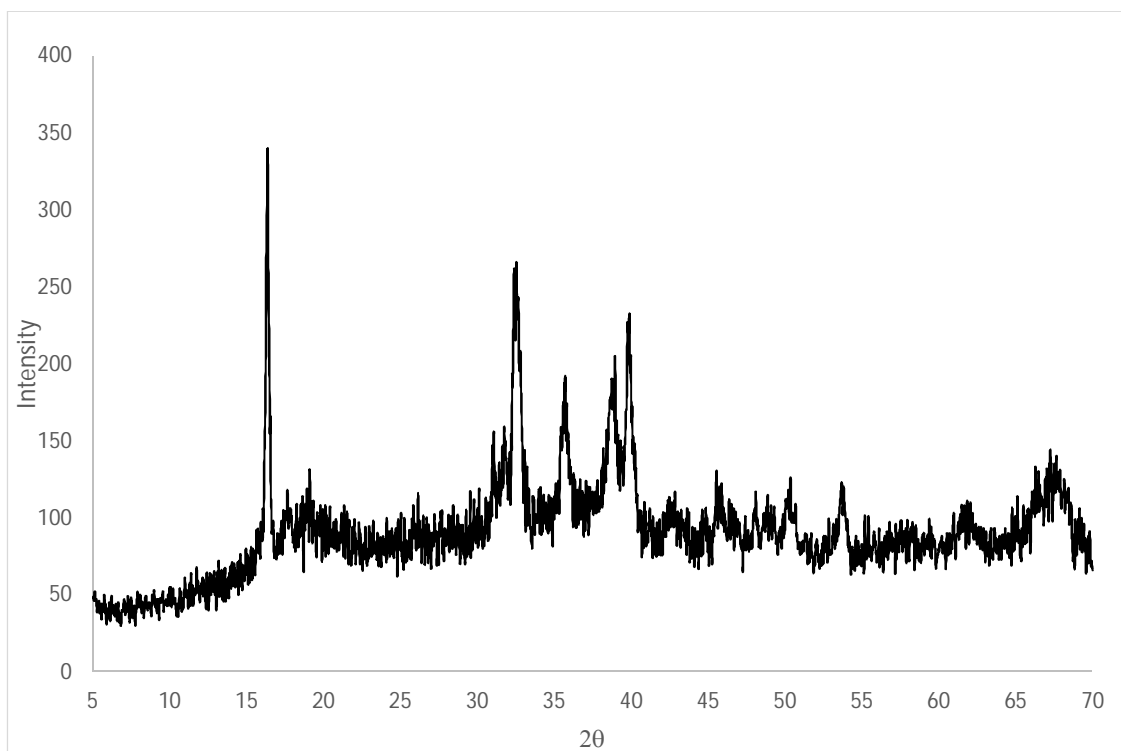


Figure 3.2: XRD of copper oxide supported by alumina

3.4.1.1 Calculation of Crystal Size:

The crystallite size of prepared CuO NPs were calculated from the full width at half maximum (FWHM), using the Debye-Scherrer formula.

$$t = \frac{0.9\lambda}{B \cos \theta}$$

Where B is the full width at half maximum (FWHM) of the XRD all Peaks, t is the crystallite size, λ is the wave length of the X-ray and θ is Bragg's angle

$$\lambda = 0.15405 \text{ nm}$$

$$\theta = 16.22^\circ$$

$$B = 0.9 * 3.14 / 180 \text{ radian}$$

From the equation $t = 9.19 \text{ nm}$

3.4.2.SEM Resultsof Copper Oxide and Copper Oxide supported by alumina

SEM micrographs of the synthesized CuO are shown in the figure 3.3 (A,B,C,D,E,F and G). From the figure it is quite evident that there is no definite morphology in the sample. It seems that the particles were agglomerated and form a cluster. As the particle size calculated from the XRD is in Nano range and not getting any exact information about the surface morphology of the sample from the SEM micrograph. The morphology observed in the sample not showing any hard grains which gives the idea that size of the particle is small and has a single phase

In figure 3.4(A,B,C,D, and F) the observed morphology of CuO in figure3.3 is greatly changed in the photograph of copper oxide support in alumina.

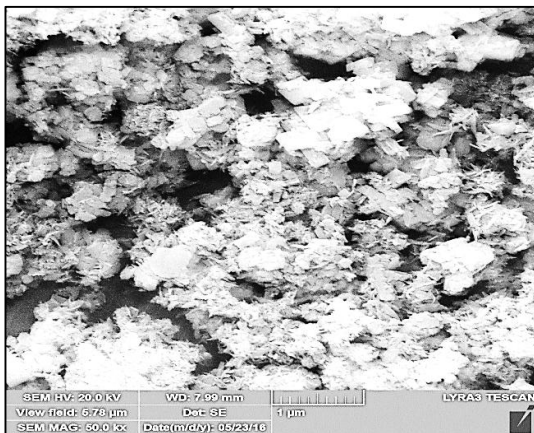


Figure 3.3A

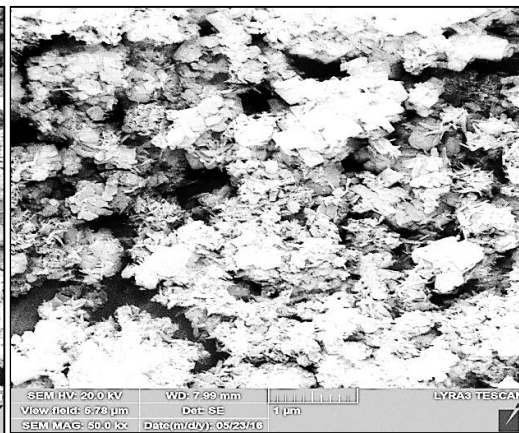


Figure 3.3B

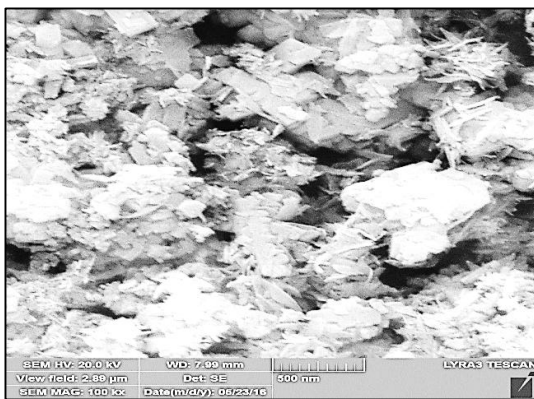


Figure 3.3C

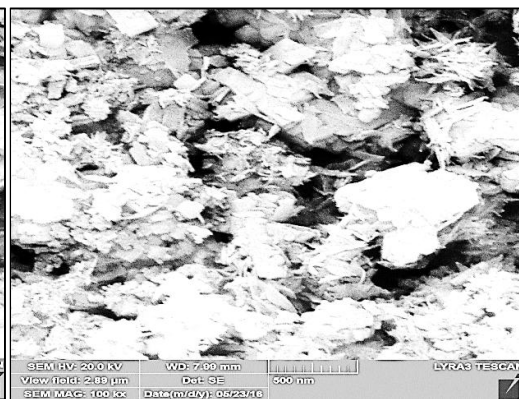


Figure 3.3D

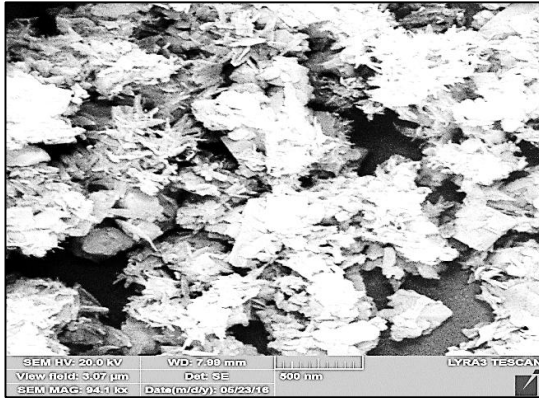


Figure 3.3E

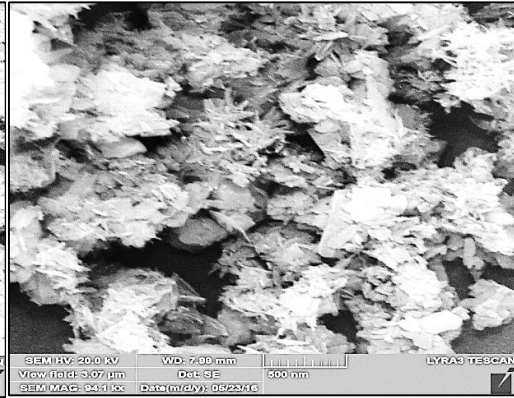
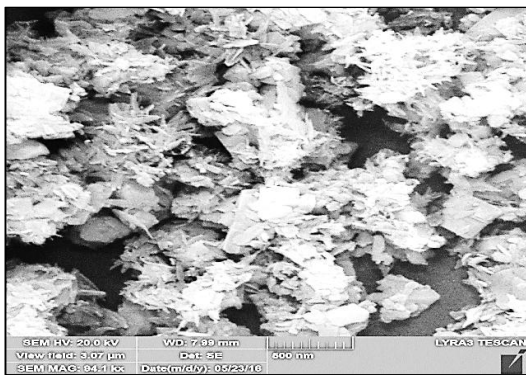


Figure 3.3F



3.3G

figure 3.3: (A,B,C,D ,E,F and G): SEM Result of Copper Oxide NPs

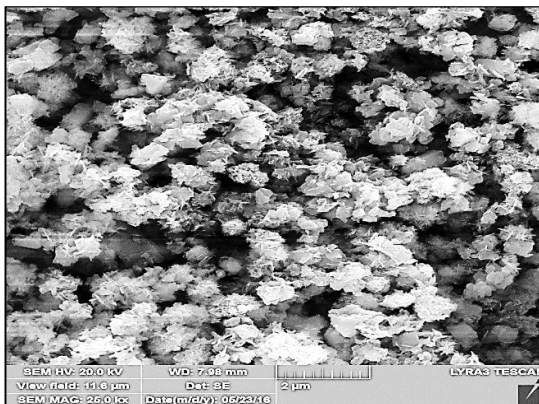


Figure 3.4A

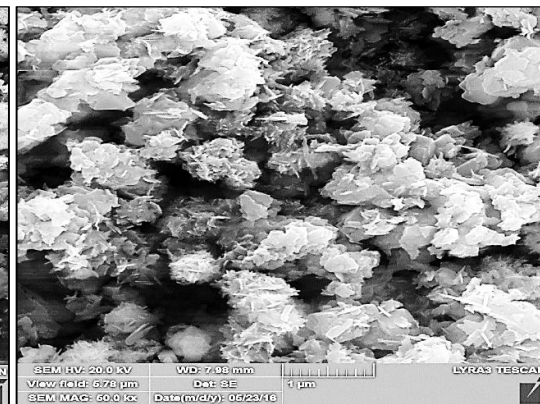


Figure 3.4B

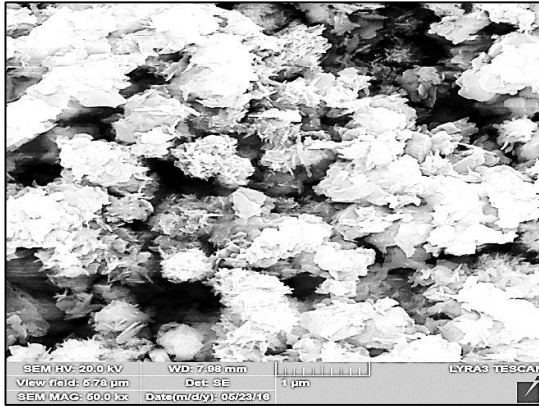


Figure 3.4C

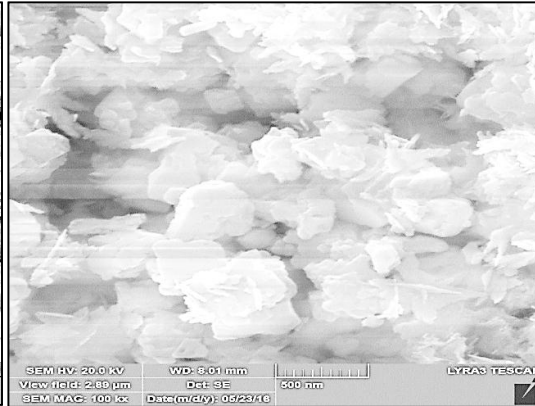


Figure 3.4D

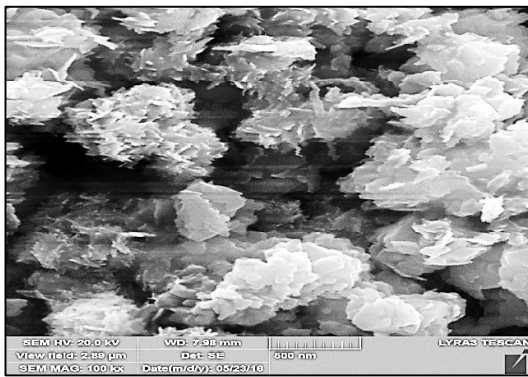


Figure 3.4F

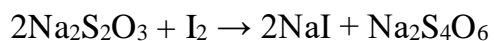
Figure 3.4: (A,B,C,D and F):SEM Result of CuO NPs /Al₂O₃

3.4.3 Determination of Copper Oxidepercentage

By using titration method the percentage of copper in the sample of copper oxide NPs was found = 67.38 %

This result was closed with the standard review which is 70-75 % **(H.Rechardson-1997)**

The chemical Equation



3.5 Practical weight of Tetraethyl orthosilicate

3.5.1 by using catalyst

The obtained practical weight of Tetraethyl orthosilicate was 0.82g and the calculated percentage yield was 30%, this result is in agreement with the expected yield (Adam.H et al ,2016)

3.5.2 by direct method without catalyst

The obtained practical weight of Tetraethyl orthosilicate was 0.72g and the calculated percentage yield was 26.6%. (Andersonin, 1974)

4 Conclusion

Copper nanoparticles synthesized using SOL- GEL method is a simple and environmental benign method. This method has many advantages such as economic viability, ease to scale up and less time consuming. In this research Copper oxide nanoparticles were prepared and used as catalyst for synthesis of Tetraethyl orthosilicate after supporting in alumina.

The experiment revealed that the presence of copper nanoparticles is necessary for increasing the rate of the reaction.

5 Recommendation

- To use transmission electron microscope (TEM) in characterization
- To use another carrier materials such as silicon and zeolite.
- To use CuO/Al₂O₃ as catalyst in other reactions

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