Chapter One

1. Introduction and Literature Review

1.1Silicon

Silicon is the element to thank for the computer you're using to read these words. A crucial component in microelectronics and computer chips, this extremely common element is also responsible for warm, white beaches — silica, an oxide of silicon, is the most common component of sand90[1].Silicon is the seventh-most abundant element in the universe and the second-most abundant element on the planet, after oxygen, according to the Royal Society ofChemistry. About 25 percent of the Earth's crust is silicon; weirder spots where this element appears include menstrual cups, breast implants and oven mitts· In nature, silicon is no longer. It's usually found linked up with a pair of oxygen molecules as silicon dioxide, otherwise known as silica. Quartz, an abundant ingredient in sand, is made up of non-crystallized silica· Silicon is neither metal nor non-metal; it's a metalloid, an element that falls somewhere between the two. The category of metalloid is something of a gray area, with no firm definition of what fits the bill, but metalloids generally have properties of both metals and non-metals. They look metallic, but conduct electricity only intermediately well. Silicon is a semiconductor, meaning that it does conduct electricity. Unlike a typical metal, however, silicon gets better at conducting electricity as the temperature increases (metals get worse at conductivity at higher temperatures)[1].

Silicon was first isolated in 1824 by Swedish chemist Jones Jacob Berzelius, who also discovered cerium, selenium and thorium, according to the Chemical Heritage Foundation. Berzelius heated silica with potassium to purify silicon, according to the Thomas Jefferson National Accelerator Facility, but today the refinement process heats carbon with silica in the form of sand to isolate the element [1].

Silicon is a main ingredient in very low-tech creations, including bricks and ceramics. But the high-tech stuff is where the element really makes its mark. As a semiconductor, silicon is used to make transistors, which amplify or switch electrical currents and are the backbone of electronics from radios to I phones.

Silicon has unique properties [2] which can be summarizes in the below table (1.1)

1.1.1 Properties of Silicon:

Table 1.1: Properties of Silicon

Atomic Number (number of protons in the nucleus)	14
Atomic Symbol (on the Periodic Table of Elements)	Si
Atomic Weight (average mass of the atom)	28.09
Density	2.3296 grams per cubic centimeter
Phase at Room Temperature	Solid
Melting Point	2577 degrees C^0
Boiling Point	5909 degrees
Number of isotopes	24
Most common isotopes	Si-28

1.1.2 Distribution of Silicon in Earth:

27.6% of the Earth's crust is made up of silicon. Although it is so abundant, it is not usually found in its pure state, but rather its dioxide and hydrates. (SiO_2) is silicon's only stable oxide, and is found in many crystalline varieties. It's pure form being quartz, but also as jasper and opal. Silicon can also be found in feldspar, micas, olivine's, pyroxenes and even in water (Figure 1.1). In another allotropic form silicon is a brown amorphous powder most familiar in "dirty" beach sand. The crystalline form of silicon is the foundation of the semiconductor age [2].

Figure 1.1: Silicon in earth

1.1.3. Silicon Isotope:

Silicon isotopes are used in a variety of applications. Si-28 has been suggested to improve the thermal conductivity of semiconductors. Si-29 is used extensively in NMR spectroscopy. Si-30 has been used to produce the radioisotope Si-31. Si-30 has also been used to study the self-diffusivity of Silicon and it has been used to study the isotope effect on superconductivity [3].

Table 1.2: Stability isotopes of silicon

Isotope	**Mass /Da**	**Natural abound. (Atom %)**	**Nuclear spin (I)**	**Nuclear magnetic moment (μ/μ_N)**
^{28}Si	27.9769271 (7)	92.2297 (7)	0	0
^{29}Si	28.9764949 (7)	4.6832 (5)	½	-0.55529
^{30}Si	29.9737707 (7)	3.0872 (5)	0	0

1.1.4. Uses of Silicon:

Silicon is one of man's most useful elements. In the form of sand and clay it is used to make concrete and brick; it is a useful refractory material for high-temperature work, and in the form of silicates it is used in making enamels, pottery, etc. Silica, as sand, is a principal ingredient of glass, one of the most inexpensive of materials with excellent mechanical, optical, thermal, and electrical properties. Glass can be made in a very great variety of shapes, and is used as containers, window glass, insulators, and thousands of other uses. Silicon tetrachloride can be used as iridize glass. Hyper pure silicon can be doped with boron, gallium, phosphorus, or arsenic to produce silicon for use in transistors, solar cells, rectifiers, and other solid-state devices which are used extensively in the electronics and space-age industries Hydrogenated amorphous silicon has shown promise in producing economical cells for converting solar energy into electricity. Silicon is important to plant and animal life. Diatoms in both fresh and salt water extract Silica from the water to build their cell walls. Silica is present in the ashes of plants and in the human skeleton. Silicon is an important ingredient in steel; silicon carbide is one of the most important abrasives and has been used in lasers to produce coherent light of 4A [4].

Silicon is also used to make silicones. These are silicon-oxygen polymers with methyl groups attached. Silicone oil is a lubricant and is added to some cosmetics and hair conditioners. Silicone rubber is used as a waterproof sealant in bathrooms and around windows, pipes and roofs. The element silicon is used extensively as a semiconductor in solid-state devices in the computer and microelectronics industries. For this, hyper pure silicon is needed. The silicon is selectively doped with tiny amounts of boron, gallium, phosphorus or arsenic to control its electrical properties [5].Silicon is very important in silicon alloys. An alloy is simply a mixture of a metal and at least one other element, created to add strength or improve processing of the metal. Steel is a common example of an alloy, where iron and carbon have been combined. Silicon is also commonly combined with iron in the process of making steel. In fact, the alloy ferrosilicon is the number one use of silicon in the world. 80% of all crude silicon worldwide goes into this application. Silicon can also take the form of silicon carbide. This combination of silicon and carbon has been in production since the 19th century. It is virtually indestructible, almost as hard as diamond, and can withstand the highest temperatures without melting. It is used in numerous industrial applications, including abrasives, grinding, polishing, cutting, kilns, body armor, and the aerospace industry [6].

1.2.Organic Silicon:

Oregano silicon compounds are organic compounds containing carbon–silicon bonds. Oregano silicon chemistry is the corresponding science exploring their properties and reactivity. Most oregano silicon compounds are similar to the ordinary organic compounds, being colorless, flammable, hydrophobic, and stable. The first oregano silicon compound, tetraethylsilane, was discovered by Charles Friedel and James Crafts in 1863 by reaction of tetrachlorosilane with diethyl zinc. The carbosilicon carbide is an inorganic compound [7]

1.2.1 Properties of Si–C, Si–O:

In most oregano silicon compounds, Si is tetravalent and tetrahedral. Carbon–silicon bonds compared to carbon–carbon bonds are longer (186 pm vs. 154 pm) and weaker with bond dissociation energy 451 kJ/mol vs. 607 kJ/mol.[8] The C–Si bond is somewhat polarized towards carbon due to carbon's greater electro negativity (C 2.55 vs. Si 1.90). The Si–C bond can be broken more readily than typical C–C bonds. One manifestation of bond polarization in organosilanes is found in the Sakurai reactioncertain alkyl silanes can be oxidized to an alcohol in the Fleming–Tamayo oxidation[9]Another manifestation is the β-silicon effect describes the stabilizing effect of a β-silicon atom on a carbonation with many implications for reactivity's–O bonds are much stronger (809 kJ/mol compared to 538 kJ/mol) than a typical C–O single bond. The favorable formation of Si–O bonds drives many organic reactions such as the Brook rearrangement and Peterson olefination.

1.2.2. Functional Groups:

Silanols, siloxides, and siloxanes

Silanols are analogues of alcohols. They are generally prepared by hydrolysis of silyl chlorides and oxidation of sillyhydrides[10].

$R_3SiCl + H_2O \rightarrow R_3SiOH + HCl$……. (1.1)

Less frequently they are prepared by oxidation of silly hydrides:

$2\ R_3SiH + O_2 \rightarrow 2R_3SiOH$……….… (1.2)

The parent R_3SiOH is too unstable for isolation, but the many organic derivatives are known including $(CH_3)_3SiOH$ and $(C_6H_5)_3SiOH$. They are about 500 xs more acidic than the corresponding alcohols. Siloxides (silanoates) are the deprotonated derivatives of silanols[10].

$R_3SiOH + NaOH \rightarrow R_3SiONa + H_2O$… (1.3)

Silanols tend to dehydrate to give siloxanes:

$2\ R_3SiOH \rightarrow R_3Si\text{-}O\text{-}SiR_3 + H_2O$…….... (1.4)

Polymers with repeating siloxane linkages are called silicones. Compounds with a Si=O double bond called silanones are extremely unstable.

1.2.3. Silicates:

Silicon is most commonly found in silicate compounds. Silica is the one stable oxide of silicon, and has the empirical formula SiO_2. Silica is not a silicon atom with two doublebonds to two oxygen atoms. Silica is composed of one silicon atom with four single bonds tofour oxygen molecules (Figure 1.2).

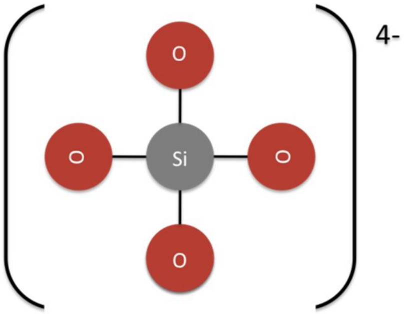

Figure 1.2: The net charge of silica is minus

Silica, i.e. silicon dioxide, takes on this molecular form, instead of carbon dioxide's characteristic shape, because silicon's 3p orbital's make it more energetically favorable to create four single bonds with each oxygen rather than make two double bonds with each oxygen atom. This leads to silicates linking together in -Si-O-Si-O- networks called silicates. The empirical form of silica is SiO_2 because, with respect to the net average of the silicate, each silicon atom has two oxygen atoms [11].

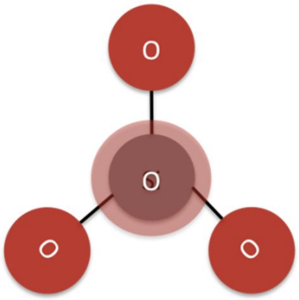

Figure 1.3: This is a representation of the tetrahedral silica complex

The tetrahedral SiO_4^{4-} complex (see Figure 1.3), the core unit of silicates, can bind together in a variety of ways, creating a wide array of minerals. Silicon is an integral component in minerals, just ascarbon is an essential component of organic compounds.

1.2.4.Sorosilicates:

In sorosilicates two silicates tetrahedral join together by sharing an oxygen atom at one of their corners. The core structure of a sorosilicate is a pair of silica tetrahedral. (See Figure 1-4).

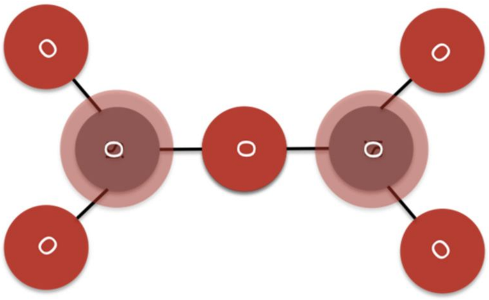

Figure 1.4: The core of a sorosilicate

1.2.5.Cyclosilicates:

In cyclosilicates three or more silica tetrahedral share two corners of an oxygen atom. The core structure of a cyclosilicate is a closed ring of silica tetrahedral [11]. (See Figure 1.5)

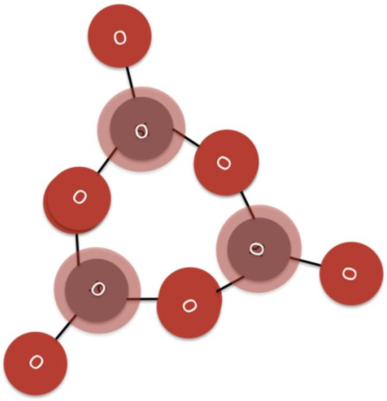

Figure 1.5: The core of a cyclosilicate

1.2.6. Phyllosilicates:

Phyllosilicates are silica complexes where each tetrahedralshare three corners and creates a sheet of silicon and oxygen. (See Figure 1.6) The core complex of a phyllosilicate is an infinite sheet of connected silica tetrahedral [11]

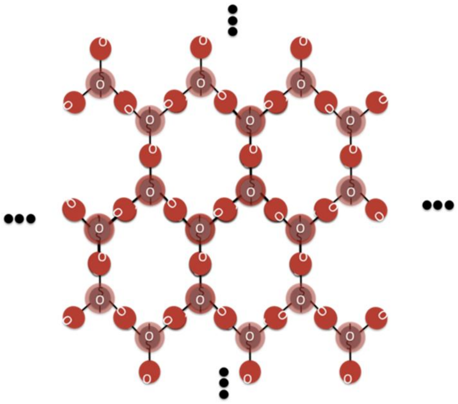

Figure 1.6: The core of phyllosilicate

1.3. Siloxane:

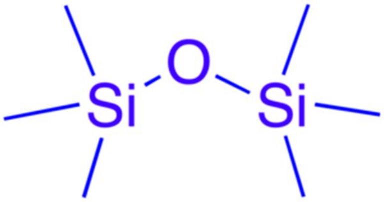

Figure 1.7: Siloxane

A siloxane is a functional group in organic silicon chemistry with the Si–O–Si linkage. The parent siloxanes include the oligomeric and polymeric hydrides with the formulae H $(OSiH_2)_{nOH}$ and $(OSiH_2)_n$.[12] Siloxanes also include branched compounds, the defining feature of which is that each pair of silicon centers is separated by one oxygen atom. The siloxane functional group forms the backbone of silicones, the premier example of which is polydimethylsiloxane.[13] The functional group $(RO)_{3Si}$ is called siloxy.

Siloxanes have long been sought after for their combination of desirable physical properties. Originally developed for their thermal stability characteristics, siloxaneelastomers are commonly marketed to keep flexibility at temperatures as low as-100°C, while siloxane fluids can retain physical properties up to 200°C. Also touted is the low surface tension of the fluids class of siloxanes. This is particularly important when applied to surfaces with variable surface topography. With the combination of heat stability and surface tension, it's not surprising that siloxanes would be of interest in coatings technology. A third characteristic that has served to promote the use of siloxanes in coatings are their release properties. Even the most aggressive adhesives do not adhere well to siloxanes. The combination of these properties has allowed for the development of siloxanes as mold release agents for rubber, plastics, and die-casting, as well as release liners for adhesive face stock. In addition to release from organic adhesive and casting substrates, siloxanesare used within the non-impact printing industry. The application of siloxane to the process of non-impact printing allows fuser rolls to release from the thermoplastic ink toner. Figure 8 illustrates the general components comprising a fuser roll used inn on-impact printing.

Thermal degradation and viscosity increase is often explained by hemolyticbond cleavage (bond dissociation between Si-CH_3 yielding radicals available to participate in chain extension and/or cross linking reactions and thus the viscosity increase. While siloxane polymers and organo-functional silicone co-polymers have been developed for use as fuser oils, the incorporation of heat stabilizers has been limited due to poor compatibility of various agents in the siloxane medium. The purpose of this work was to develop a synthetic route to produce a siloxaneco-polymer that contains a heat stabilizer bonded to the chain, allowing the heat stabilizer to be compatible with the parent siloxane fluid. The siloxane additive, when mixed with commonly used fuser fluids, contained an aromatic amine as theorgano-functional group that functioned as the antioxidant. Prior research has indicated that the ratio of dimethyl units to aromatic amine containing units should be approximately 10 to 1, respectively, with the polymer end units being trimethylsilyl.

The functionalized polymer was miscible with polydimethylsiloxane and organomodifiedsiloxanes such as amino and Mercator fluids. The additive was characterized via 1H and 29Si NMR as well as FT-IR. Finally, the material was tested to evaluate the efficacy via heat age studies. The synthetic additive was compounded with othersiloxane release agents and compared to an iron actuate industry standard stabilizer fluid [14].

There are several different properties that Siloxane might have. It might be composed of either branched or unbranched backbones that consist of silicon alternating with oxygen atoms. This creates Si-O-Si-O, with side chains of R that attach themselves to the silicon atoms. There are also more complicated structures of atoms within different types of Siloxanes, so there are many different components that might be used for them. All in all, there are many variations of Siloxane that can be seen and that can be used Although Siloxane is a compound that is widely known and widely used, it is something that is a chemical compound that might be difficult to understand. It is important to know that Siloxane is not a single product, but is a group of products. There are several different types of Siloxanes that are used for different things. All in all, Siloxane is a compound that can be most useful to people in various solutions and solvents [15].

1.4.Sol gel Chemistry:

Sol-gel polymerization of tetra-alkoxysilanes, $Si(OEt)_4$ (TMOS), is a mild and convenient method for the synthesis of amorphous silica gels. The sol-gel process is the name given to any one of number of processes in which solution or sol undergoes a sol-gel transition. At this transition, the solution becomes a rigid non-fluid mass. A specific example of a sol-gel process is the polymerization of TEOS in ethanol and water. Following addition of a catalyst this homogenous solution undergoes a sol-gel transition to a rigid gel consistent of silica (SiO_2) and solvent filled pores. The chemical steps involved in sol-gel polymerization, hydrolysis and condensation, result in formation of a network Si-O-Si chemical linkage form the alkoxysilane[16].(figure 1.8).

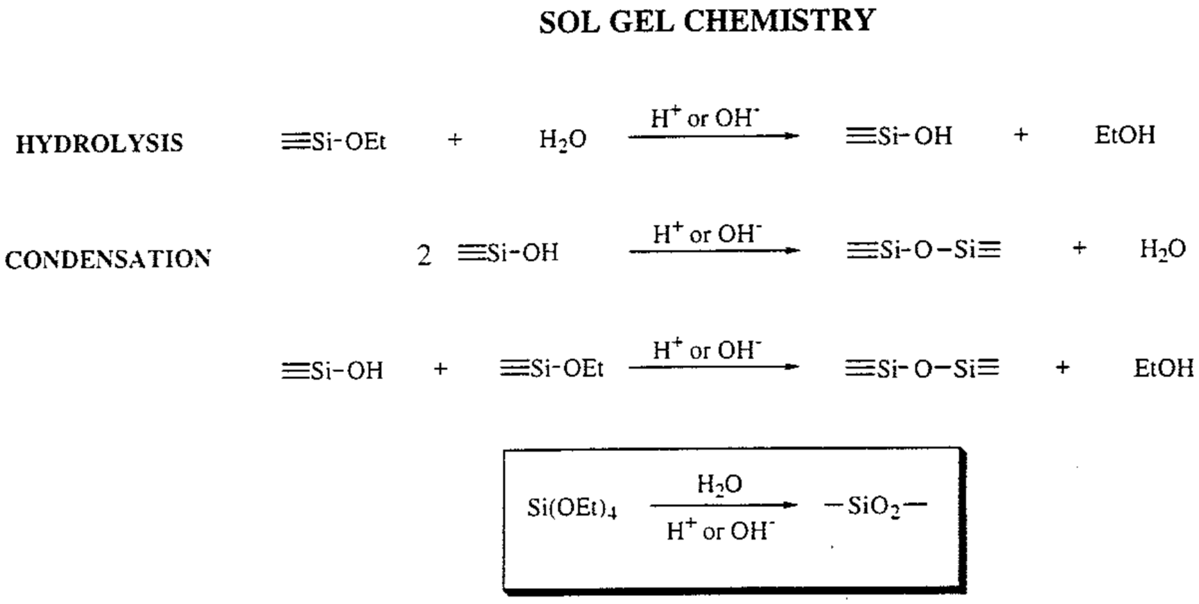

Figure 1.8: Summary of the Key Steps in Sol-gel ofethoxysilanes

Sol = a stable suspension of colloidal solid particles or polymers in a liquid.

Gel = porous, three-dimensional, continuous solid network surrounding a Continuous liquid phase.

Colloidal (particulate) gels = agglomeration of dense colloidal particles

Polymeric gels = agglomeration of polymeric particles made from subcolloidal Units.

Agglomeration = covalent bonds, van der Walls, hydrogen bonds, polymeric chain Entanglement [17].

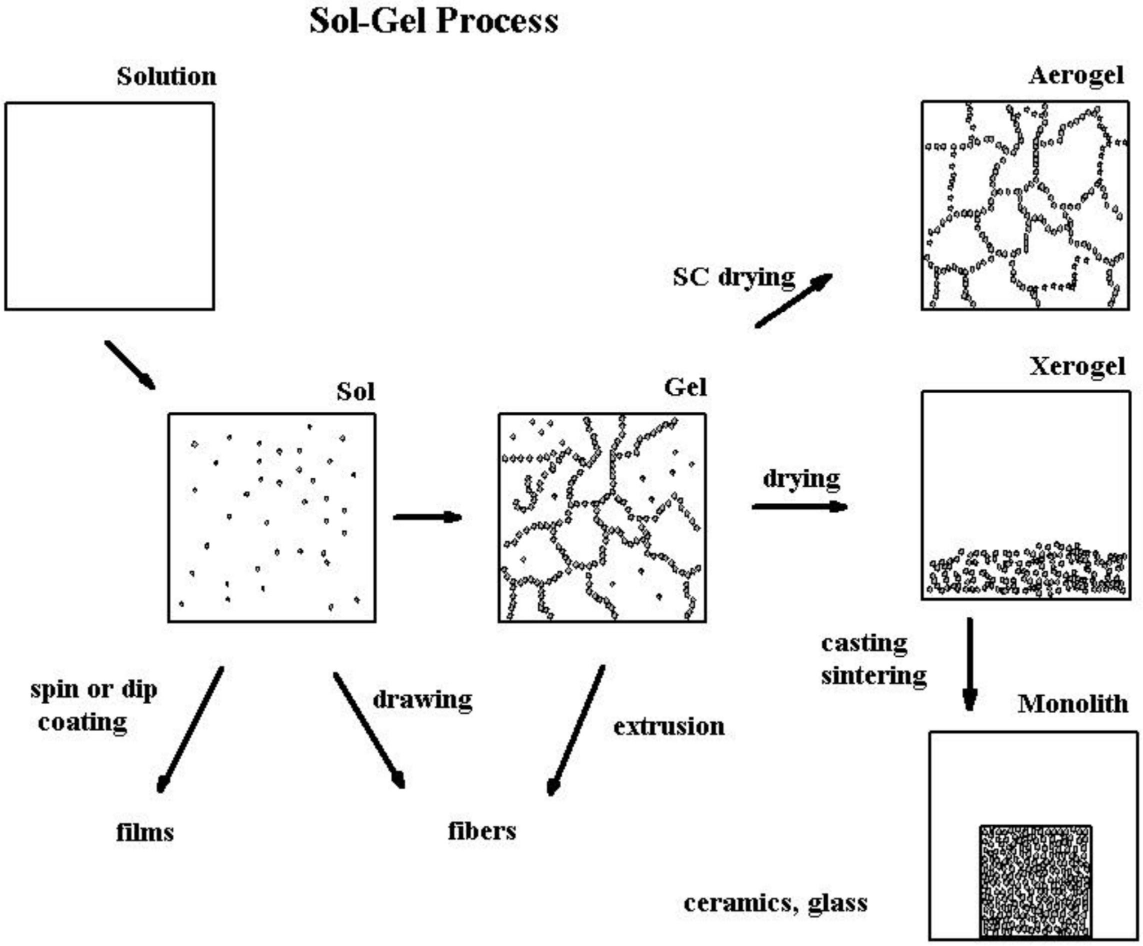

Figure 1.9: Sol-gel Process

1.5. TetraethylOrthosilicate:

Tetraethyl orthosilicate is the chemical compound with the formula Si $(OC_2H_5)_4$. Often abbreviated TEOS, it is a colorless liquid that degrades in water. TEOS is the ethyl ester of orthosilicic acid, Si $(OH)_4$. It is a prototypical alkoxide.

TEOS is a tetrahedral molecule. Like its many analogues, TEOS is prepared by alcoholysis of silicon tetrachloride:

$$SiCl_4 + 4\ EtOH \rightarrow Si(OEt)_4 + 4\ HCl \ldots.(1.5)$$

TEOS is mainly used as a crosslinking agent in silicone polymers and as a precursor to silicon dioxide in the semiconductor industry [18]. TEOS is also used as the silica source for synthesis of zeolites [19]. Other applications include coatings for carpets and other objects. TEOS is used in the production of aerogel. These applications exploit the reactivity of the Si-OR bonds [20].

1.6. Catalysis:

1.6.1.Description of Catalyst:

A catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst, and leaves itunaltered such that it is available for the next reaction. Infact, we can describe the catalytic reaction as a cyclic event in which the catalystparticipates and is recovered in its original form at the end of the cycle. Let us consider the catalytic reaction between two molecules A and B to give productP; (Fig. 1.10).The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state [21]. Catalysis is a technology which increases the rate of a chemical reaction. This technical field employs both scientists and engineers. Catalysts are the materials used by these persons to explore the phenomenon of catalysis. Catalysts are materials which speed up chemical reactions without the catalyst being consumed; they are materials which induce change. More specifically, catalysts are materials which change the rate of attainment of chemical equilibrium without themselves being changed or consumed in the process. Catalysts also provide selectivity or specificity to particular products which are more desirable than others. All these attributes about catalysis and catalysts translate to energy savings, less pollution, fewer side products, lower cost reactor materials, and ultimately products which reduce global warming. It has been said (A. Mittasch) that "chemistry without catalysis would be a sword without a handle…or a bell without sound [22].

1.6.2. Work of Catalyst:

- All chemical reactions require bond breaking, and bond making.
- Breaking the bonds requires energy known as the activation energy. The energy supplied must be higher than the activation energy, in order for the reaction to occur.

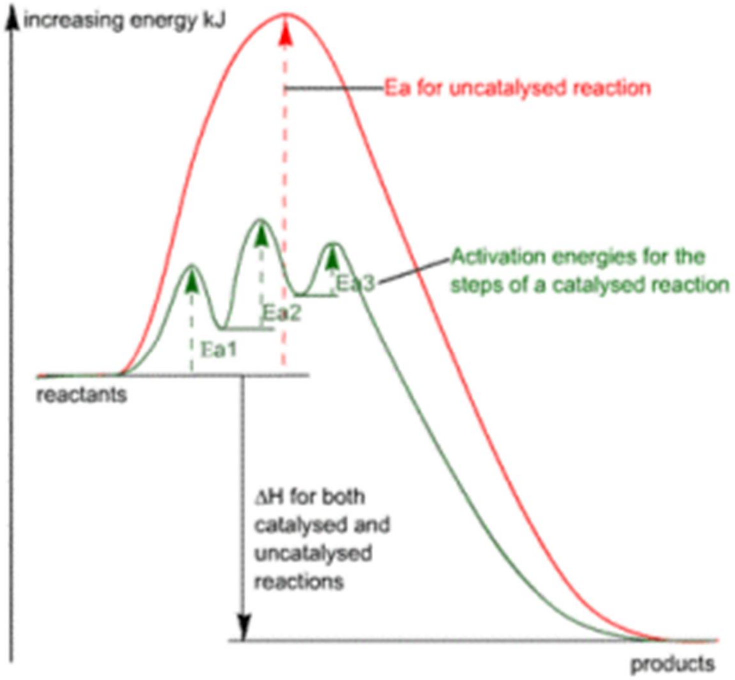

Figure 1.10: Work of catalyst

- If the activation energy is high, very few molecules will have enough energy to overcome it, and so the reaction will take place at a slow rate.
- Catalysts speed up chemical reactions by providing an alternative pathway for breaking and remaking bonds.
- In the reaction above, the activation energy is made lower, and so more bonds can be broken and reformed, hence a faster reaction [23].

1.6.3.Most Important Properties of Catalysts:

- A catalyst increases the speed of a reaction, and it also improves the yield of the intended product.
- A catalyst actually takes part in the reaction even though it itself is not consumed or used up in the course of the reaction.
- A catalyst makes the reaction faster by providing an alternative pathway with lower activation energy.

- A catalyst is reaction-specific. It may not be effective in another reaction even if the two reactions are of similar type.
- In a reversible reaction, a catalyst accelerates both the forward and the reverse reactions. So, the inclusion of a catalyst does not alter the equilibrium constant of a reversible reaction [24].

1.7. Copper Oxide Supported On Silica Catalyst:

Copper oxide supported on silica catalyst have be used in many chemical reactions and widely used in organic silicate. In this research used copper oxide supported on silica as catalyst to product tetrethyleorthosilicate and can be describe as follow:

Among the many applications of glass-metal composites, one of the most important is as catalysts. Silica-supported copper catalysts have been reported as excellent catalysts in the NO reduction [25-27].Stabilization of the active phase in supported catalysts depends on the support and its preparation method; among the preparation methods the sol-gel technique offers some advantages. With this preparation method copper species are effectively uniform incorporated into the ionic oxide network [28, 29] and may lead to more stable catalysts than those prepared by conventional methods. The sol-gel polymerization of the metal alkoxides in the presence of inorganic salts leads to the formation of ceramic oxide materials that exhibit important microstructure properties.The main aim of this work is to explore the microstructure of the support material (glass) and the evolution of the metallic species in the glass network under heat treatments. Silica xerogel were prepared by the sol-gel route and annealed at different temperatures. In order to get powder samples, gels were grounded after the annealing. The samples were used to obtain information about the structural modifications, at molecular level, induced by the doping element and the heat treatments, and mainly to understand the metal species evolution as well as metal-glass interaction. Silica xerogel samples were doped using two different copper precursors: copper nitrate and copper particles chemically synthesized. Amounts of copper nitrate and copper particles were determined in order to obtain final silica glasses of $CuO\text{-}SiO_2$ and $Cu\text{-}SiO_2$with concentrations of the doping element of 30 %w [30].

The preparation of silicon alkoxide can be catalysis by acid or base catalysis. The proposed mechanism for this reaction can be proceeding as follow:

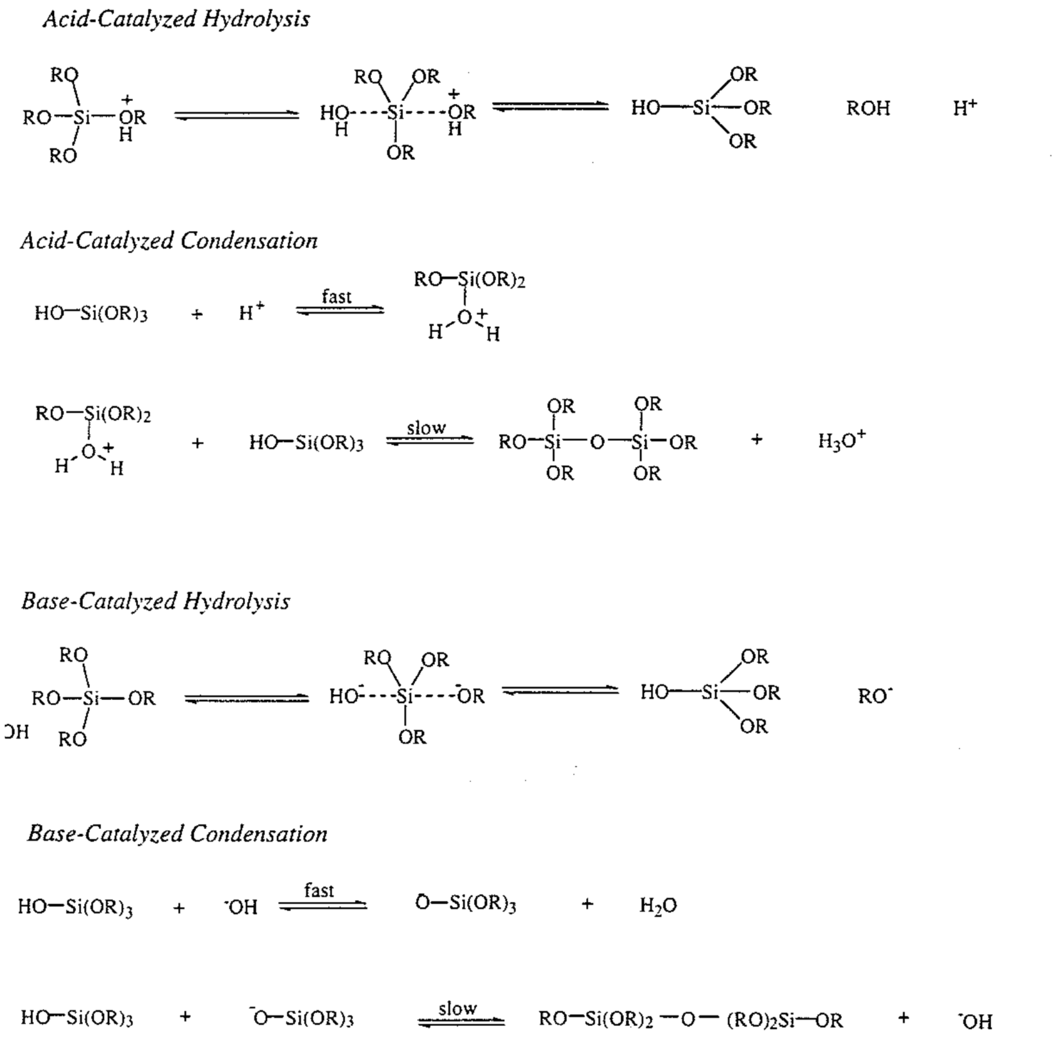

Figure 1.11 Acid base catalysts of Tetraethoxysilane

1.8. Objectives:

The objective of this study can be divided into three parts which can be

Summarized as follows:

- Preparation of tetraethyl orthosilicate by directs method.
- Preparation of tetraethylorthosilicate by using silica supported copper oxide catalyst.
- Characterization of tetraethylorthosilicate (TOES) using FT-IR Spectroscopyand comparison method between tetraethyl orthosilicate which prepared by direct method and by using catalyst.

Chapter two

2. Experimental

2.1 Materials:

2.1.1Apparatuses and Equipment:

- Beakers (50 ml) (Pyrex type).
- Porcelain crucible.
- Heatingmantle (SHIMADZU).
- Glass watch.
- Fourier transform -Infrared spectroscopy (FT-IR spectroscopy) (SHIMADZU).
- Measuringcylinder.
- Whattmannfilterpaper.
- Balance (SHIMADZU JAPAN).

2.1.2Chemicals:

All chemicals used were of analytical grade type and it is includes:

- Hydrochloricacid (HCl).
- Diethyl ether (Et_2O).
- Distilled water.
- Sodiumsilicates (Na_2SiO_3).
- Sodium bisulphate ($NaHSO_4$).
- Copper oxide supported on silica catalyst (Cu_2O/SiO_2).

2.2Methods:

2.2.1 Preparation of Ultra-Pure Silicon Dioxide:

30 g of sodium silicates were weighted and poured into a beaker (250 ml), dissolved in 50 ml of hydrochloric acid, 50 ml of water were added then shacked until the solution is completely dissolved, 35 g of sodium bisulphate were dissolved in 100ml water, the solution was stirred

vigorously with glass rode until it's completely dissolved. The contents of the first beaker was poured into the second one and mixed thoroughly until a thick jelly-like precipitate was formed. The precipitate was poured into a porcelain crucible, heated, dried, and weighted; the percentage of yield was calculated, as following equation:

$$\text{Yield\%} = (W_{Prac}/W_{Theo})\ X100\ldots\ldots\ (2.1)$$

Where:

W_{prac} practical weight

W_{Theo}Theoratical weight

W_{Theo} can be calculated from the theoretical number of moles of sodium silicates and sodium bisulphate.

2.2.2Synthesis of Silicon Alkoxide by Direct Method:

1.0g of ultra-pure silicon dioxide which prepared above (method 2.3.1) was weihgted, 20 ml of diethyl ether and 25 ml of hydrochloric acid were added, the solution was left until the precipitation was completed, the precipitate was filtered and weighted, then was subjected to FT-IR, IR charts for the sample was recorded, finally the percentage yield was calculated,as following equation which explainedabove (method 2.3.1).

Where:

W_{Theo} can be calculated from the theoretical number of moles of silicon dioxide, diethyl ether and hydrochloric acid.

2.2.3Synthesis of Silicon Alkoxide by Using Copper Oxide Supported On Silica Catalyst:

1g of ultra-pure silicon dioxide which mentioned above (method 2.3.1) was weighted, few amount of copper oxide supported on silica catalyst was added, 20 ml of diethyl ether and 25 ml of hydrochloric acid were added, the solution was left until the precipitation was completed, theprecipitate was filtered and weighted, then was subjected to FT-IR,finally the IR charts was recorded, finally the percentage yield was calculated, asequation(2.1).

2.3 Melting Point of Tetraethylorthosilicate.

The melting point of the obtained products by direct method and by using catalystwas carried out using the melting point apparatuses (BIBBY U.K).

2.3.1Percentage of Yield:

The precipitate with catalyst (2.2.2) was subtracted from that without catalyst (2.2.3), the precipitate of actual increasing in the amount of precipitate was calculated, as following equation:

$$(A-b) * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

2.3.2Rate of Reaction of Silicon Alkoxide:

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

$$(Wt/time)\ g/sec \ldots\ldots\ldots\ldots\ldots (2.3)$$

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

2.3.3. FT-IR Spectroscopy:

IR Spectroscopy was used to elucidate the structure and characteristic peak of the silicon Alkoxide which formed in the latter two method (2.2.2 and 2.2.3), and the spectrums were recorded.

Chapter Three

3. Results and Discussion:

3.1. Preparation Method:

3.1.1. Practical Weight of Silicon Dioxide:

The obtained silicon dioxide has amorphous crystal structure, white and the melting point was equal 1650 ^{0}C.

The obtained practical weight of silicon dioxide was 15.002g and the calculated percentage yield was 89.3%,].The reaction equation for this preparation can be represented by the following equation:

$$Na_2SiO_3+NaHSO_4 \xrightarrow{HCL} H_4SiO_3 \xrightarrow{\Delta} SiO_2 \ldots\ldots\ldots\ldots (3.1)$$

From these results this method can be considerable good procedure to production pure silicon dioxide[31], [32].

3.1.2. Practical weight of SiliconAlkoxide by direct method:

The obtained practical weight of siliconAlkoxide was 0.72g and the calculated percentage yield was 26.6%, this result in agreement with the expected yield [33].This reaction can be describe asfollow equation:

$$SiO_2 + (Et_2)_2O \xrightarrow{excess\ (HCL)} TEOS \ldots\ldots\ldots\ldots (3.2)$$

3.1.3. Practical weight of siliconAlkoxide by using catalyst:

The obtained practical weight of siliconAlkoxide was 0.81g and the calculated percentage yield was 30%, this result in agreement with the expected yield [33].

3.2. Characterization Methods:

3.2.1. Rate of Reaction:

3.2.1.1. Time of Initially Formation of Silicon Alkoxide:

Time/sec	90

3.2.1.2. Time of Initially Formation of Silicon Alkoxideby using catalyst:

Time/sec	30

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.

Reactions can be sped up by the addition of a catalyst, including reversible reactions involving a final equilibrium state. Recall 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.

Catalysts are compounds that accelerate the progress of a reaction without being consumed. Common examples of catalysts include acid catalysts and enzymes. Catalysts allow reactions to proceed faster through a lower-energy transition state. By lowering the energy of the transition state, which is the rate-limiting step, catalysts reduce the required energy of activation to allow a reaction to proceed and, in the case of a reversible reaction, reach equilibrium more rapidly. 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 0.81g from tetraethyl orthosilicate at using catalyst, but without catalyst formed 0.72g for 90sec, this indicating that, the tetraethyl orthosilicate which prepared by using catalyst is better than prepared without catalyst. These resultsresemble to the information's in paper [34].

3.3. FT-IR:

3.3.1.FT-IR of TetraethylOrthosilicate Which Prepared by Direct Method:

Infrared spectroscopy is used to study the vibration motions of molecules. As shall be described shortly, it turns out that different motion among different groups of atoms cause the molecule to absorb different amounts of energy. Studying these transitions can sometimes allow us to determine what kinds of atoms are bonded or grouped in an unknown compound, which in turn gives clues as to the molecular structure.

Absorption of energy in the infrared region (ν– = 4000 - 200 cm-1) arises from changes in the vibration energy of the molecules. There are two types of vibrations that cause absorptions in an IR spectrum. Stretching involves rhythmical displacement along the bond axis such that the interatomic distance alternately increases and decreases. Bending involves a change in bond angles between two bonds and an atom common to both.One important condition is that only those vibrations that produce a change in the electric dipole moment of the molecule will be observed in the infrared spectrum. For example, stretching vibrations in homonuclear diatomic molecules like O2, N2, and Br2 do not produce a change in dipole moment and hence these molecules do not give rise to an IR spectrum. On the other hand, CO and IBr produce IR spectra because these molecules contain a permanent dipole moment that will change as the bond is stretched or compressed. CO2, a linear molecule that does not have a permanent electric dipole, nevertheless produces an IR spectrum because the two C=O bonds can stretch in an asymmetric fashion and also bend to produce changes in the dipole moment.

In this research FT-IR Spectroscopy was used to characterize the characteristic band of the obtained product.

The obtained results of FT-IR Spectroscopy of tetraethylorthosilicate which prepared by direct method was describe in **figure (3.3)**

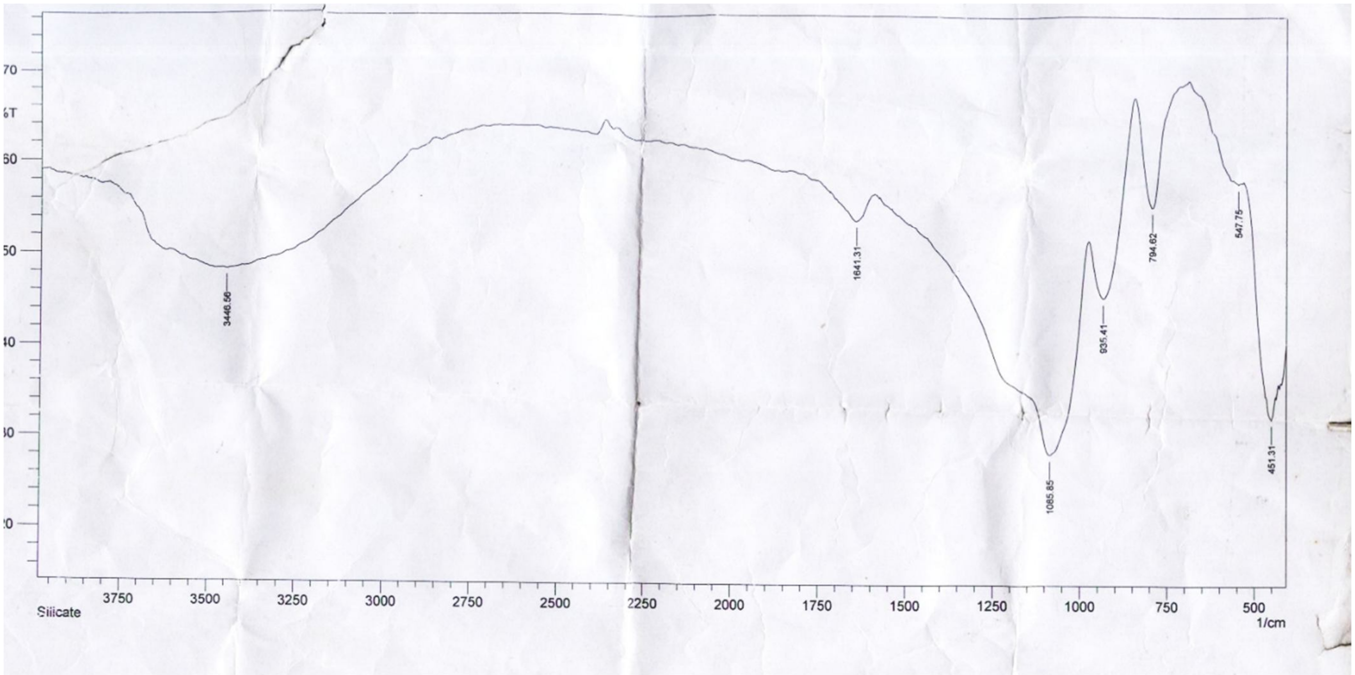

Figure 3.1: IR of TetrethylorthosilicateWhich Prepared By Direct Method

The strong peak at about 3400-3450 cm^{-1} after hydrolysis of TEOS with water is ascribed to hydroxyl group on the surface of the silica. Siloxanes show one or more very strong infra-red band in the region 1130-1000, 700-800 cm^{-1} corresponded to symmetric st.vib of Si-O-Si bond, then 1641.31cm^{-1} corresponded to a symmetrical st.vib of Si-O-Si bond. 450-460cm^{-1} associated with Si-O-Si bond ben.vib. This result was corresponding the IR of TOES was analyzed by Philip J.Launer [35].

3.3.2. FT-IR of TetraethylOrthosilicate Which Prepared By Using Catalyst:

The effect of catalyst in tetraethyl orthosilicate was studied and shows that:

It is clear that, the absorption of Si-O-Si bond increased, it can be seen that, this peak shift toward higher frequencies indicating the strength of the network and the degree of connection in the membranes.

The obtained results of FT-IR Spectroscopy of tetraethylorthosilicate which prepared by using catalyst was describe in **figure (3.4)**.

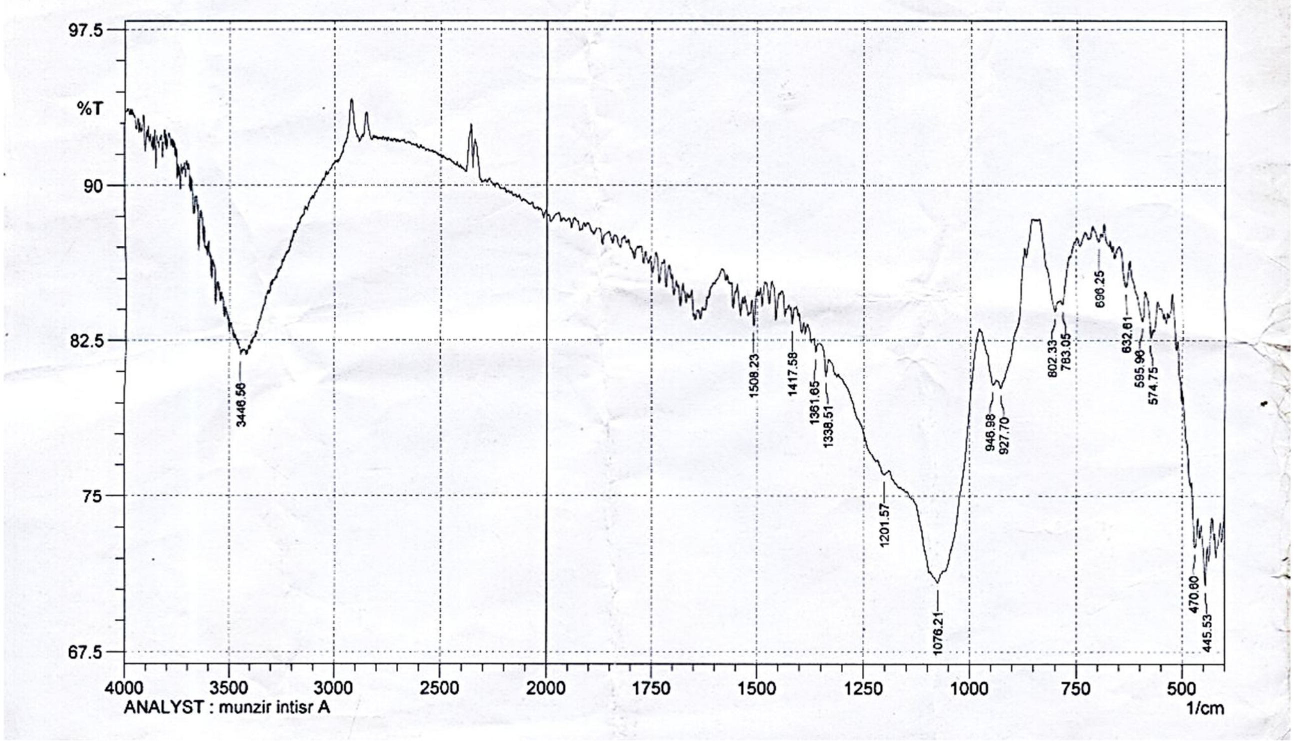

Figure 3.2: IR of Tetrethylorthosilicate Which Prepared By Using Catalyst

High intensities of 3446.56cm^{-1} is presence indicating large amount of free silanol group on it is surface. The hydrolysis and polymerization of a non-catalyzed silica sol was investigated by Fourier Transform Infrared Spectroscopy (FT-IR) and deconvolution of the infrared spectra. The hydrolysis was followed by the 1201.57 and 802.33 cm−1 bands which have been observed that decrease continuously with the reaction time, and they disappear showing the complete hydrolysis. The bands located at 1200 and 1076.12 cm−1 are assigned to polymerization of Si-

OH groups forming Si-O-Si bonds in cyclic or linear structures respectively. Both bands increase with time and are present simultaneously in the spectra showing that both kind of cross-linking of Si-OH groups are taking place in the sol to form the gel. In the gel the presence of Si-OH groups and Si-O− free broken bonds have been detected by means of the bonds located at 946.98and 927.70 cm^{-1} respectively. The spectra of all the samples show the absorption band at about 470 cm-1which corresponds to the Si-O rocking vibration where theoxygenatom moves perpendicular to the Si-O-Si plane. The band appeared at about 800 cm^{-1}may be due to the Si-O bending vibration where the oxygen move atrightangleto the Si-Si lines in the Si-O-Si plane The peak appeared at about 3400 $cm^{-1}$is related to the O-H stretching vibration of H_2O in the sample (figure3.4).this IR peaks resemble to the IR Which carried out by Singh andAugier[36], [37].

In this research was used FT-IR Spectroscopy technical to characterize the product of tetraethylorthosilicate due to the wavelength accuracy or Connes' advantage. The wavelength scale is calibrated by a laser beam of known wavelength that passes through the interferometer. This is much more stable and accurate than in dispersive instruments where the scale depends on the mechanical movement of diffraction gratings. In practice, the accuracy is limited by the divergence of the beam in the interferometer which depends on the resolution [38]. As seen from the operations description above, the interferometer does not separate energy into individual frequencies for measurement. Each point in the interferogram contains information from each wavelength of light being measured. Every stroke of the moving mirror equals one scan of the entire infrared spectrum, and individual scans can be combined to allow signal averaging. In the dispersive instrument, every wavelength across the spectrum must be measured individually as the grating scans. This can be a slow process, and typically only one spectral scan of the sample is made in a dispersive instrument. The multiplex advantage means many scans can be completed and averaged on an FTIR in a shorter time than one scan on most dispersive instruments. Another minor advantage is less sensitivity to stray light that is radiation of one wavelength appearing at another wavelength in the spectrum. In dispersive instruments, this is the result of imperfections in the diffraction gratings and accidental reflections. In FT instruments there is no direct equivalent as the apparent wavelength is determined by the modulation frequency in the interferometer [39].

4. Conclusion:

Tetra ethylorthosilicate was prepared by direct method and by using catalyst, then the characteristic method was applied for two methods. The reaction between silicon and absolute ethanol does not take place without using any catalyst due to the silica present on silica surface. Silica supported copper oxide catalyst (Cu_2O/SiO_2) was found to be most effective catalyst to the reaction which takes place as follow:

$$Si + 4C_2H_5OH \rightarrow Si(OC_2H_5)+2H_2\uparrow \ldots..(10)$$

The tetraethoxysilane has been isolated in high purity from above reaction is indicated by FT-IR analysis. The mechanism of this reaction shows that the catalyst breaks down the silica layer to give teraethoxysilane.

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