

Chapter One

1. Introduction

Silica is silicon dioxide, one form of which is commonly known as sand .it is, by definition, inorganic. However, some plants absorb silicon compound, such as monosilicic acid, from the soil, which are then converted by the plants into a non-crystalline form of silica called a phytolith. phytoliths could be considered "Organic Silica" since they are manufactured by plants, but, strictly speaking, to a chemist, they are still inorganic, since the chemical structure does not contain carbon. The term organic is ambiguous: to a chemist, it must contain carbon, to a biologist, it is "related to, or derived from living organisms"[1].

It is conceivable that silica could be hydrolyzed, in mammalian gastrointestinal tracts to orthosilicic acid, which could be bioavailable, but the extent to which this occurs is unknown. According to the Framingham and Framingham offspring studies, the main food sources for silicon in humans are beer, bananas, and string beans. However, giving foods to human volunteers and then measuring the absorption of silicon compounds gave some results that conflicted with the epidemiological figures, such as regarding bananas:

Food-based, phytolithic silica is digested and absorbed from the gastrointestinal tract. Silicon in grain and grains products (rice, breakfast cereals ,breads and pasta) was readily absorbed , as indicated by the mean urinary excretion of $49 \pm 34\%$ of intake (range: 10–100%). However , except for green beans and raisins , the silicon in vegetables and fruit was less readily absorbed , as indicated by the mean urinary excretion of $21 \pm 29\%$ of intake (range : 0–40%) . Surprisingly, silicon uptake was low ($2.1 \pm 1.2\%$ of intake) from bananas, which are high in silicon (5.4mg Si/100g edible portion) and were one of the highest contributors to silicon intake in the Framingham cohorts. This suggests either that silicon is mainly present in an unavailable form from bananas or that this silicon is absorbed late from the gastrointestinal tract (after 6 h). In general, however, silicon was readily available from foods and in many cases, it showed absorption

similar that of silicon from fluids [2]. There may be a human nutritional requirement for silicon, but not for silicon per se. This subject has been the subject of scientific controversy for decades.

There is no conceivable way that silica itself could be considered essential, since there is no known method by which it can be absorbed or used as such in the human body other than by being converted into soluble silicon compounds.

French scientist J. Loeper, of the Laboratoire de Medicine Experimental in Paris, and UCLA's Dr. Edith Muriel Carlisle, published numerous studies over a period of decades touting the importance of silicon in human nutrition. Loeper hypothesized that a deficiency contributed to numerous diseases. As described by Forrest Nielson of the USDA's Agriculture Research service in 2003, Silicon was actually first reported as possible being an essential nutrient more than 30 years ago. For the next 25 years, the battle of bringing attention to the nutritional importance was fought, not too successfully, by a scientist who promoted the hypothesis that inadequate dietary silicon could contribute to diseases associated with aging such as atherosclerosis, high blood pressure, osteoarthritis and osteoporosis. After this scientist's death, studies examining the nutritional importance of silicon came to a standstill until about 2 years ago.

Then several research groups reported new findings indicating that silicon is important for joint cartilage and bone formation and maintenance, thus boosting the suggestion that silicon is a nutrient of concern for osteoporosis, and perhaps osteoarthritis [3].

"Alternate" health practitioners and advocates make numerous claims for "silica," touting its supposed efficacy in preventing and treating various diseases, such as the claims being made below. Note that, except for the Jugdaohsingh article, found in a 2007 issue of Journal of nutrition, health and aging, the sources cited are secondary and non-scientific, and many of the claims are speculative:

1.1 Organic Silica

It aids in bone cartilage growth, accelerates healing, prevents bone injuries and helps with arthritis. Some skeletal diseases such as osteomalacia and osteoporosis are due to calcium deficiency however calcium supplementation alone does not help. This is due to the fact that

silica allows the body to absorb calcium. Silica has been shown to improve joint function, strengthen connective tissue and reduce swelling of joints [4]. The mineral may also help in maintaining the tissues found in the human digestive tract which in turn may reduce stomach and intestinal inflammation [5]. Cardiovascular health such as keeping blood vessels supple and strong, help clear up plaque as well as prevent heart disease may be helped with organic silica [6]. A deficiency in organic silica increases the risk of arteriosclerosis, however it has been found people who do not have heart disease have up to fourteen times more silica in their bodies [7]. Regular consumption of organic silica has been shown to help and prevent kidney disease, kidney stones and urinary tract health [8]. Silica is also an essential part of skin and hair health since it is found in collagen. An ample supply of organic silica in the body removes irritation and inflammation of skin, improving its overall appearance and preventing sagging, reduces hair loss, accelerates and strengthens nail growth. Signs of old age can be caused by a silica deficiency such as dry and wrinkled skin, weakened teeth and gums, hair loss and frail bones [9].

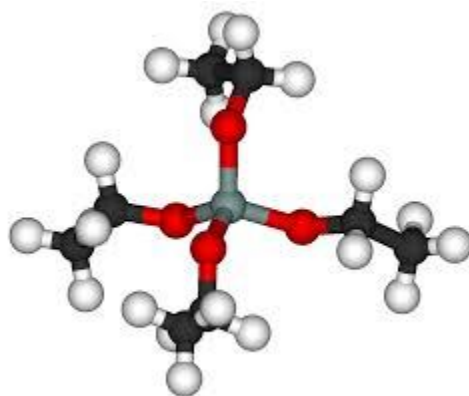
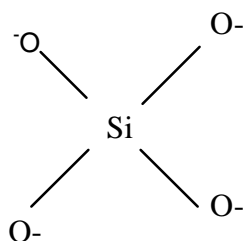


Figure 1.1: Organic Silicates

1.1.1 Structure of the Silicates

Organosilicon compounds with Si-O-Si bonds may show [10] arrangement of structural features. Silicon, unlike carbon, almost never forms double bonds - chemists only recently succeeded in

making a double-bonded compound of silicon by special and complex methods. The basic chemical unit of silicates is [11] the (SiO_4) tetrahedron shaped an ionic group with a negative four charge (-4). The central silicon ion has a charge of positive four while each oxygen has a charge of negative two (-2) and thus each silicon - oxygen bond is equal to one half (1/2) the total bond energy of oxygen. This condition leaves the oxygen's with the option of bonding to another silicon ion and therefore linking one (SiO_4) tetrahedron to another and another etc. The silicates tetrahedron form complicated structures. They can form as single unit, double units, chains, sheets, rings and frame work structures [12] . So we must picture each silicon atom forming [13] single bonds to four separate oxygen atoms, with each oxygen atom linked to two separate silicon atoms, thus:



Actually, in three dimensions the silicon sits at the center of a tetrahedron, with oxygen at each of the four corners. This is true of almost all metal silicates. Obviously the silicon oxygen tetrahedra can bond to each other, and indeed must do so in the solid silicates, for the oxygen atoms are bivalent and must attach to two silicon atoms. This leads to chains and rings of linked (Si-O) tetrahedra, and even to continuous sheets of such linked tetrahedra. As for the mineral silicates [there are also non mineral silicates Which are volatile liquids; such as ethylsilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$.p.168.5°C these are esters of orthosilicic acid, $\text{Si}(\text{OH})_4$], they are of several distinct types:

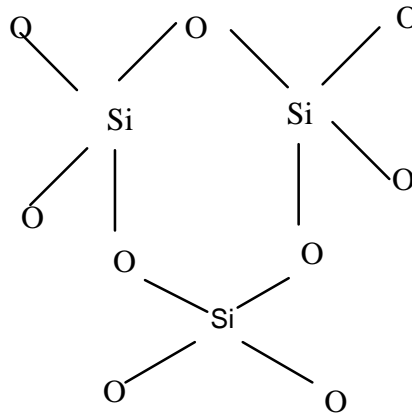
1. Silicates with discrete negatively-charged silicates ions, as in:

a. Those in which there are discrete orthosilicate ions, SiO_4^{4-} (no oxygen atoms are shared by other silicate tetrahedra; all four charges are balanced by positively-charged ions of metal such

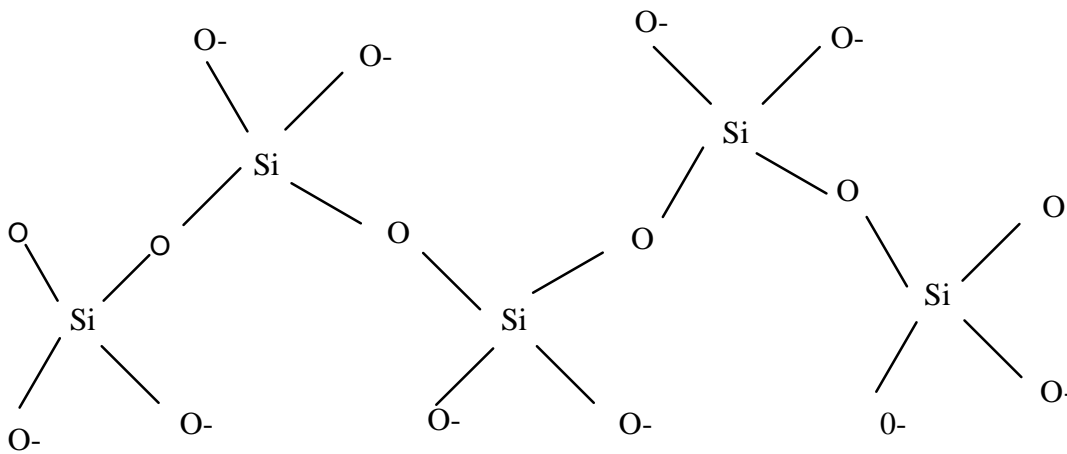
as $\text{Na}^+.\text{K}^+.\text{Ca}^{2+}.\text{Mg}^{2+}.\text{etc...}$). The gem mineral, zircon ZrSiO_4 , is an example.

b. Those in which there are discrete disilicate ions, $\text{Si}_2\text{O}_7^{6-}$, in which two silicate tetrahedra share one corner.

c. Those containing cyclic polysilicate ions in which three or more tetrahedra share two corners, as in:



2. Silicate with infinite chains of tetrahedra, each sharing two corners with the outside oxygen atoms bearing negative charges:



Such ions and the ones in 1.C, have the average composition $(\text{SiO}_3)^{2n-}$, are all tailed metasilicates.

3. Silicates in which the tetrahedra share three corners, leading to flat sheets of alternate silicon and oxygen atoms. This conformation is typical of the layered minerals. Such as the clays and micas.

The different ways that the silicate tetrahedra combine is what makes the silicate class the largest, the most interesting and complicated class of minerals, and also give them their characteristic properties which allow them to be used widely.

1.1 Organic Silicates

1.1.2 Physical Properties of Organic Silicates

Organic silicates exhibit great differences in physical properties [14] (Table 1.1) depending primarily on the position of the metal in the Periodic Table, and secondarily on the alkyl group.

Table 1.1: Physical Properties of Some Metal Ethoxides:

Alkoxide	Colour & Physical Form	m.p. °C	h.p. °C/pa ^b	Solubility in Organic Solvents
LiOC ₂ H ₅	White solid	20-24	n.d.	+
NaOC ₂ H ₅	White solid	260	n.d.	+
KOC ₂ H ₅	White solid	250	n.d.	+
Mg(OC ₂ H ₅) ₂	White solid	270	n.d.	(+) ^d
Ca(OC ₂ H ₅) ₂	White solid	270	n.d.	+
Ba(OC ₂ H ₅) ₂	White solid	270	n.d.	+
U(OC ₂ H ₅) ₅	Dark-brown liquid	–	160	+
Ce(OC ₂ H ₅) ₄	Yellow solid	200		–
Sn(OC ₂ H ₅) ₄	White solid	Un meltable	n.d.	+
U(OC ₂ H ₅) ₆	Dark-red liquid	–	72/0.13	+

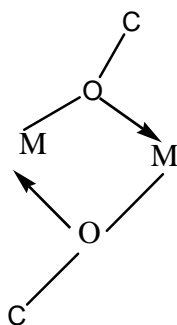
b = to convert pa to mml lg divide by 133.3.

n.d. = not distilable.

d = less soluble.

The alkoxyderivatives of metals have at least one (M-O-C) system. due to the strongly electronegative character of oxygen (electronegativity value, 3.5 on the Pauling scale), alkoxides

of metallic elements exhibit strongly polar character [15]. Thus M- O bond in these derivatives could be expected to have about 65% ionic character for metals with electronegativity values of 1.5 -1.3 (e.g. Al) to about 80% for more electropositive metals with electronegativity values of the order of 1.2 -0.9 (on Pauling scale) (e.g, alkali metals and alkaline earths). However, most of these alkoxides show a fair degree of volatility and solubility in common organic solvents; properties which can be considered as, characteristic of covalent compounds. The two factors which have been postulated [14-15] for explaining the attenuation in the polarity of the (M-O) bond, are the inductive effect of the alkyl or aryl groups at the oxygen atom (this increases with the branching of the alkyl chain) and the formation of oligomers through-dative association of the type:

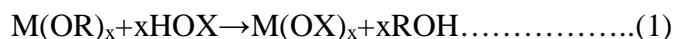


The later tendency is expected to decrease with the ramification on the alkyl group due to steric factors. The applications of more sophisticated spectroscopic and magnetic techniques have thrown clearer light on the structures of organic silicates.

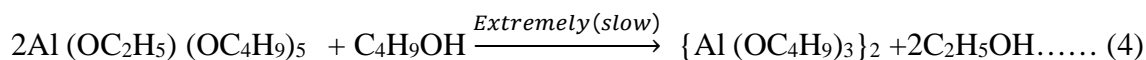
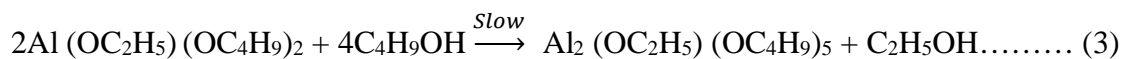
1.1.3 Chemical Properties of Organic Silicates

Alkoxysilanes are characterized by the presence of (Si-O-Si) functional groups, which show similar common reactions depending on the nature of the alkoxy group and substituent. Alkoxysilanes are very reactive species which may be due to the presence of electronegative alkoxy groups making the metal atoms highly prone to nucleophilic attack. The metal alkoxides are, therefore, extremely susceptible to hydrolysis by atmospheric moisture and require careful

handling. Metal alkoxides readily react with excess. of hydrogen halides or acylhalides giving the metal halides. However, by using stiochiometric amounts of these halides, the metal halide alkoxides may be prepared. Alkoxides readily react with the protons of a large number of organic hydroxyl compounds such as alcohols [15-16], glycols[15-17-18], carboxylic acid, hydroxyacid, β -diketones, alkanolamines etc., containing reactive hydroxyl groups with replacement of the alkoxy group by the new organic ligand:



These reactions are quite versatile, and appear to be subject mainly to kinetic factors, e.g., the reaction with highly ramified alcohol arc generally slower and may be even sterically hindered in some cases.



Also the alkoxides are sometimes reactive towards other molecules having reactive protons such as those having -NH or -SH. In these cases, the reactions are controlled by thermodynamic factors and are governed by the comparative stability of (M-O), (M-N) and (M-S) bonds. Metalalkoxides sometimes behave as weak Lewis acids forming coordination compounds. with suitable ligands, although, in general, the metal atoms in alkoxides prefer to attain the high coordination state through intermolecular alkoxy bridge formation rather than by coordination with an external reagent. Also the unsaturated substrates like A=B readily insert across the (M-O) bonds of certain metal alkoxides with molecular re-arrangement resulting in the formation of insertion products [15]. It was established [19] that Bu₃SnH effectively catalyzed the silicon hydride reductive cyclization of enals and enones. Employing Bu₃SnH as a catalyst for

transformation requires the use of stoichiometric amount of a second metal hydride capable of regenerating Bu_3SnH from tributyltinalkoxide.

Silicon hydrides react with alkoxides to afford in hydrides and silyl ethers, provide the basis anew catalytic process [19-20].

1.1.4 Uses of Organic Silicates

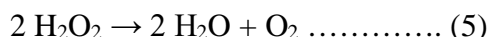
The uses of metal alkoxides depends on their chemical reactivity in common organic solvents [15]. The chemical reactivity is manifest in the variety of catalytic applications of the alkoxides ranging from redox catalysts (Aluminium alkoxides), to accelerators for the drying of paints and inks. Ultimately the alkoxides are valuable precursors of high purity metal oxides through hydrolysis, pyrolysis or combustion. Aluminum alkoxides and other organic aluminum compounds are used as dryers in paints. Silicon alkoxides copolymers are used as protective forming media and in thermally stable inorganic polymers. Dihydro carbonyltris (triphenylphosphine) ruthenium (Ru) catalysed copolymerisation of disiloxane compounds [21]. Alkoxides of aluminum could be used for water-proofing of textiles [15-22]. Monomeric precursors may be converted through hydrolysis reaction into gels and ultimately glasses or ceramic [23-24-25]. Tetraalkoxysilanes are used for the preparation of ceramics by the sol-gel process [26]. Tetraethoxysilane is an important industrial material, it can be used as heat transfer fluid, as an electric, coolant, and can be hydrolysed under controlled conditions to form hydrolysates which act as binders for refractory grains. This latter application is particularly important in the production of precision cast material for ceramic and foundry applications [15-27]. A variety of carbocyclic derivatives of silicon which was biologically active have found a medicinal interest [28]. Purified methyl chlorosilane are used to prepare the various methyl silicone resins, oils and elastomers. Trichlorosilane HSiCl_3 is the preferred source of hyperpure silicon for the transistor and integrated circuits which go into every radio, television and telephone appliance and which are heart of every computer system [13].

1.2 Catalysis

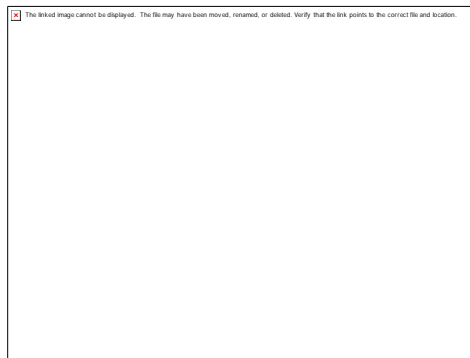
It is the increase in the rate of a chemical reaction due to the participation of an additional substance called a catalyst [29]. With a catalyst, reactions occur faster and require less activation energy. Because catalysts are not consumed in the catalyzed reaction, they can continue to catalyze the reaction of further quantities of reactant. Often only tiny amounts are required [30].

The production of most industrially important chemicals involves catalysis. Similarly, most biochemically significant processes are catalyzed. Research into catalysis is a major field in applied science and involves many areas of chemistry, notably organometallic chemistry and material science. Catalysis is relevant to many aspects of environmental science, e.g. the catalytic converter in automobiles and the dynamics of the ozone hole. Catalytic reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated, [31] as opposed to stoichiometric reactions in which all reactants are consumed and more side products are formed. Many transition metals and transition metal complexes are used in catalysis as well. Catalysts called enzymes are important in biology.

A catalyst works by providing an alternative reaction pathway to the reaction product. The rate of the reaction is increased as this alternative route has a lower activation energy than the reaction route not mediated by the catalyst. The disproportionation of hydrogen peroxide creates water and oxygen, as shown below.



This reaction is preferable in the sense that the reaction products are more stable than the starting material, though the unanalyzed reaction is slow. In fact, the decomposition of hydrogen peroxide is so slow that hydrogen peroxide solutions are commercially available. This reaction is strongly affected by catalysts such as manganese dioxide, or the enzyme peroxidases in organisms. Upon the addition of a small amount of manganese dioxide, the hydrogen peroxide reacts rapidly. This effect is readily seen by the effervescence of oxygen [32]. The manganese dioxide is not consumed in the reaction, and thus may be recovered unchanged and re-used indefinitely. Accordingly, manganese dioxide catalyses this reaction [33].



Main article: Heterogeneous catalysis

Figure 1.2: Heterogeneous

Ask the average person in the street what a catalyst is, and he or she will probably tell you that a catalyst is what one has under the car to clean up the exhaust. Indeed, the automotive exhaust converter represents a very successful application of catalysis; it does a great job in removing most of the pollutants from the exhaust leaving the engines of cars. However, catalysis has a much wider scope of application than abating pollution.

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 it unaltered such that it is available for the next reaction. In fact, we can describe the catalytic reaction as a cyclic event in which the catalyst participates and is recovered in its original form at the end of the cycle [34].

1.2.1 Catalysis in Industry

Catalysts are the workhorses of chemical transformations in the industry. Approximately 85–90 % of the products of chemical industry are made in catalytic processes. Catalysts are indispensable in:

- Production of transportation fuels in one of the approximately 440 oil refineries all over the world.
- Production of bulk and fine chemicals in all branches of chemical industry.
- Prevention of pollution by avoiding formation of waste (unwanted byproducts).
- Abatement of pollution in end-of-pipe solutions (automotive and industrial exhaust).

A catalyst offers an alternative, energetically favorable mechanism to the noncatalytic reaction, thus enabling processes to be carried out under industrially feasible conditions of pressure and temperature [34].

1.2.2 General Acid/Base Catalysis

In acid catalysis and base catalysis a chemical reaction is catalyzed by an acid or a base. The acid is the proton donor and the base is the proton acceptor. Typical reactions catalyzed by proton transfer are esterifications and aldol reactions. In these reactions the conjugate acid of the carbonyl group is a better electrophile than the neutral carbonyl group itself. Catalysis by either acid or base can occur in two different ways: specific catalysis and general catalysis.

Charge development in the TS can be decreased by either donation of a proton from general acids (like acetic acid or a protonated indole ring) to an atom such as a carbonyl O which develops a partial negative charge in the TS when it is attached by a nucleophile. Proton donation decreases the developing negativity in the TS. Alternatively, a nucleophile such as water which develops a partial positive charge in the TS as it begins to form a bond to an electrophilic C in a carbonyl can be stabilized by the presence of a general base (such as acetate

or the deprotonated indole ring). Proton abstraction decreases the developing positive charge [35]



Figure 1.3: Charge Development in the transition state for ester hydrolysis



Figure 1.4: Mechanism of general acid catalysis

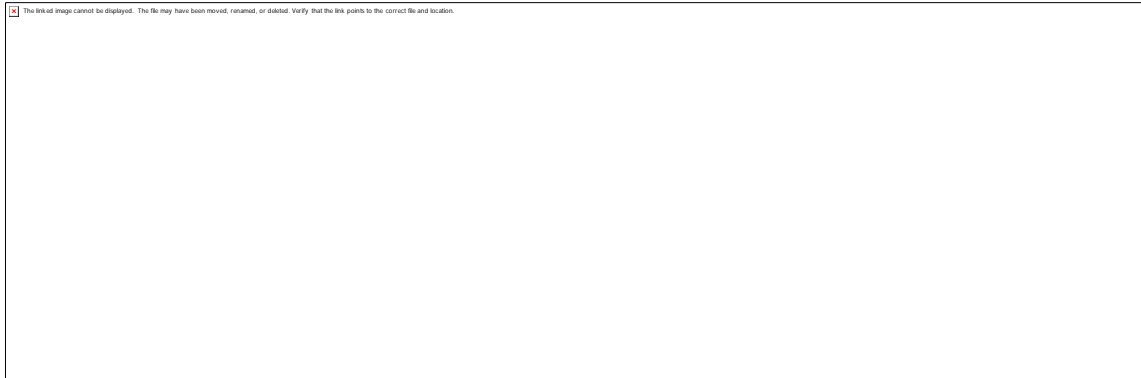


Figure 1.5: Mechanism of general base catalysis

1.2.3 Importance of Catalysis

The chemical industry of the 20th century could not have developed to its present status on the basis of non-catalytic, stoichiometric reactions alone. Reactions can in general be controlled on the basis of temperature, concentration, and pressure and contact time. Raising the temperature and pressure will enable stoichiometric reactions to proceed at a reasonable rate of production, but the reactors in which such conditions can be safely maintained become progressively more expensive and difficult to make. In addition, there are thermodynamic limitations to the conditions under which products can be formed, 600°C. Nevertheless, higher temperatures are needed to break the very strong $\text{N}\equiv\text{N}$ bond in N_2 . Without catalysts, many reactions that are common in the chemical industry would not be possible, and many other processes would not be economical. Catalysts accelerate reactions by orders of magnitude, enabling them to be carried out under the most favorable thermodynamic regime, and at much lower temperatures and pressures. In this way efficient catalysts, in combination with optimized reactor and total plant design, are the key factor in reducing both the investment and operation costs of a chemical processes. But that is not all [34].

- 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 [36].

1.3 Sol-Gel Chemistry

Sol-gel polymerization of tetra-alkoxysilanes, $\text{Si}(\text{OEt})_4$ (TEOS), 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 alkoxy silane [37] (see figure 1.6).

SOL GEL CHEMISTRY

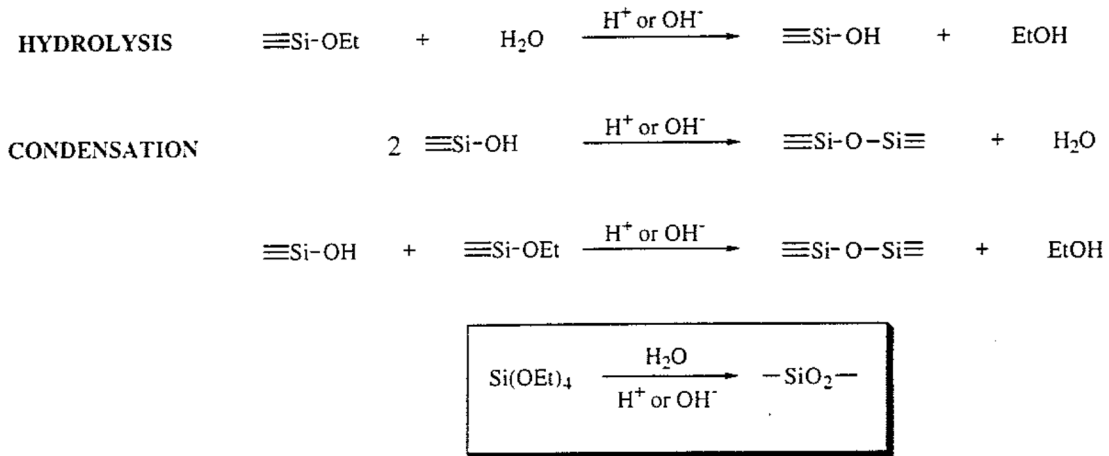


Figure 1. Summary of the key steps in sol-gel polymerization of ethoxysilanes.

Figure: 1.6 Summary of the key steps in sol-gel polymerization of ethoxysilanes

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 Waals, hydrogen bonds, polymeric chain

Entanglement [38].

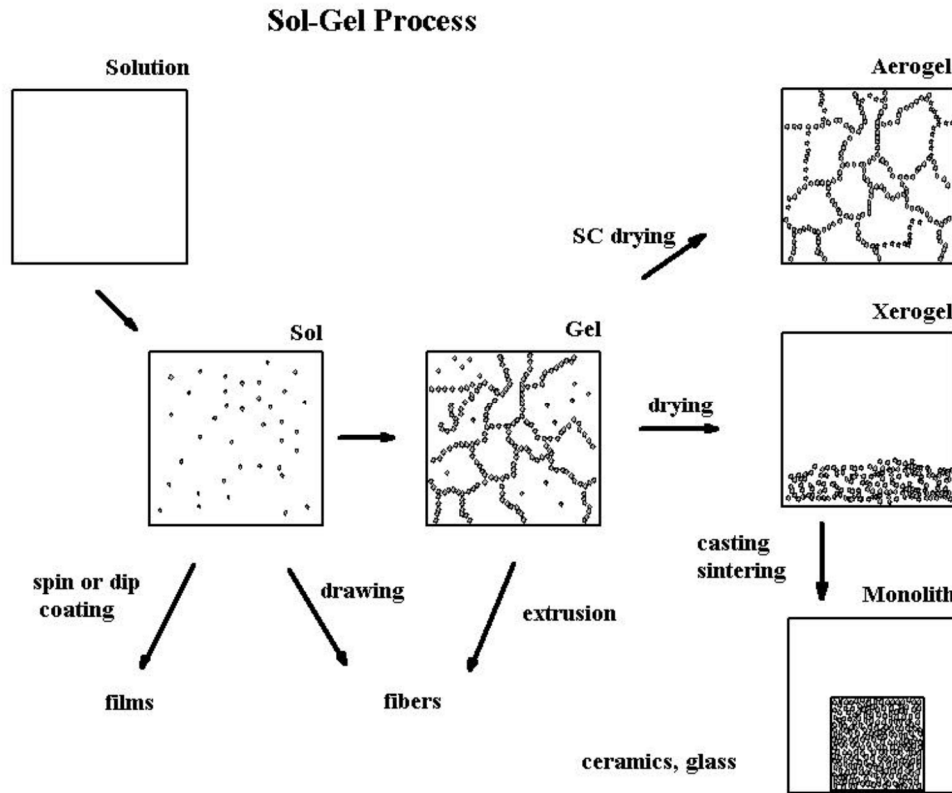
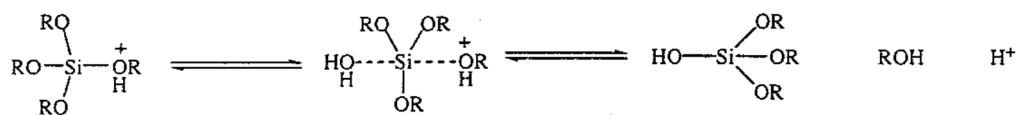


Figure: 1.7 Sol-gel Process

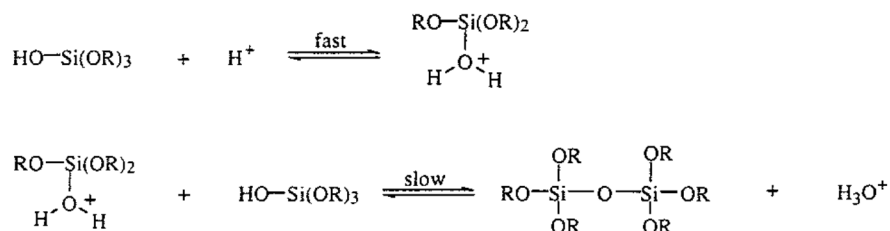
1.3.1 Sol -Gel Polymerization of Tetra ethylorthosilicate

Sol gel polymerization of TEOS involves hydrolysis and condensation reactions. Hydrolysis occurs when TEOS and water are mixed in a mutual solvent, generally ethanol. The intermediates that are produced include Si – OH groups, which are called silanols. Complete hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ to $\text{Si}(\text{OH})_4$ would give silicic acid, but this does not occur. Instead condensation may occur between either two silanols or a silanol and an ethoxy group to form bridging oxygen or a siloxane group Si-O-Si. Water or ethanol is eliminated (figure 1.8) [37].

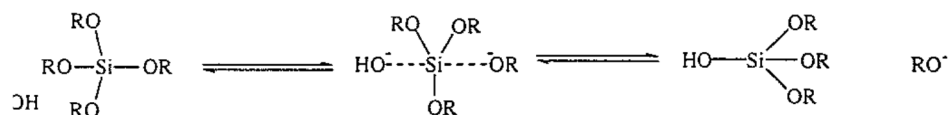
Acid-Catalyzed Hydrolysis



Acid-Catalyzed Condensation



Base-Catalyzed Hydrolysis



Base-Catalyzed Condensation

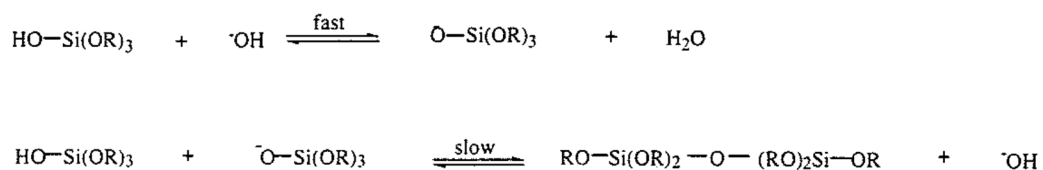


Figure: 1.8 Mechanism of hydrolysis and condensation of alkoxy silanes

1.4 Tetra ethyl OrthoSilicate

Tetraethyl orthosilicate is the chemical compound with the formula $\text{Si}(\text{OC}_2\text{H}_5)_4$. Often abbreviated TEOS, it is a colorless liquid that degrades in water. TEOS is the ethyl ester of orthosilicic acid, $\text{Si}(\text{OH})_4$. It is a prototypical alkoxide.

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



where Et = C₂H₅

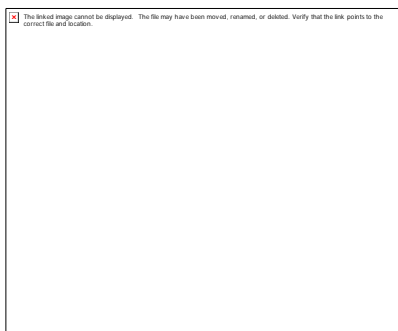
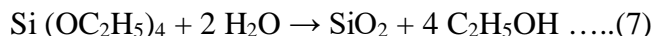


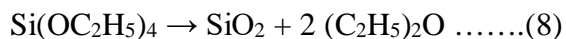
Figure 1.9: Tetraethyl OrthoSilicate

TEOS easily converts to silicon dioxide. This reaction occurs upon the addition of water:



This hydrolysis reaction is an example of a sol-gel process. The side product is ethanol. The reaction proceeds via a series of condensation reactions that convert the TEOS molecule into a mineral-like solid via the formation of Si-O-Si linkages. Rates of this conversion are sensitive to the presence of acids and bases, both of which serve as catalysts. The Stöber process allows the formation of monodisperse silica particles.

At elevated temperatures (>600 °C), TEOS converts to silicon dioxide:



The volatile coproduct is diethyl ether.

1.4.1 Properties of Tetraethyl OrthoSilicate

Table 1.2: Properties of Tetraethyl OrthoSilicate:

Chemical formula	SiC ₈ H ₂₀ O ₄
Average mass	208.327 Da
Monoisotopic mass	208.113083 Da
Molar mass	208.33 g mol ⁻¹
Appearance	colourless liquid
Odor	sharp, alcohol-like[39]
Density	0.933 g/mL at 20 °C
Melting point	-77 °C (-107 °F; 196 K)
Boiling point	168 to 169 °C (334 to 336 °F; 441 to 442 K)
Solubility in water	reacts with water, soluble in ethanol, and 2-propanol
Vapor pressure	1 mmHg[39]

1.4.2 Application of Tetraethyl OrthoSilicate

TEOS is mainly used as a crosslinking agent in silicone polymers and as a precursor to silicon dioxide in the semiconductor industry [40]. TEOS is also used as the silica source for synthesis of zeolites [41]. 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 [42].

1.5 Other Study about Copper Oxide Supported On Alumina and Silica Catalyst

Ethyl silicates is a chemical substance which has been known to be excellent precursor (starting material) for production of metal oxides [43] which are vital in electronics and ceramics industries for fabrication of electronics, glassy and ceramic materials. Sol – gel process has been used as novel method for preparation of these oxides materials from ethyl silicates [44]. High quality oxide prepared by this procedure depends mainly on optimization of ethyl silicates synthesis and physico – chemical factors that affect in hydrolysis of ethyl silicates to form these metal oxides. Therefore, ethyl silicates have been tested in industrial practice for the production of ferroelectrics and related materials, of dielectrics, solid electrolytes, heat – resistant material, high temperature super conductors, protective coatings, films with specific optical and electro physical properties, and catalysts [45] . 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. Previously [44] ethyl silicates can be prepared by the reaction of tetrachlorosilane and ethanol as follows:-
$$\text{SiX}_4 + 4\text{ROH} \rightarrow \text{Si}(\text{OR})_4 + 4\text{HX} \dots (9)$$

(Where R is an alkyl or aryl group, and X is a halogen). When anhydrous ethanol is used the product is tetraethoxysilane, but when industrial spirit or aqueous ethanol is used, the product is technical ethyl silicates [46]. Technical ethyl silicates is a mixture of ethoxypolysiloxanes, comprising hexaethoxydisiloxane and the higher oligomers. The reason that ethoxypolysilicates are formed is that the condensation – polymerization reactions occur in the presence of small amounts of water in the reaction mixture which are catalyzed by the hydrogen chloride by product.

The vast development of industry and the increasing demands for human needs lead unintentionally to the increase of environmental pollution. For such reasons the concerned authorities have begun issuing strict laws which enforce industries to reduce the prevalent pollution which is the result of their factories or the engines which they manufacture. The European Union strict laws, for example, enforced automobile industry to reduce the amounts of prevalent soot pollutants emitted from the road vehicles. Therefore since 1993 petrol cars use in their exhaust effective catalyts which decrease the rate of pollution caused by these engines. The catalysis system has now extended to diesel vehicles. Hence the purpose of this study is to prepare and characterize catalyts formed from CuO, CeO₂ and Al₂O₃. The oxides of transition metals combined with other oxides such as that of zinc, chrome, thorium and cerium have been extensively studied [47-48], and the catalytic properties of these catalyts are result of active centers surrounded by an electronic hole, the ability of the hydroxyl roots to move on the surface of the catalyst and finally the catalyst capacity to store hydrogen or oxygen in its structure. These properties are the outcome of the nature of the support and the conditions in which the catalyst are handled and activated. Cerium oxide has been widely used as a support [49-50] because it has two oxidation numbers: Ce⁺³ and Ce⁺⁴, which enable it to form nonstoicheometric oxides CeO_{2-x} [51-52]. The lack of oxygen in this type of oxides leads to the formation of electronic holes which makes these oxides semi-conductors. But in fact these holes are capable of easily receiving or giving oxygen, and play a role as a regulator of existing oxygen in the catalyts used in petrol exhaust cars [53-54]. It has been revealed that the presence of cerium delays the glassing process of active phase in catalyts and improves the stabilities of aluminum oxide γ at high temperatures [55-56]. Aluminum oxide is also used as a support in various catalyts especially when its specific area is high [57-58].

Tetraethoxysilane was prepared using the direct synthetic procedure in presence of magnesium ethoxide, tin tetrachloride and tin oxide as catalyts. Magnesium ethoxide was prepared firstly, identified by spectral analysis and then used in the preparation of tetraethoxysilane. The method Adopted is reliable and significant as far as synthetic routes are concerned. The product obtained was analyzed using infra-red spectroscopy and gas-liquid chromatography, these indicated that the final reaction production can be obtained in high Spectral analysis obtained are in good agreement with reported data for tetraethoxysilane [46].

1.6 The Aim of the Study

- i. Preparation of tetraethylorthosilicate by direct method.
- ii. Preparation of tetraethoxysilan by using copper oxide supported on alumina catalyst.
- iii. Characterization of tetraethylorthosilicate (TOES) using FT-IR spectroscopy and comparison between tetraethylorthosilicate which prepared by direct method or by using catalyst.

Chapter Two

Materials and Methods

2. Materials

2.1 Apparatuses and Equipments

- Beakers (50 ml) (Pyrex type).
- Porcelain crucible.
- Heating mantle (SHIMADZU).
- Glass watch.
- Fourier transform -Infrared spectroscopy (FT-IR spectroscopy) (SHIMADZU).
- Measuring cylinder.
- Whattmann filter paper.
- Balance (SHIMADZU JAPAN).

2.2 Chemicals

All chemicals used in this research were of analytical grade type and it includes:

- Hydrochloric acid (HCl).
- Diethyl ether (Et₂O).
- Distilled water.
- Sodium silicates (Na₂SiO₃).
- Sodium bisulphate (NaHSO₄).
- Copper oxide supported on Alumina catalyst (Cu₂O/AlO₂).

2.3 Preparation Methods

2.3.1 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 shaken until the solution is completely dissolved, 35 g of sodium bisulphate were dissolved in 100ml water, the solution was stirred

vigorously with glass rod 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 and heated, dried and weighted, the percentage of yield was calculated, as following equation:

$$\text{Yield\%} = (W_{\text{Prac}}/W_{\text{Theo}}) \times 100 \dots\dots (10)$$

Where:

W_{prac} practical weight

W_{Theo} Theoretical weight

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

2.4 Synthesis Method

2.4.1 Synthesis of Silicon Alkoxide by Direct Method

1g of ultra-pure silicon dioxide which prepared above (method 2.3.1) was weighted, 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 explained above (method 2.3.1).

Where:

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

2.4.2 Synthesis of Silicon Alkoxide by Using Copper Oxide Supported On Alumina Catalyst

1g of ultra-pure silicon dioxide which mentioned above (method 2.3.1) 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, the solution was left until the precipitation was completed,

the precipitate was filtered and weighted, then was subjected to FT-IR, finally the IR charts was recorded, finally the percentage yield was calculated, as following equation which explained above (method 2.4.1).

2.5 Characterization Methods

2.5.1 Melting Point of Tetraethylorthosilicate Which Prepared By Two Methods

The melting of the obtained products was carried out using the melting point apparatuses (BIBBY U.K).

2.5.2 Comparison between Tetraethylorthosilicate Which Prepared By Direct Method and By Using Catalyst

2.5.2.1 Percentage of Yield

The precipitate with catalyst (2.4.1) was subtracted from that without catalyst (2.4.2), the precipitate of actual increasing in the amount of precipitate was calculated, as following equation:

$$(A-b) * 100 \dots \dots \dots (11)$$

2.5.2.2 Rate of Reaction

2.5.2.2.1 Rate of Reaction of Silicon Alkoxide

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

$$(Wt/time) \text{ g/sec.}$$

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

2.5.3 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 (2.4.1 and 2.4.2), 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 °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:

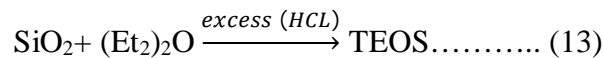


Silicon dioxide is stable in water and at high temperature. This chemical stability and good electrical insulation properties are the major reason that is needed to fabricate excellent semiconductor devices. The properties of silicon dioxide nano particles such as high surface areas are highly desirable as catalytic support because high surface area provides more active sites for gas or solid interactions

From these results this method can be considerable good procedure to production pure silicon dioxide [60-61].

3.1.2 Practical weight of Silicon Alkoxide by direct method

The obtained practical weight of silicon Alkoxide was 0.72g and the calculated percentage yield was 26.6%, this result in agreement with the expected yield [62]. This reaction can be described as follow equation:



3.1.3 Practical weight of silicon Alkoxide by using catalyst

The obtained practical weight of silicon Alkoxide was 0.82g and the calculated percentage yield was 30%, this result in agreement with the expected yield [63].

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.

3.1.3.1 Reaction energetic

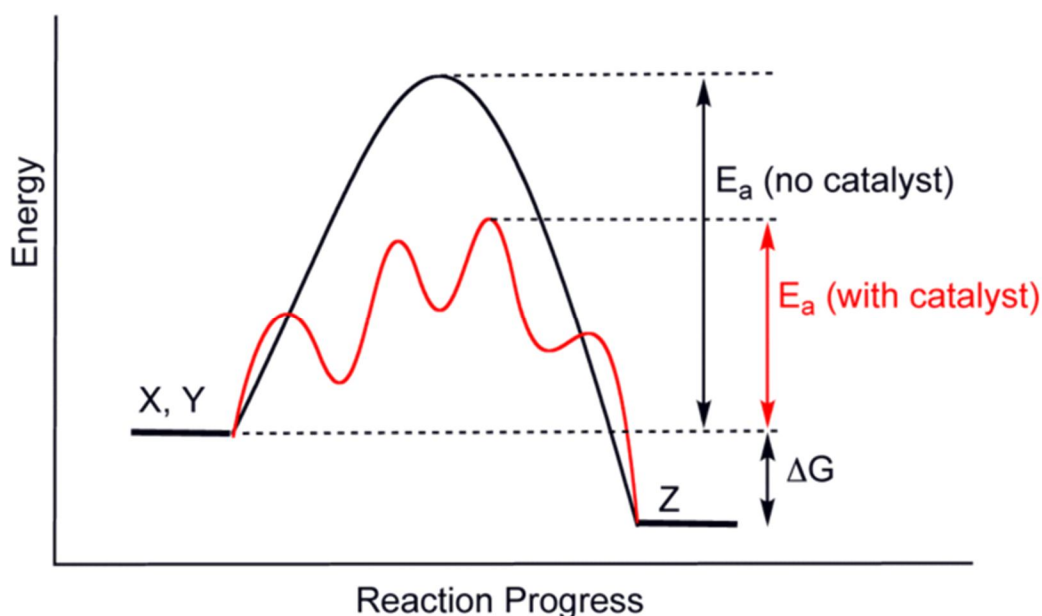


Figure 3.1: Effect of a Catalyst on Equilibrium

3.2 Characterization Methods

3.2.1 FT-IR

3.2.1.1 FT-IR of Tetraethyl Orthosilicate 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 ($\nu = 4000 - 200 \text{ cm}^{-1}$) 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 O_2 , N_2 , and Br_2 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. CO_2 , a linear molecule that does not have a permanent electric dipole, nevertheless produces an IR spectrum because the two $\text{C}=\text{O}$ 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 (3.2)**.

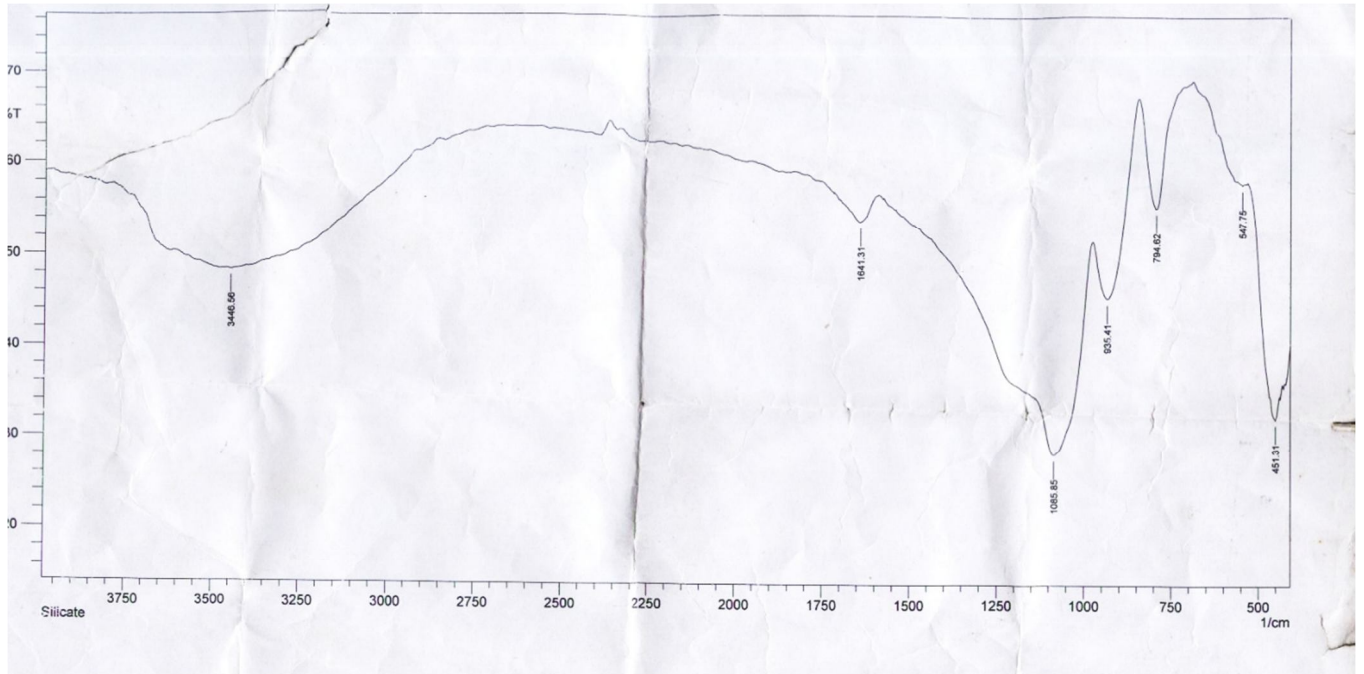


Figure 3.2: IR of Tetraethylorthosilicate Which Prepared By Direct Method

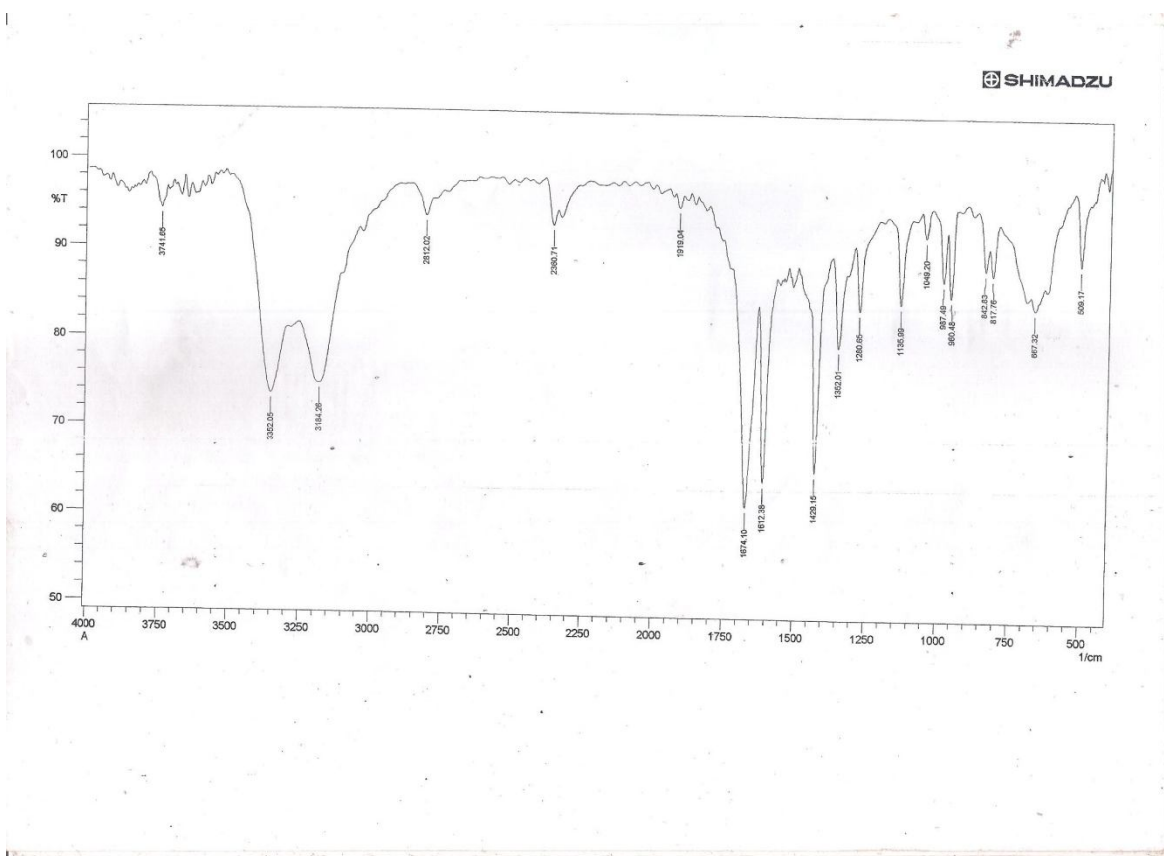
The strong peak at about $3400\text{-}3450\text{ cm}^{-1}$ after hydrolysis of TEOS with water is ascribed to hydroxyl group on the surface of the silica. Siloxanes show one or more very strong infra-red band in the region $1130\text{-}1000, 700\text{-}800\text{ cm}^{-1}$ corresponded to symmetric st.vib of Si-O-Si bond, then 1641.31 cm^{-1} corresponded to a symmetrical st.vib of Si-O-Si bond. $450\text{-}460\text{ cm}^{-1}$ associated with Si-O-Si bond ben.vib. This result was corresponding the IR of TOES was analyzed by Philip J.Launer [64].

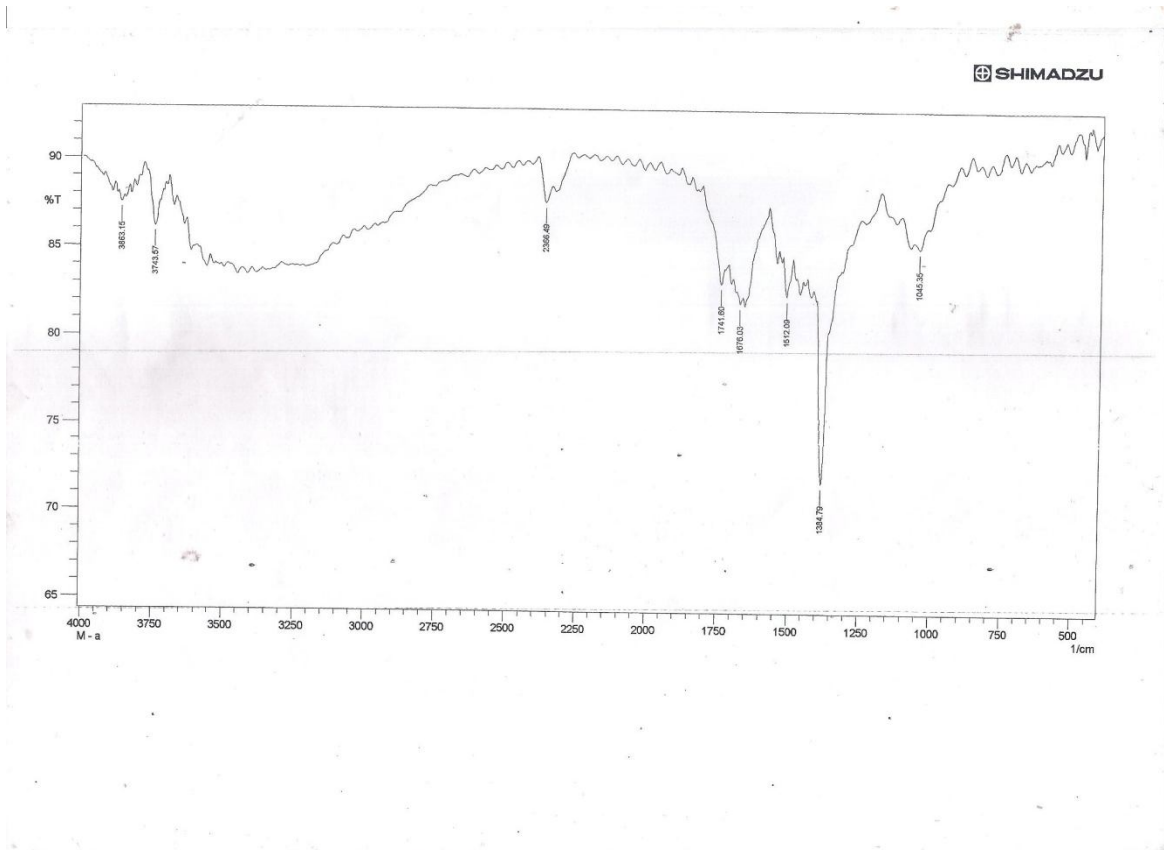
3.2.1.2 FT-IR of Tetraethyl Orthosilicate Which Prepared By Using Catalyst:

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 (3.3)**.





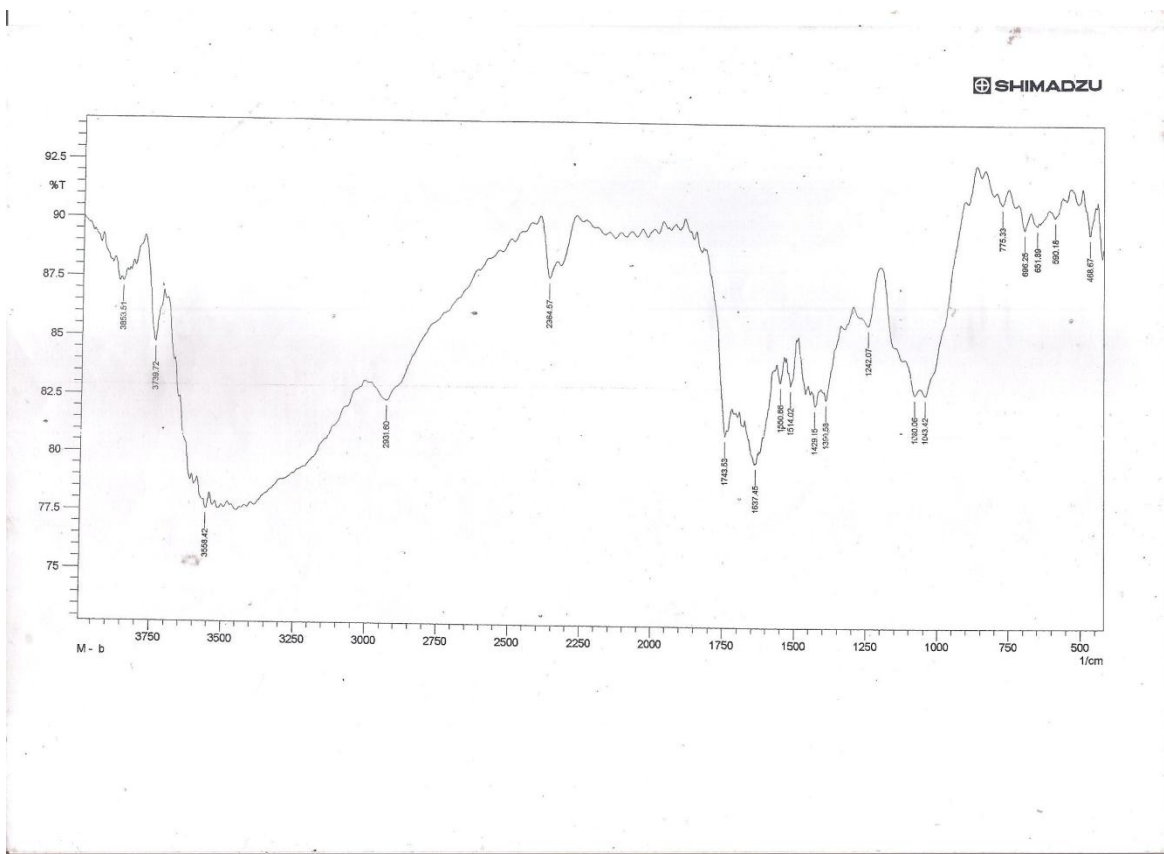


Figure 3.3: IR of Tetrethylorthosilicate Which Prepared By Using Catalyst

High intensities of 3446.56 cm^{-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} band 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 946.98 and 927.70 cm^{-1} respectively. The spectra of all the samples show the absorption band at about 470 cm^{-1} which corresponds to the Si-O rocking vibration where the oxygen atom 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 at right angle to 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 H₂O in the sample (See figer3.3).this IR peaks resemble to the IR Which carried out by Singh and Augier [64-65].

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 [66]. 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 [67].

3.3 Rate of Reaction

3.3.1 Time of Initial Formation of Silicon Alkoxide

Time/sec	90
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3.2.2 Time of Initial Formation of Silicon Alkoxide by 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.

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. 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 0.82g 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 results resemble to the information's found in literature [68].

4. Conclusion

Tetra ethylorthosilicate has been prepared from silicon dioxide and diethyl ether using direct method Synthesis of Silicon Alkoxide and indirect method using catalyst copper oxide supported on alumina. The reaction between silicon and absolute ethanol does not take place without using any catalyst due to the silica present on silicon surface. Alumina supported copper oxide ($\text{Cu}_2\text{O}/\text{AlO}_2$) was found to be the most effective catalyst to the reaction which takes place as follows:



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 tetraethoxysilane.

3.5 Recommendations

- To obtain new method for study copper oxide supported on Alumina as catalyst.
- To use copper oxide supported on Alumina as catalyst in preparation of tetraethylorthosilicate.

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