

Synthesis and Characterization of Organic Silicates Using Appropriate Catalysts

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Abstract:

Tetraethoxysilane (TEOS) was prepared from elemental silicon and liquid ethanol using silica or alumina supported copper oxide catalysts .The effects of catalyst, reaction conditions were studied . Moreover, the product characterized by IR, GLC, H¹NMR and scanning electron microscope (SEM), also Silica and alumina supported copper oxide catalysts were prepared and characterized by the analytical and spectroscopic methods. The results indicated that silica or alumina supported copper oxide were effective catalysts for the direct synthesis of tetraethoxysilane . Moreover, tetraethoxysilane has been isolated in high yield and purity as showed by H¹NMR and GLC analyses.

Keywords: Tetraethoxysilane, Catalyst, Elemental Silicon, Ethanol.

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1. Introduction

Ethyl silicates is a chemical substance which has been known to be excellent precursor (starting material) for production of metal oxides [1] 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 [2]. 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 [3] .

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 [2] ethyl silicates can be prepared by the reaction of tetrachlorosilane and ethanol as follows:-

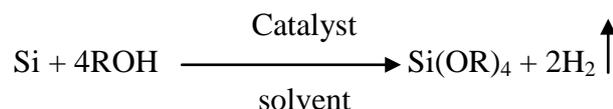


(Where R is an alkyl or aryl group, and X is a halogen).

When anhydrous ethanol is used the product is tetraethoxysilane, but when industrial spirit or aqueous ethanol is used, the product is technical ethyl silicates [4]. 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.

1.1 The elemental route to tetraethoxysilane:

The halosilane route to tetra alkoxy silanes is a source of many difficulties concerning control of pollution [5], chlorine which is used in the manufacture of silicon tetrachloride, is a hazardous material. So also is silicon tetrachloride. Both can cause severe pollution. The hydrogen chloride by – product decreases the overall yield by initiating series side reactions. However, an alternative recent route has been developed for the production of tetraalkoxy silanes, by a direct method which is based on reacting elementary silicon with a corresponding alcohol [6] using suitable catalyst. The reaction can be represented as follows:



The use of metal alkoxides as catalysts in production of tetraethoxysilane from silicon metal and the corresponding alcohol has been reported [7]. The preferred metal alkoxides are those of alkali metals particularly those of sodium and potassium, a method is described for production of tetraethoxysilane as follow: stir suspension of silicon powder in large volume of catalytic solution preheated to 150 – 160 oC, dry ethanol is then added batch wise. The catalytic solution [8-9] has sufficient thermal capacity to maintain the temperature catalyzed the reaction, and to discharge tetraethoxysilane as vapor together with ethanol and hydrogen gas. The thermal capacity can be maintained by step wise addition of reactions .

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, so a considerable effort has been expended [10-11] to develop the direct synthesis for production of tetraethoxysilane due to its industrial uses or applications.

1.2 Silica supported copper oxide catalysts:

The effect of catalyst on the reaction between silicon and ethanol, has been investigated [12-13] the catalyst , has to be freshly prepared by carefully dissolving clean directly

1.3 The catalyzed reaction of silicon with alcohols:

Tetraethoxysilane was prepared from reaction involving silicon, ethanol and a silica and alumina supported copper oxide catalyst in a suitable solvent at 100 °C:



It is now well established that all previous attempts [4] to activate the silicon in a vapour phase reaction by presence of copper and /or Zinc or by carrying out the reaction under Pressure, have been largely superseded by liquid phase procedures using silica or alumina supported copper oxide catalysts. The success of this investigation lay in the development of a simple model reaction system which was capable of good reproducibility and the results of which form a firm basis for comparison. The use of novel silica and alumina supported copper oxide catalysts for this reaction shows that silica supported copper oxide and alumina supported copper oxide will function as catalysts for initiating and propagating the reaction between silicon and liquid ethanol .

1.4 Selection of a model reaction and procedure:

Silicon normally does not react with alcohols, but catalysts are necessary to activate or cause the silicon to react with alcohols to produce tetraethoxysilane and hydrogen. Thus to achieve a practical reaction rate, silicon powder is reacted with alcohols in the liquid phase at temperature of 80 – 100 °C in the presence of a catalyst using a suitable solvent.



To a stirred suspension of silicon powder in a large volume of catalyst solution and solvent (500Cm³ per mole Si) preheated to 150 °C, absolute ethanol is added

continuously below the liquid as evidenced by hydrogen evolution. Silicon is added batch wise, while ethanol addition is drop wise at a rate determined in response to the reaction temperature and progress. The product is periodically distilled out of the reaction vessel in the form of an ethanol /tetraethoxysilane mixture, separated by fractional distillation with ethanol being recycled. The most important aim of this study to elucidate the composition and the structure of freshly prepared silica and alumina supported copper oxide catalysts. In addition to that to investigate the influence of the catalyst precursor, type of support on the catalyst activity in the direct reaction between elemental silicon and absolute ethanol to produce tetraethoxysilane. To achieve these goals, series of three samples with a Cu concentration 10 w% have been examined in detail with several physicochemical techniques. Most of these techniques have been successfully used to study copper system. However, considerable controversy still exists as to the exact nature of the Cu responsible for their catalyst activity.

2. Experimental

2.2 Materials and methods:

All chemicals used were of analytical grade and used as received.

2.3 Preparation of tetraethoxysilane (TEOS) by direct route:

2.3.1 Preparation of (TEOS) using silica supported copper oxide catalyst prepared from copper hydroxide salt:

In 3- necked round bottomed flask 100 ml absolute ethanol was added to 1.0 g silicon powder followed by addition of tiny amounts of silica supported copper oxide catalyst. Then the reaction mixture was refluxed about 36 hrs. With effective stirring using stirrer and the reading of thermometer was adjusted at 78 °C. At the end of the experiment, the reaction mixture was filtered to separate unreacted silicon and the catalyst. A colorless liquid was observed in the reaction container. Then this liquid solution was fractionated to separated product at its boiling temperature. The obtained product was characterized by IR; GLC. This experiment was summarized in Table (1).

Table (1): Summary of the direct reaction between silicon and absolute ethanol using silica supported copper oxide catalyst prepared from copper hydroxide salt.

| | |
|---|---------------------|
| Time /hours | 36 |
| Ethanol /mL³ | 100 |
| silicon/ g | 1.0 |
| Silica support copper oxide catalyst | Tiny amounts |
| Product /g | 1.41g |

2.3.2 Preparation of tetraethoxysilane (TEOS) using alumina supported copper oxide catalyst prepared from copper nitrate trihydrate salt:

Using similar reaction system and procedure, 100 ml of absolute ethanol was added to 1.0 g silicon powder in 3 – neck round bottomed flask and followed by the addition of tiny amount of alumina supported copper oxide catalyst. Then the reaction mixture was refluxed about 36 hrs. with effective stirring using stirrer and the reading of thermometer was adjusted at 78 °C. At the end of the experiment, the reaction mixture was filtered to separate unreacted silicon and the catalyst. A colorless liquid was observed in the reaction container. Then this liquid solution was fractionated to separated product at its boiling temperature. The obtained product was characterized by IR; GLC. This experiment was summarized in Table (2).

Table (2): Summary of the direct reaction between silicon and absolute ethanol using alumina supported copper oxide catalyst.

| | |
|--|---------------------|
| Time /hours | 36 |
| Ethanol /ml | 100 |
| Silicon/ g | 1.0 |
| Alumina support copper oxide catalyst | Tiny amounts |
| Product /g | 1.13g |

Direct synthesis of metal alkoxide catalysts as well as novel catalysts such as silica or alumina supported copper oxide catalysts prepared by impregnation method. In comparison with halosilane route, the direct synthesis of tetraethoxysilane from silicon and ethanol permits the isolation of a relatively high purity product.

2.2.3 Preparation of silica and alumina supported copper oxide catalysts by impregnation method[12-13]:

10% w/w silica and alumina supported copper oxide catalysts were prepared by impregnation method using copper nitrate trihydrate as precursor of catalyst.

3.Results and Discussion

3.1 X- Ray Powder Diffractometer: Silica & alumina supported copper oxide catalysts:

The X-ray diffraction data for silica and alumina supported copper oxide catalysts are listed in figures from the diffraction pattern, the values of 2θ were converted into d-values using Braggs equation:

$$n \lambda = 2d \sin\theta$$

Where, n is integer (order of diffraction). λ is the wave length of radiation . d is the distance between the plane . θ is diffraction angle . The diffractograms of CuNS and CuNA catalysts are displayed in figures (1) & (2) it is quite clear that tiny patterns occur at $2\theta = 16,32$ and $2\theta = 16,32,36$ good peaks of CuO and Cu₂O could be detected, especially those at American Standard for Testing Material (ASTM) card (5 – 661) and (5 – 667), respectively. Good peaks were characteristic for copper species at $2\theta = 16, 36, 39$, these were obtained at ASTM card (5 – 661) /8]Y 67; patterns indicate the presence of crystalline CuO.

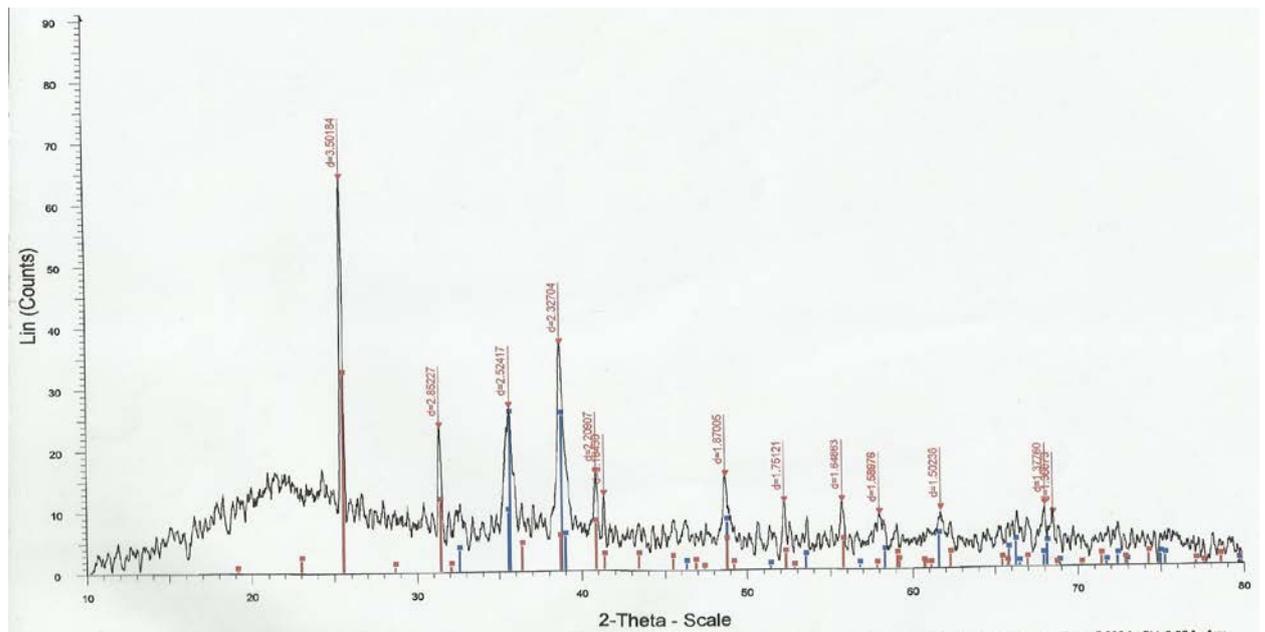


Fig (1) X-ray powder diffraction of Copper nitrate trihydrate Impregnated silica at10% loading level and 500 °C Calcined temperature

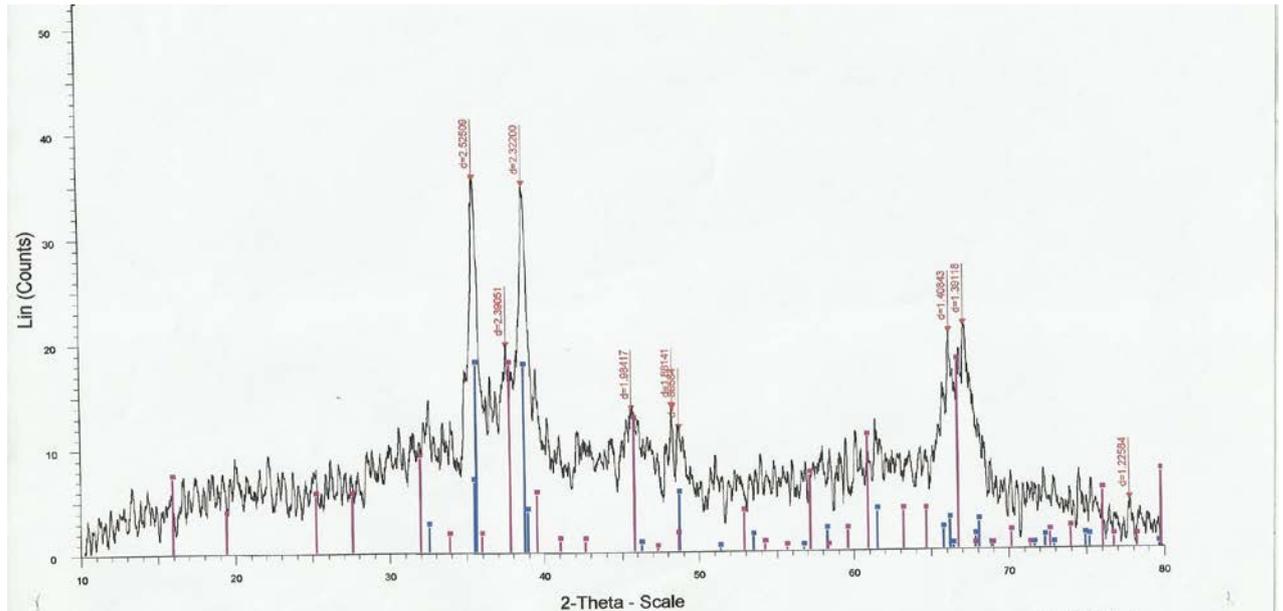


Fig (2) X-ray powder diffraction of Copper nitrate trihydrate Impregnated alumina at 10% loading level and 500 °C Calcined temperature

3.2. Infrared spectra:

Figures (3) & (4) show the FTIR spectra for CuNS, CuNA samples. FTIR measurements were done using KBr method at RT. The observed spectra located at 1157 cm^{-1} , 1120 cm^{-1} , 985 cm^{-1} , 814 cm^{-1} , 467 cm^{-1} for silica supported. However, small band observed in the 500 °C spectrum at 3520 cm^{-1} has no association with the OH lengthening. This can be elucidated by Lopez et al. ⁽¹⁴⁾, who reported that 3484 cm^{-1} an asymmetric and rather intense band appear, to be assigned to an OH lengthening in the hydroxide groups for the sample. This is supported by the fact that this band observed sharply diminishes intensity. In fact the small band observed in the 600 °C spectrum at 3600 cm^{-1} has no association with OH lengthening at all. It is a typical signal for terminal silanol groups. They appear during calcination and may cause shifts in the micro – crystallinity of the materials during calcination. They may also be related to the signals at 985 cm^{-1} , which in turn modifies its intensity during dehydroxylation. Furthermore a band is generated at 467 cm^{-1} due to the formation of oxygen bridges in the silica surface. Other observation was that the peaks located at 675 cm^{-1} , 615 cm^{-1} , 694 cm^{-1} due to the formation of copper oxide in silica supported catalyst system.

Fig. (1):

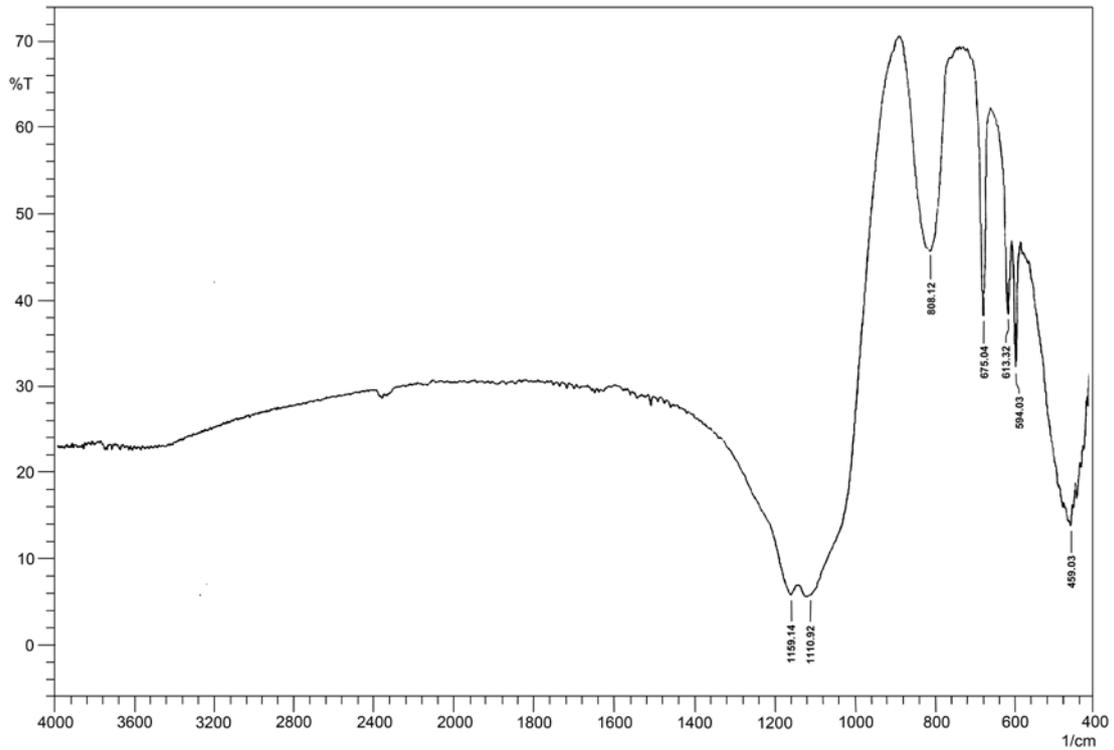


Fig. (3): infrared spectrum of copper nitrate trihydrate impregnated silica at 10% loading level and 500 °C calcined temperature

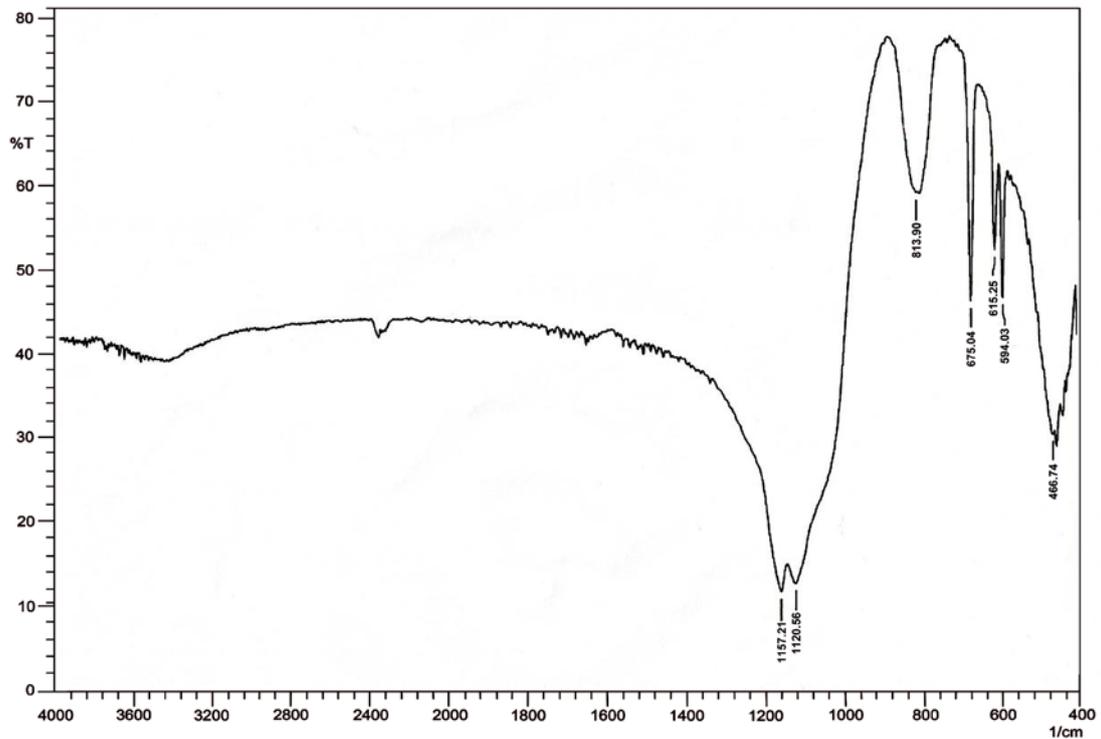


Fig. (4): infrared spectrum of copper trihydrate impregnated alumina at 10% loading level and 500 °C calcined temperature

3.3 Characterization of Catalyst's surface morphology by scanning electron microscopy:

The morphologies of CuNS and CuNA catalysts surfaces before and after use in the reaction of elemental silicon and absolute ethanol were examined using SEM. SEM pictures for these catalysts were shown in Figures (5,6,7,8). These pictures have showed that the surface morphology of the catalysts were change before and after their using in the above mentioned reaction. The change in the surfaces of these catalysts which were observed in SEM photographs indicated that the novel catalysts worked well in the direct synthesis of tetraethoxysilane.



Fig. (5): SEM picture of CuNS catalyst before

Fig.(6): SEM picture of CuNS catalyst after

use in direct synthesis of tetraethoxysilane.

use in direct synthesis of tetraethoxysilane



Fig (.7): SEM picture of CuNA before use in direct synthesis of tetraethoxysilane

Fig. (8): SEM picture of CuNA catalyst after

use in direct synthesis of tetraethoxysilane

3.4. Surface area determinations:

The specific surface area was measured for CuNS, CuNA samples using single point S_{BET} method (figures {9), (10)}. It was found that the specific surface area values were $137 \text{ m}^2/\text{g}$, & $82 \text{ m}^2/\text{g}$ for CuNS, CuNA samples respectively. The low surface area ($137 \text{ m}^2/\text{g}$) for CuNS sample is due to the coating of the surface of silica by CuO. Alumina supported copper oxide catalyst (CuNA) sample has the lower surface area value ($82 \text{ m}^2/\text{g}$) compared with the sample of silica supported copper oxide catalyst. This is due to the partially formation of copper aluminate CuAl_2O_4 by Strong Metal Support Interaction (SMSI).

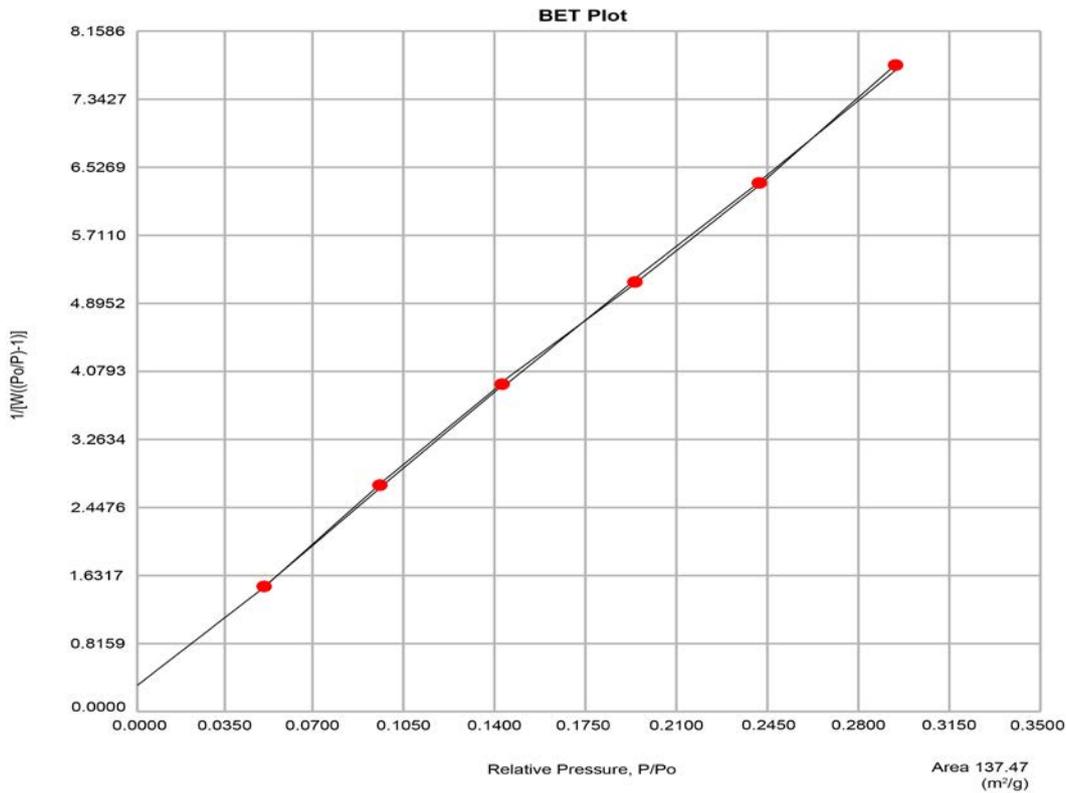


Fig.(9): S_{BET} (m^2/g) for CuNS catalyst calculated from Nitrogen adsorption at $-196 \text{ }^\circ\text{C}$

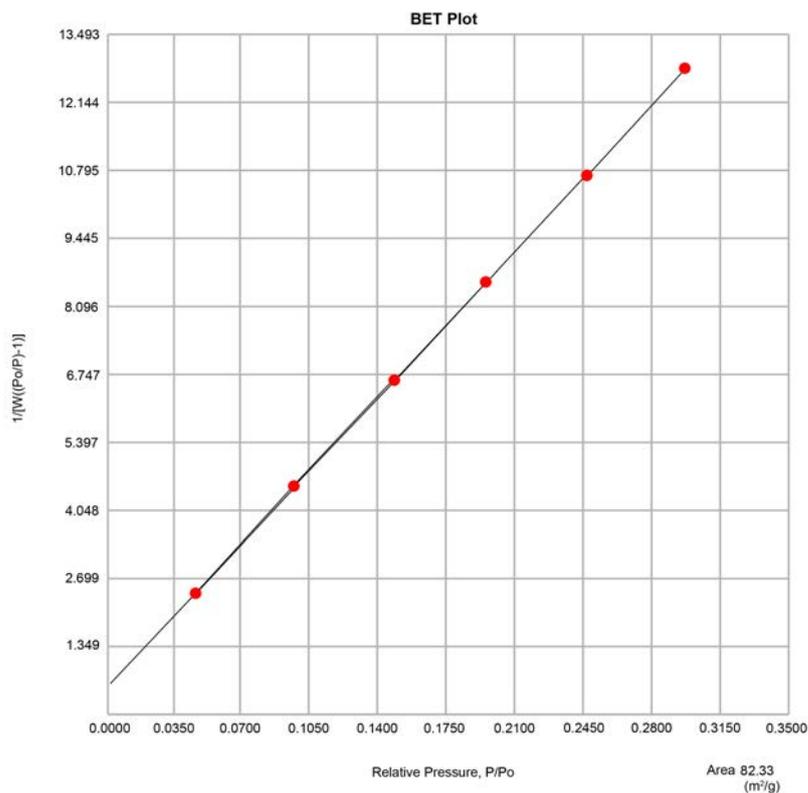


Fig.(10): S_{BET} (m²/g) for CuNA catalyst calculated from Nitrogen adsorption at – 196 °C

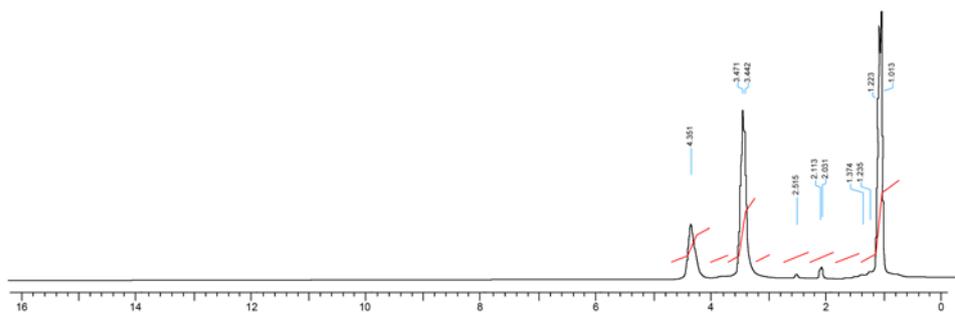


Fig.(11): ¹H NMR spectra of the product obtained from the reaction between absolute ethanol and silicon using silica supported copper catalyst

Fig (11): shows a high field methyl triplet (CH₃ – CH₂) proton at $\delta = 1.06$ ppm and low field methylene quartet signal, (CH₃ – CH₂) proton at $\delta = 3.45$ ppm for the material examined. The chemical shift are in good agreement with the reference values[7], indicating the presence of the tetraethoxysilane.

3.5 Gas – Liquid Chromatography:

The GLC results of final reaction mixture, where the a silica or alumina supported catalysts, have generally indicated the presence of ethanol, tetraethoxysilane (figure 12).

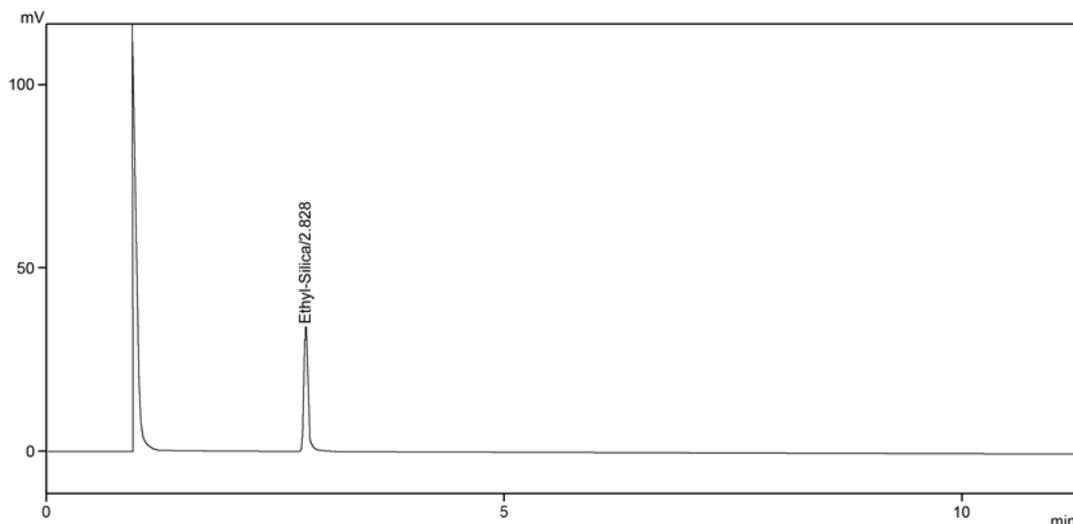


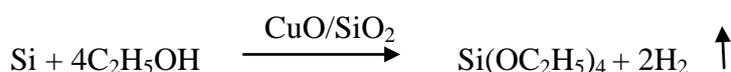
Fig.(12): GLC Analysis of the product obtained from reaction between absolute ethanol and silicon metal using catalyst.

Table : (8.31) GLC Analysis of the product obtained from reaction between C₂H₅OH and silicon metal using sodium ethoxide catalyst.

| Peak number | Assignment |
|-------------|-------------------|
| 1 | Ethanol |
| 2 | Tetraethoxysilane |

4.Conclusions

The reaction between silicon and absolute ethanol does not take place without using any catalyst due to the silica present on silicon surface . Silica supported copper oxide (CuNS) 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 as indicated by FTIR, ¹H NMR & GLC analysis. The mechanism of this reaction shows that the catalyst breaks down the silica layer to give tetraethoxysilane.

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