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A Novel Method for Synthesis of Ethylsilicates and its Applications

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A new method of preparing tetraethoxysilane from silicon and ethanol is established. An alumina-supported copper oxide catalyst was used successfully to enhance the facile reaction of silicon with ethanol to produce tetraethoxysilane and hydrogen, avoiding any halosilane intermediate. Thus, a new effective catalyst is confirmed. The final reaction mixture, tetraethoxysilane is hydrolyzed in presence of a suitable base, acid, or both, to produce a mixture suitable for coating and binding refractory materials. Surface coatings based on ethyl silicate binders are categorized as inorganic coatings.

Keywords: Tetraethoxysilane, Ethylsilicate, Binding material, Coatings, Catalysts.

INTRODUCTION

Ethyl silicate, which is the common name for tetraethoxysilane (TEOS), hexaethoxydisiloxane and lower silicon oligomers, has found worldwide acceptance in applications when a liquid precursor of silica (SiO_2) is needed. Ethyl silicate produces very fine particles of silica, which can act as a binder to adhere refractories into ceramic shapes or provide corrosion-resistant coatings in combination with zinc dust. When vapourized and thermally decomposed upon the surfaces of semiconductor chips, ethyl silicate forms electrically insulating layers of silica glass which are necessary in the fabrication of integrated circuits. The chemical applications of ethyl silicate, including cross-linking of silicones, are numerous and new applications for this versatile chemical are constantly being developed.

Alkyl silicates, especially ethyl silicate in either the monomer or the polymer form, have found widespread applications as liquid precursors of silicon-based materials [1-4]. They can be hydrolyzed and condensed to produce silica colloids to act as binding agents in the manufacture of ceramic materials that are resistant to highly corrosive environments and have mechanical strength, heat resistance and high dielectric properties [5,6].

Ethyl silicate is the semi-hydrolyzed product of tetraethylorthosilane, comprising tetraethoxysilane, the monomer, hexaethoxydisiloxane, the dimer and probably light silicon oligomers. These mixtures can be hydrolyzed in acidic or basic media to give a hydrolyzate suitable for use in binding refractory materials [1].

In the current work, ethyl silicate was prepared directly from elemental silicon and absolute ethanol in the presence of a novel catalyst [3,6,7]. Part of this work has been carried out previously and is repeated here for confirmation of results [8,9]. It has been shown that the sequence is hydrolysis followed by poly condensation to produce a gel-like slurry material, which can be used in refractory materials. The previous methods used for the preparation of ethyl silicates involve the use of halo silane intermediates which ultimately release hydrogen chloride as an environmentally unacceptable by product [5], as shown in the following equation:

$$SiCl_4 + 4C_2H_5OH \longrightarrow Si\,(OC_2H_5)_4 + 4HCl\uparrow$$

If dry ethanol is used, the sole products are TEOS and hydrogen [6], as indicated in the following equation:

$$Si + 4EtOH \longrightarrow Si(EtO)_4 + H_2\uparrow$$

As alkyl silicates have no binding ability on their own, they must first be hydrolyzed and a gel formed from the resulting hydrolyzate. This gel is the actual binding agent. Alkyl silicates and water are usually immiscible, so a mutual solvent such as ethanol is required. Hydrolysis is normally performed under acidic or basic conditions, or even both will do.

EXPERIMENTAL

All chemicals used were of analytical grade and used as received without further purification. Double distilled water was used throughout the experiments.

Preparation of silica and alumina-supported copper oxide catalysts by impregnation [10,11]: Ten per cent w/w silica and alumina-supported copper oxide catalysts were prepared by the impregnation method. The precursors include copper nitrate and copper hydroxide. The mixture was heated at 500 °C under nitrogen in order to obtain a constant mass of silica and alumina-supported copper oxide catalysts. The final products were kept in a desiccator until used.

Preparation of tetraethoxysilane from silicon and ethanol: In a 250 mL round-bottomed flask, 1 mol (58.4 mL) of absolute ethanol was added to 0.25 mol (7 g) of silicon powder followed by the addition of tiny amounts of silica-supported alumina oxide catalyst. The reaction mixture was refluxed for about 40 h with effective mechanical stirring and the thermometer reading was adjusted to 90 °C. The reaction was monitored until the steady evolution of hydrogen gas ceased. The final reaction mixture was filtered off to separate unreacted silicon and the catalyst. A resulting colourless liquid solution was fractionated to separate the desired product (TEOS) at its boiling temperature. The purity of the products was established by recording the boiling point, infrared spectrum, ^{1}H NMR spectrum and by comparing the gas-liquid chromatography (GLC) retention time with that of an authentic sample. The experiment is summarized in Table-1.

TABLE-1
SUMMARY OF THE DIRECT REACTION BETWEEN SILICON AND ABSOLUTE ETHANOL USING ALUMINA-SUPPORTED COPPER OXIDE CATALYST

Time (h)	40
Ethanol (mL)	58.4
Silicon (g)	7.0
Alumina-supported copper oxide catalyst (g)	1
Product (g)	6.13

Preparation of ethylsilicate from tetraethoxysilane: Using a similar procedure [12] (Table-2). The final reaction product was isolated and used to prepare ethylsilicate. 30 mL of TEOS was poured into a beaker followed by the addition of 5 mL of double distilled water, 1 mL of 0.10 M HCl, catalyst and 5 mL of absolute ethanol as solvent. The mixture was stirred periodically for 20 h until a viscous slurry mixture was obtained. When this final reaction mixture was left to dry at room temperature, a gel was formed, which was dried and weighed [2]. The prepared sample was characterized by Fourier transform infrared (FTIR) spectroscopy, thermal analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM).The surface morphology and nanostructure of the prepared samples was evaluated using SEM.

TABLE-2
SUMMARY OF PREPARATION OF ETHYLSILICATE FROM TEOS

Reactants, product and hydrolysis time	Value
Tetraethoxysilane (TEOS)	30 mL
Hydrochloric acid (HCl)	1 mL, pH = 1
Distilled water (H_2O)	5 mL
Ethanol (C_2H_5OH)	5 mL
Hydrolysis time	20 h
Product weight	9.685 g

Preparation of gel by base catalyzed hydrolysis of TEOS: The gel was prepared by adding 30 mL of TEOS into a beaker followed by the addition of 3 mL of 0.10 M ammonium hydroxide, 5 mL of absolute ethanol and 5 mL of double distilled water. The mixture was stirred periodically for 25 h at room temperature until a finger of gel was formed. The gel was then dried and weighed [2], before being characterized by infrared (IR), XRD and thermal analysis. The surface morphology and nanostructure of the prepared samples was evaluated using SEM. A summary of gel preparation by the base catalyzed hydrolysis of TEOS is shown in Table-3.

TABLE-3
SUMMARY OF GEL PREPARATION BY BASE CATALYZED HYDROLYSIS OF TEOS

Reactants, product and gelation time	Value
Tetraethoxysilane (TEOS)	30 mL
Ammonium hydroxide	3 mL, pH = 13
Distilled water	5 mL
Ethanol	5 mL
Gelation time	216 h
Product weight	4.505 g

Preparation of gel using acid and base together: Similar procedures were repeated using a 1:1 acid:base ratio. To the reaction mixture, 1 mL of HCl was added drop-wise, then 3 mL ammonium hydroxide was added. A similar gel was obtained in a shorter time than from either base or acid catalysis alone as described earlier.

RESULTS AND DISCUSSION

The direct reaction of elemental silicon with ethanol was carried out using an alumina-supported copper oxide catalyst. Results listed in Table-4 indicate that the catalyst was very effective. The feasibility of the reaction is indicated by the high yields of products (approx. 80 %; GLC results). The reaction was continuously monitored by the evolution of hydrogen gas which was taken periodically using an IR gas cell. The spectral results show the presence of hydrogen and a total absence of ethanol vapour. This procedure was repeated many times with similar lines, as indicated above.

TABLE-4
GLC ANALYSIS OF THE PRODUCT OF THE REACTION BETWEEN C_2H_5OH AND SILICON METAL USING ALUMINA-SUPPORTED CATALYST

Peak number	Assignment
1	Ethanol
2	Tetraethoxysilane

GLC analysis: The final reaction products were characterized by GLC analysis, which indicated the presence of TEOS at high yield and purity, in good agreement with the values reported in the literature [1]. The GLC results are shown in Table-4.

^{1}H NMR: ^{1}H NMR results show a triplet CH_3 at low field δ 1.3 and CH_2 at high field δ 3.4, ascribed to ethoxy groups.

Infrared spectra: IR analysis using a KBr disk indicated the presence of tetraethoxysilane with good comparison with the values reported in the literature (Table-5).

TABLE-5
INFRARED DATA OF REACTION BETWEEN C_2H_5OH AND SILICON USING ALUMINA CATALYST

Frequency (cm^{-1})	Assignment
3344 b	O–H stretch
2974 s, 2883 m	C–H asymmetric stretch
2540 w, 1925 s	C–H symmetric stretch
1655 w	O–H bend
1448 m, 1379 s, 1329 m	C–H bend
1275 w	CH_3 rocking
1090 s, 1049 s	C–O stretch
881 s	C–C stretch
804 w	SiO_4 asymmetric stretch
652 w	SiO_4 symmetric stretch

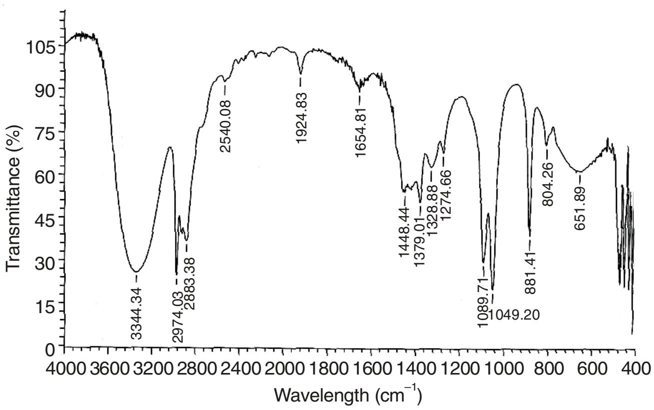


Fig. 1. Infrared spectra of C_2H_5OH and silicon reaction using alumina catalyst

SEM studies: SEM analysis provides information about the size and shape of particles and pores. The SEM photographs show that the samples consisted of small and large grains and that the surface of the silicon recovered from the reaction was badly etched away. This indicates the effectiveness of the catalyst and significantly supports the postulated catalyzed reaction of silicon and ethanol.

X-ray diffraction: The crystalline structure of the prepared gel was investigated by conventional XRD analysis. The diffraction patterns in Figs. 2 and 3 show that the gels were amorphous solids, because no crystalline phase was detected. The XRD patterns show wide peaks at 2θ angles of approximately 24°, characteristic of amorphous silica, as reported in the literature [13].

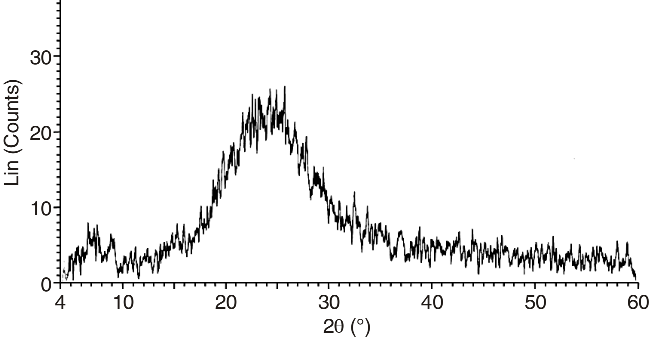


Fig. 2. X-ray diffraction pattern of the gel prepared by acid catalyzed hydrolysis of ethylsilicate

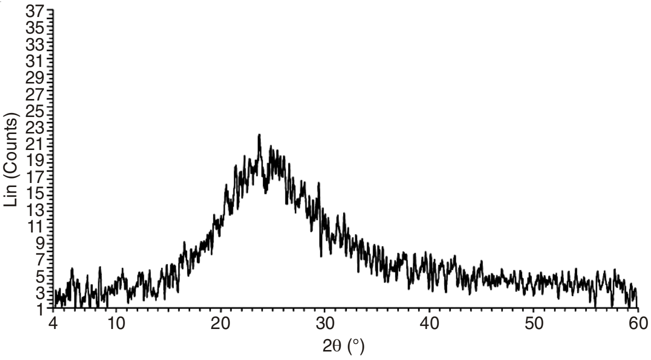


Fig. 3. X-ray diffraction pattern of the gel prepared by base catalyzed hydrolysis of ethylsilicate

XRD peaks of all samples show a typical broad halo, clearly assigned to amorphous silica, as reported in Hilonga *et al.* [15]. The broad XRD reflection peaks may be ascribed to the small size and incomplete inner structure of the particles. No well-defined peaks were observed in any samples, as indicated in literature [15]. This demonstrates that a high percentage of these particles were amorphous in of all the samples.

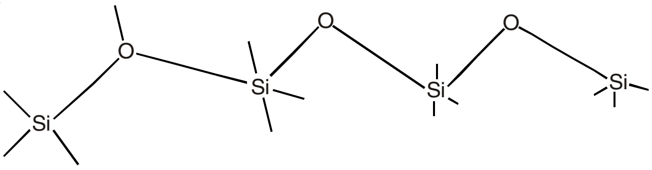
Proposed mechanism of catalysis of reaction of silicon with ethanol: All previous studies in this area have concentrated on industrial applications and the subject has been reported entirely in the patent literature. This current work has concentrated on the chemical information based on the results obtained and in line with previous work [1,16].

Studies based on SEM indicate that the facile reaction of silicon with ethanol is feasible. The mechanism of the facile reaction of elemental silicon with liquid ethanol can be proposed as follows:

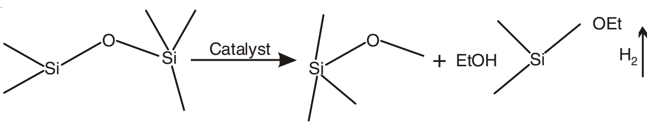
Elemental silicon is considered to be covered with an oxide layer (SiO_2) [15], which acts as a protective layer, preventing silicon from reacting with ethanol.

$$\mathrm{Si} + 4\mathrm{EtOH} \xrightarrow[\text{Solvent}]{\text{Catalyst}} \mathrm{Si(OEt)_4} + \mathrm{H_2}\uparrow$$

This silica surface can be considered to have the following structure:



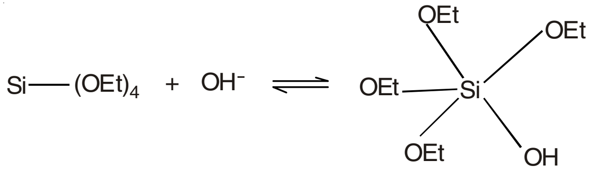
The role of the catalyst is believed to be to break through this silica layer, revealing the underlying active silicon surface and allowing it to react directly with ethanol:



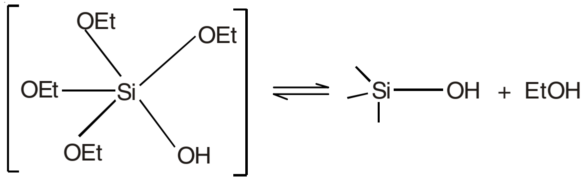
This mechanism is similar to that which prevents aluminium and magnesium from reacting with reagent like RX unless in the presence of a catalyst. In our case, the exposed silicon surface reacts with ethanol to give tetraethoxysilane and hydrogen.

Proposed mechanism of hydrolysis and condensation of ethyl silicate: In the base hydrolysis of ethyl silicate, OH^- ions attack the silicon on the vacant 3d orbitals and a penta covalent complex is formed as follows:

Step-I:



Step-II:



Step-III:

$$\equiv Si{-}OH + \equiv Si{-}OH \longrightarrow \equiv Si{-}O{-}Si\equiv + H_2O$$

In Step-III, a silanol reactive intermediate is formed, then condenses with itself to give siloxane products and water.

Conclusion

It has been found that elemental silicon is partially oxidized by atmospheric oxygen, thus covered with a film of silica (SiO_2). This oxide layer prevents silicon from reacting directly with ethanol, so a catalyst is required to break this sheath and to expose the active silicon centre or under lying silicon surface, which then reacts directly with ethanol. It has been confirmed that an alumina-supported catalyst is effective in catalysing the direct reaction of silicon and ethanol to give tetraethoxysilane and hydrogen. This is a clean method avoiding contamination of the system by any halosilane intermediate.

Ethylsilicate was prepared from the product obtained by addition of 80 % double distilled water in the presence of base or acid or both *in situ*, to produce a hydrolyzed mixture suitable for coating and binding refractory materials.

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REFERENCES

1. K.D. Biddle, A.K. Das, K. Jones and H.G. Emblem, *J. Appl. Chem. Biotechnol.*, **27**, 565 (1977).
2. V.G. Kessler and M.I. Yanovskaya, The Chemistry of Metal Alkoxides, Kluwer Academic, London (2002).
3. P.A. Shcheglov and D.V. Drobot, *Russ. Chem. Bull.*, **54**, 2247 (2005).
4. D.C. Bradley, R.C. Mehrotra, I.P. Rothwell and A. Singh, Alkoxo Derivatives of Metals, Academic Press, London (2001).
5. H. Adam, Ph.D. Thesis, University of Elfashir (2011).
6. K. Chandran, R. Nithya, K. Sankaran, A. Gopalan and V. Ganesan, *J. Bull. Mater. Sci.*, **29**, 173 (2006).
7. Y.O. Omer, Ph.D. Thesis, University of Manchester (1989).
8. E.V. Suslova, N.Y. Turova, A.S. Mityaev, A.V. Kepman and S. Gohil, *Russ. J. Inorg. Chem.*, **53**, 665 (2008).
9. E.V. Suslova, N.Y. Turova, V.G. Kessler and A.I. Belokon, *Russ. J. Inorg. Chem.*, **52**, 1682 (2007).
10. M.G. Voronkov, *J. Glass Phys. Chem.*, **35**, 231 (2009).
11. M.E. Simonsen and E.G. Søgaard, *J. Sol-Gel Sci. Technol.*, **53**, 485 (2010).
12. A.H.E. Yousif, O.Y. Alhussein, E.A.M. Elgorashi, M.S. Ali and W.I. Eldogdu, *Int. J. Innov. Sci. Eng, Technol.*, **3**, 259 (2016).
13. A. Hilonga, J.-K. Kim, P.B. Sarawade and H.T. Kim, *J. Alloys Comp.*, **487**, 744 (2009).
14. G. Parashar, D. Srivastava and P. Kumar, *Prog. Org. Coat.*, **42**, 1 (2001).
15. S. Satapathy, G.C. Mohanty and P.L. Nayak, *Adv. Appl. Sci. Res.*, **3**, 3981 (2012).