

CHAPTER I

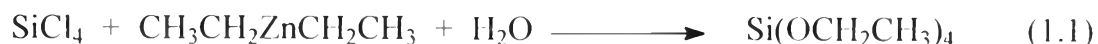
INTRODUCTION

1.1. Background

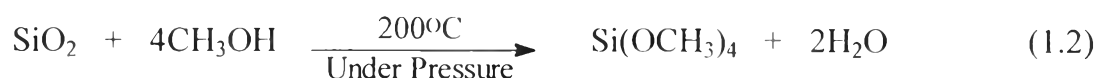
Even though silicon and carbon are in group IV, still the silicon chemistry falls far apart from the carbon chemistry. Silicon has an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^2$ similar to carbon in the form of tetrahedral compounds (Craig *et al*, 1952). However, the availability of 3d orbital of silicon brings about some striking differences from carbon in terms of forming compounds through sp^3 hybridization. Furthermore silicon forms very few coordination complexes with organic molecules.

Organosilicon compounds are nowadays of great importance in such diverse fields as organic synthesis (chemistry reagents), ceramics, polymers, and glasses. Many more simple starting inorganics and organometallics, which are missing, must be developed by chemists in order to realize the potential of inorganic and organometallic polymer chemistry. Moreover, the Si-O bond in silica is one of the strongest bond in nature [128 kcal (535kJ)/mol]. The advantage of this bond is good thermal, oxidative stability, and chemical resistance, thus curing of Si-O bonds is interesting and important. Unfortunately, the primary problem with developing any large-scale industrial process is based on silica. Raw material of silica is plentiful and extremely low cost, accounts for about 25% of the earth's crust which is an ideal starting material for new route to silicon feedstock chemistry.

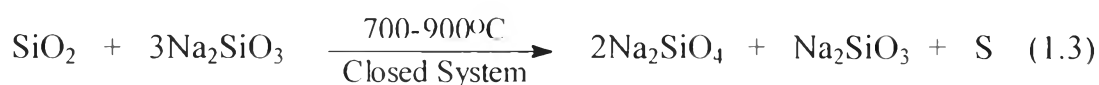
Friedel and Crafts (1863) were the first group who discovered the synthesis of tetraethylsilane from diethylzinc and silicon tetrachloride, as showed in equation (1.1).



Kitahara and Asano (1973) showed that SiO_2 could be dissolved to a higher extent in anhydrous methanol than in water, with the solubility being at a minimum at around 80% CH_3OH to 20% H_2O , as showed in equation (1.2).

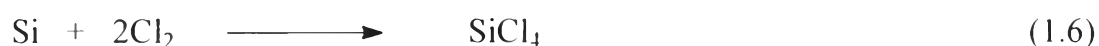


In 1966, Holmquist and Iler, 1979, showed that the dissolution of silica in strong base could provide access to a wide variety of inorganic silicates, as illustrated in equation (1.3) and (1.4), respectively.



where M is alkali metal

Stark *et al.*, 1982, and Hardman and Torklson, 1987, showed the carbothermal reduction of SiO_2 to metallurgic grade silicon, see equation (1.5), which was then converted into tetrachlorosilane (SiCl_4) by reacting with Cl_2 , as illustrated in equation (1.6).



The other way is the reaction with alkyl (most typically CH_3Cl) or aryl chlorides in the presence of Cu/Sn as catalyst at 200-350°C, as illustrated in equation (1.7).



Moreover, Si metal can react with a variety of acids, for example, HCl, to obtain related compounds, as illustrated in equation (1.8).



Tetrachlorosilane is used as feedstock in the preparation of $\text{Si}(\text{OEt})_4$. Whereas trichlorosilane is disproportionated according to reaction (1.9) to form silane, the primary source of electronic grade Si metal.



The tetrachlorosilane was also employed by Grignard reaction to form organosilanes, as illustrated in equation (1.10).



The reaction of tetrachlorosilane and a Grignard reagent is complicated and expensive. In 1949, Rochow and Muller independently discovered the "direct or Rochow process" of organic halides with silicon metal in the presence of Cu as catalyst. The most common reaction product is dimethyldichlorosilane, which is an important precursor to produce polydimethylsilanes-silicon rubbers, as illustrated in equation (1.11).



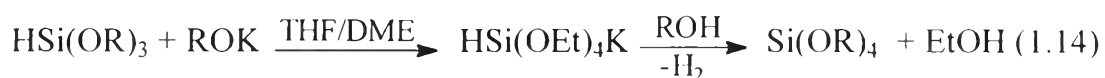
Kenney and Goodwin (1987, 1988) demonstrated the formation of tetraethoxysilane, $\text{Si}(\text{OCH}_2\text{CH}_3)_4$, from ordinary Portland cement and other mineral silicates followed by careful azeotropic distillation to remove water from the system, as illustrated in equation (1.12). Unfortunately, some rehydrolysis occurs invariably and yields are relatively poor.



Suzuki, Akiyama, and Ono (1993) synthesized tetramethoxysilane, $\text{Si}(\text{OCH}_3)_4$, from silica and dimethyl carbonate, as the source of alkoxide at $500^\circ\text{-}600^\circ\text{C}$, with high yield. However, dimethyl carbonate is very expensive, as illustrated in equation (1.13).

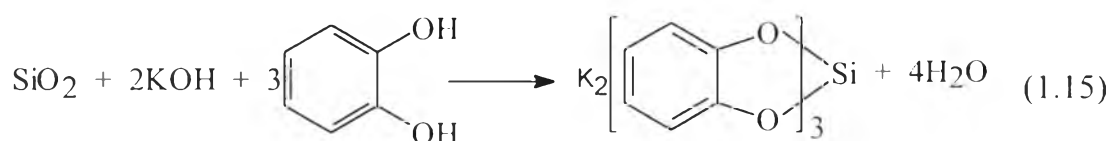


The direct reaction of alkoxy or aryloxy silanes (Becher *et al.* 1989 and Corriu *et al.* 1991) with the corresponding potassium alkoxides or aryl oxides afforded the anionic pentacoordinate hydridosilicate, which was used to react with alcohols with rapid evolution of hydrogen gas to form tetraalkoxysilane, as illustrated in equation (1.14).

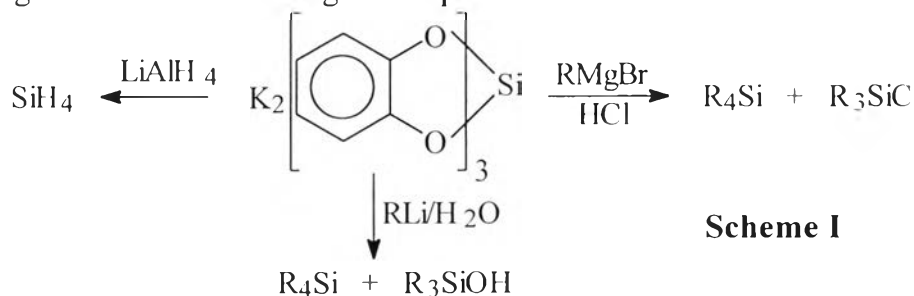


where R : Me, Et, Bu^n , Pr^i , and Ph.

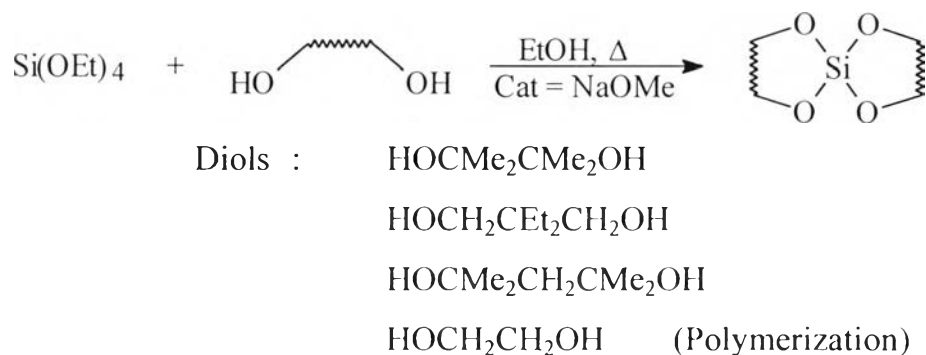
Rosenheim and coworkers (1931) were the first group to find that catechol could be used to transform a wide variety of metal oxide and silica into catecholato complexes, as illustrated in equation (1.15).



Corriu *et al.* found new synthesis routes to silicon containing compounds from tricatecholato silicates by reacting with strong nucleophiles, such as aryl or alkyl Grignard or lithium reagents, as indicated in **Scheme I**. Unfortunately, tricatecholato silicate is quite robust and reacts only under forcing condition with strong nucleophiles.



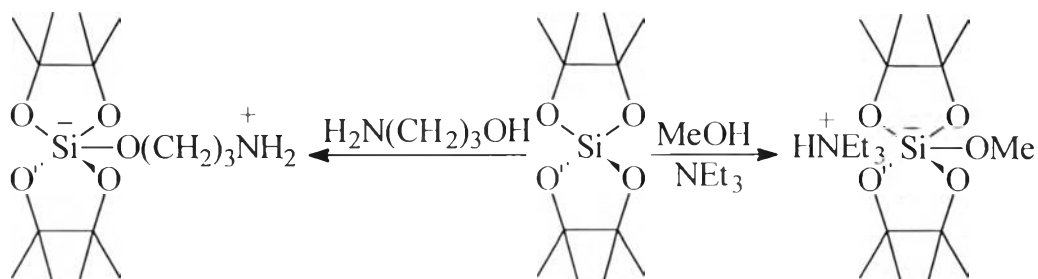
In late 60's Frye reported that the preparation of spiro-siloxane from tetraethoxysilane, $\text{Si}(\text{OEt})_4$, and 1,2-diols, was quite facile, if the reactions were run in ethanol with small amount of sodium methoxide, NaOMe , as catalyst. However, Frye found that with ethylene glycol, the product obtained was polymeric species, as showed in **Scheme II**.



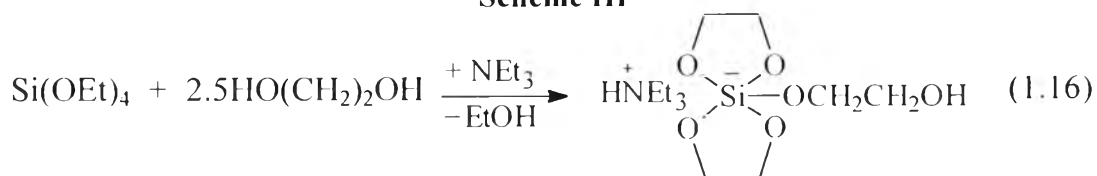
Scheme II

He also discovered that in the presence of amine bases at ambient temperature, novel pentacoordinate species would be formed, **Scheme III**. However, these species reverted to the tetra-coordinated spiro-silicate, when the temperature was higher than 100°C .

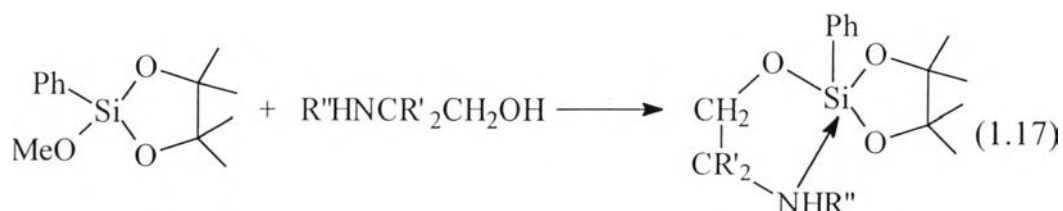
In this instance, even ethylene glycol gave a monomeric, penta-alkoxy silicate containing one monodentate and two bidentate glycol, as illustrated in equation (1.16).



Scheme III

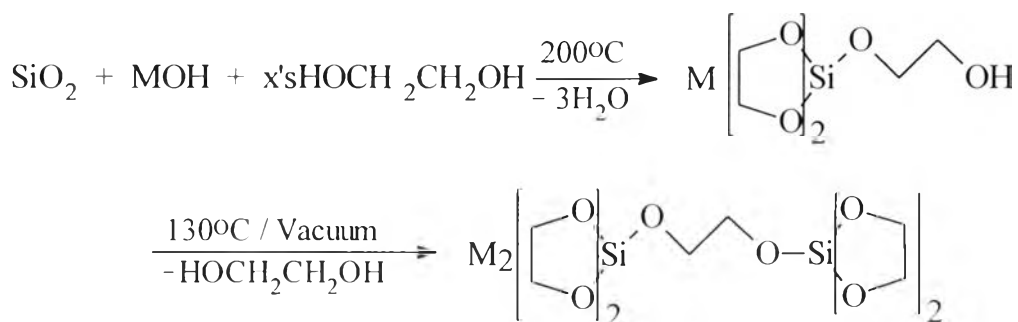


He also synthesized bispinacoloxo salts (pentacoordinated silicon derivatives) from heterocyclic pinacol derivative and alkanolamines. The result showed the partial bond between silicon and nitrogen atom, as illustrated in equation (1.17).

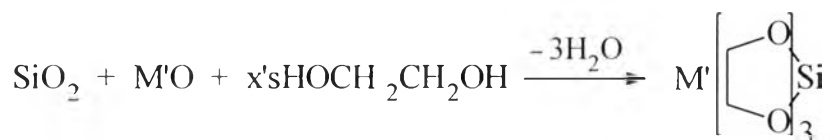


where: $\text{R}' = \text{H}$ and CH_3 , and $\text{R}'' = \text{H}$ and CH_3

Laine, *et al.* (1991) synthesized penta-coordinated spirosilicates, at 200°C directly from silica and ethylene glycol using group I metal hydroxide or group II metal hydroxide as base, followed by drying under vacuum at 130°C , 0.1mmHg (**Scheme IV**).



where $\text{M} = \text{Li}, \text{Na}, \text{K},$ and Cs

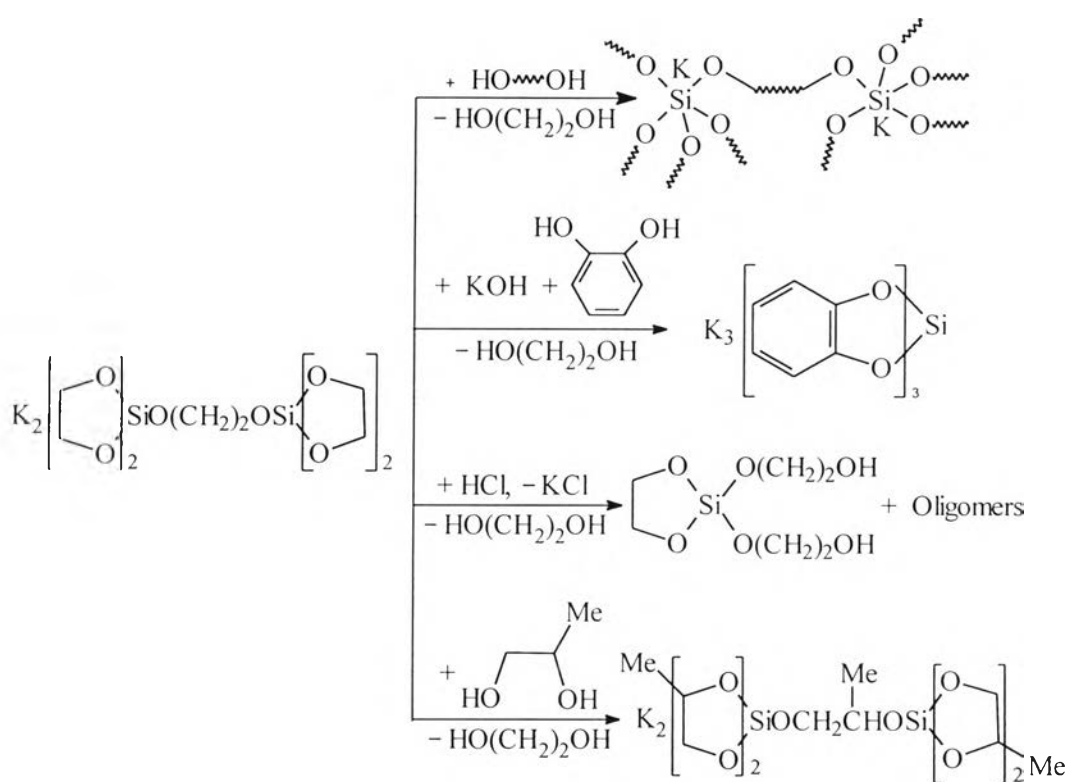


where $\text{M}' = \text{Mg}, \text{Ca},$ and Ba

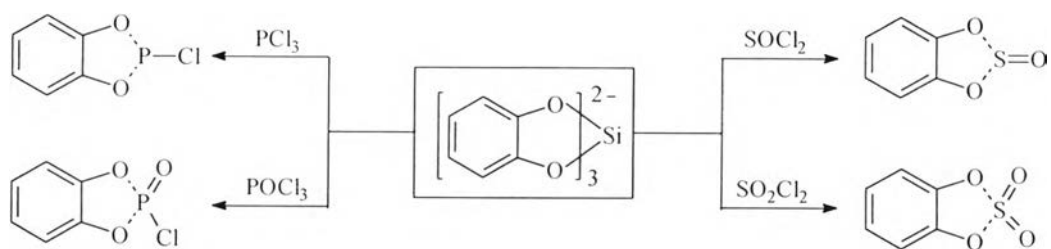
Scheme IV

The glycol groups were easily exchanged, unlike the triscatecho silicate. It permitted readily replacement of the glycol ligands with other diols. Thus, refluxing the potassium silicate in excess 1,2-propanediol, pinacol (2,3-methylbutane-2,3-diol) or catechol (within equivalent of base)

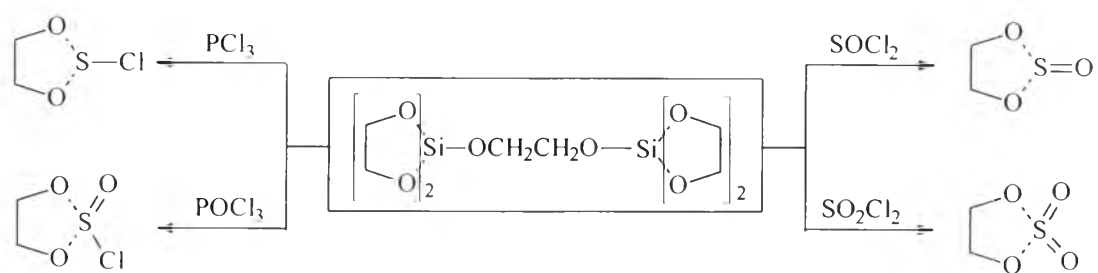
gave quantitative yields of new diol complexes. An interesting point was the fact that if 1,3 or larger "bite" diols (e.g. polyethylene glycol) were used in place of 1,2-diol, then it was possible to prepare ionic polymers containing penta-alkoxy silicate centers. In this instance, it was necessary to distill out displaced glycol in order to force the reaction forward (**Scheme V**). Unfortunately, the procedures to synthesize these materials need strong bases, which are also expensive and low environmental stability.



In 1997, Kingston and Sudheendra Rao, found that both tris (catecholato) silicate, $M_2[Si(o-C_6H_4O_2)_3]$ $\{M = Na, Et_3NH\}$, **Scheme VI** and glycolato silicate, $K_2[Si(O_2C_2H_4)_5]$, **Scheme VII** react with PCl_3 , $POCl_3$, $SOCl_2$, and SO_2Cl_2 at room temperature to give a variety of all purpose materials, such as polymers precursors and additives, surfactants, antiviral reagents, hydroxy alkylating agents, biological model compounds as well as reagents in organic synthesis.



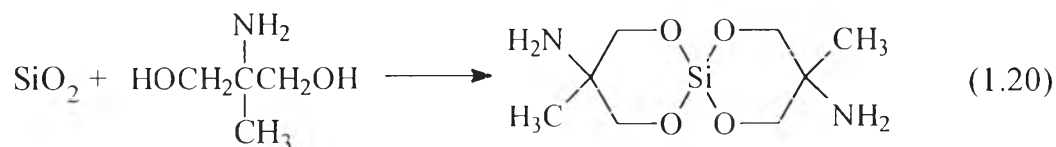
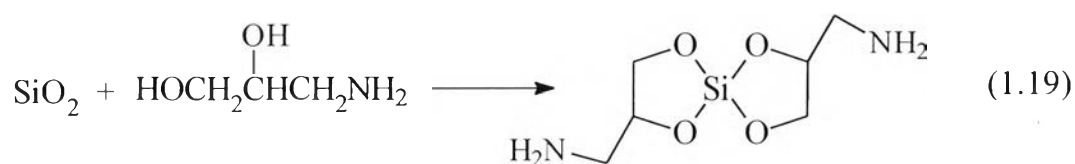
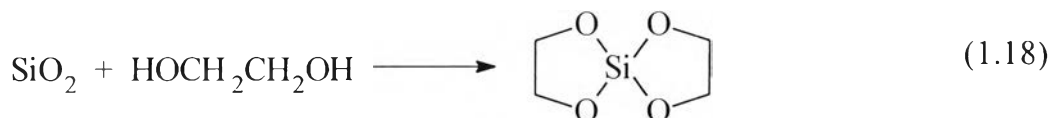
Scheme VI



Scheme VII

1.2 Research Objectives

The purposes of this research were firstly to synthesize and characterize glycolato spiro-silicate or bis(ethane-1,2-diyldioxy) silane (as showed in equation 1.18), directly from silica (SiO_2) and ethylene glycol, bis (3-aminopropane-1,2-diyldioxy)silane (as showed in equation 1.19), and bis (2-amino-2-methylpropane-1,3-diyldioxy)silane (as showed in equation 1.20) directly from silica and 3-amino-1,2-propanediol and 2-amino-2-methyl-1,3-propanediol, respectively, using triethylenetetramine (TETA) as catalyst and solvent with/without alkali base as co-catalyst.



These aminospirosilicates were then used to react with para-formaldehyde and phenol to obtain benzoxazine derivatives.