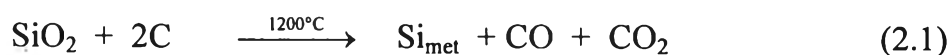# CHAPTER II
LITERATURE SURVEY

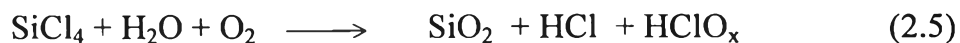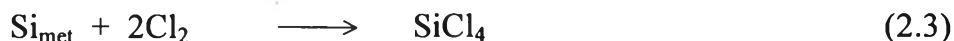The primary silicon-based feedstock chemicals may be derived from the carbothermal reduction of silica to silicon metal (Si_{met}), as illustrated in eq. (2.1), (Kirk-Othemer Encyclopedia of chemical technology, 1979).

$$SiO_2 + 2C \xrightarrow{\text{1200°C}} Si_{met} + CO + CO_2 \tag{2.1}$$

The resulting metallurgical grade silicon (90-98% purity) must then undergo further processing to make other products, for example, to provides access to organosilicon compounds via reaction of Si_{met} with alkyl or aryl chlorides in the presence of a catalyst:

$$RCl + Si_{met} \xrightarrow{\text{Cu/SnCatalyst 200-350°C}} RSiCl_3 + RSiCl_2 + ... \tag{2.2}$$

This reaction only works well when RCl is MeCl. Alternately, Si_{met} is reacted with Cl_2 (eq. 2.3) or HCl (eq. 2.4) to make $SiCl_4$ which can then be burned to make many of the industrially useful (high purity) forms of silica (eg. fumed or electronics grade silica),(eq. 2.5):

$$Si_{met} + 2Cl_2 \longrightarrow SiCl_4 \tag{2.3}$$

$$Si_{met} + HCl \longrightarrow HSiCl_3 + SiCl_4 \tag{2.4}$$

$$SiCl_4 + H_2O + O_2 \longrightarrow SiO_2 + HCl + HClO_x \tag{2.5}$$

Carbothermal reduction requires high heat and specialized equipment. The result is an energy and equipment intensive process. There are few simple, low-temperature methods of chemically modifying silica. One such
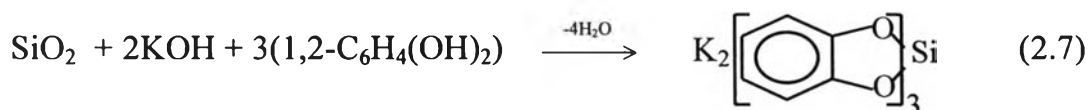
method is dissolution in strong base to give a wide variety of inorganic silicates, as illustrated in eq. (2.6), (Iler, R.K.; 1979):

$$xMOH + SiO_2 \xrightarrow[\text{-H}_2\text{O, Under pressure}]{<100°C} M_2SiO_3 + M_4SiO_4 \qquad (2.6)$$
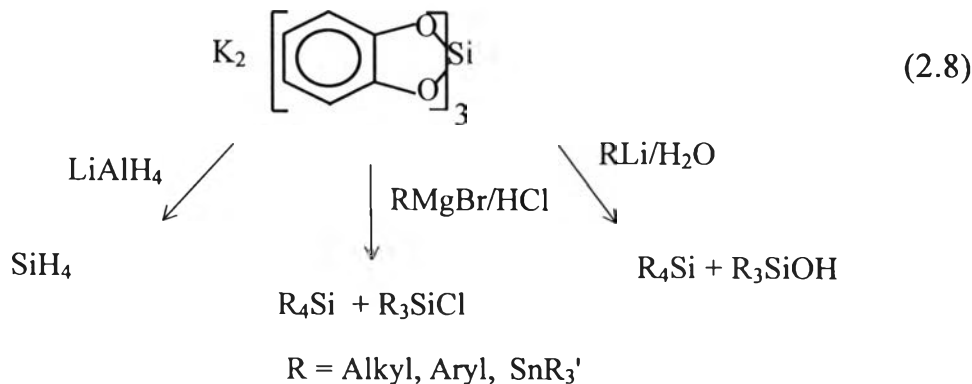
Unfortunately, this reaction has limited application for the formation of useful feedstock chemicals. If there are alternate methods for producing high molecular weight silicon-based polymers and providing commercially competitive materials, the rewards would be exceptional. Preferably, these new methods should also involve an inexpensive and readily available starting material.

The preparation of useful silicon-containing compounds has been developed which can be further reacted to produce a variety of useful soluble silicon products starting with silica and using a simple and inexpensive reaction.

Rosemheim *et al.* (Rosemheim A., 1931) reported that soluble complexes of silicon, tris(catecholato) silicate, can be prepared from silica, sand or even quartz with catechol (1,2-dihydroxobenzene) in basic media, eq. (2.7)

$$SiO_2 + 2KOH + 3(1,2\text{-}C_6H_4(OH)_2) \xrightarrow{-4H_2O} K_2\left[\begin{array}{c} \text{catecholato} \end{array}\right]_3 Si \qquad (2.7)$$
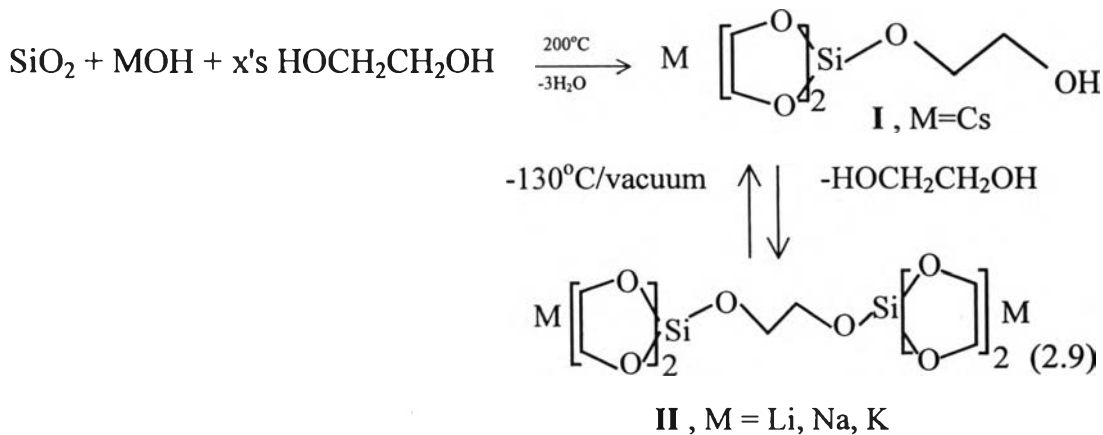
These reports showed that the reactions of silica with 1,2 aromatic diols gave hexacoordinate, monomeric silicon complex, which required lower temperature than that obtained by carbothermal reduction. Corriu and co-workers (Corriu R.J.P., 1988) were able to demonstrate that this catechol silicate complexes of reaction (2.7) can be reacted with strong nucleophiles such as aryl or alkyl grignard or lithium reagents to form three (and frequently four) new silicon-carbon bonds, eq. (2.8)

$$\text{K}_2 \left[\underset{3}{\overset{\text{Si}}{\bigcirc}} \right] \quad (2.8)$$

LiAlH$_4$ / RLi/H$_2$O

RMgBr/HCl

SiH$_4$

R$_4$Si + R$_3$SiOH

R$_4$Si + R$_3$SiCl

R = Alkyl, Aryl, SnR$_3'$

The problem of this approach is that, this catechol silicate complex is relatively expensive and so stable. It can only be modified under forcing conditions using expensive reagents, and the products are limited to tri or tetrasubstituted silicon. The large-scale utility is thus limited. Furthermore, formation of mono- and dialkyl derivatives that are primarily sought by industry for polymer synthesis, was not possible.

In principle, it would be desirable to develop more reactive complexes of silica. R. M. Laine and coworkers (Laine *et al.*, 1991) discovered a new inexpensive synthetic route to organosilicon compounds, using aliphatic 1,2 or 1,3 diols, such as ethylene glycol instead of catechol, in the presence of an alkali base. These complexes were found to contain one or more anionic pentacoordinate silicon atoms, as shown in eq. (2.9)

$$\text{SiO}_2 + \text{MOH} + \text{x's HOCH}_2\text{CH}_2\text{OH} \xrightarrow[-3\text{H}_2\text{O}]{200°\text{C}} \text{M} \left[\underset{O_2}{\overset{O}{\bigcirc}} \text{Si}^{-O} \bigvee^{O} \text{OH} \right]$$

I , M=Cs

-130°C/vacuum ↑ | -HOCH$_2$CH$_2$OH

$$\text{M} \left[\underset{O_2}{\overset{O}{\bigcirc}} \text{Si}^{-O} \bigvee^{O-} \text{Si} \overset{O}{\bigcirc} \right]_2 \text{M} \quad (2.9)$$

II , M = Li, Na, K

When M is an alkali metal such as Li, Na, or K, the product obtained was dimeric pentacoordinate anionic species (II). However, if Cs was used, the product acted as monomeric species (I). The OCH_2CH_2O groups on these pentacoordinate silicates are readily exchangable with other diol species such as tetraethylene glycol, $HO(CH_2CH_2O)_4H$ [PEG$_4$]. Refluxing these silicates in an excess of a different 1,2-diol followed by removal of excess diol and free EG by distillation results in complete ligand exchange and the formation of new dimeric materials, eq. (2.9).


$$(2.10)$$
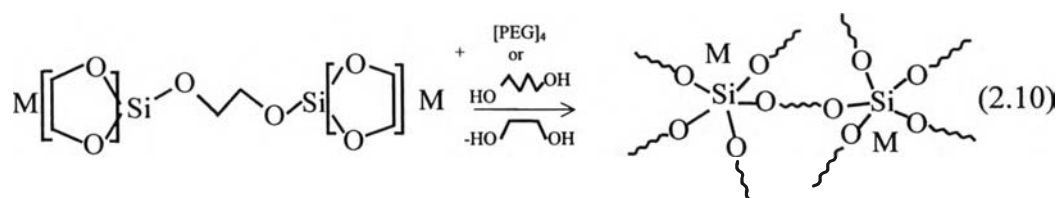
Unlike EG, the PEG$_4$ ligand is unable to function as a bidentate ligand, it rather provides crosslinks. The rheology of this polymer can be adjusted by controlling the extent to which ethylene glycol is displaced. Because of their useful rheology, they may directly be used for thin film, fibers and membranes of alkali silicate glasses and ceramics. In particular, the non-hydrolytic four-coordinate alkoxy silane complexes are of interest for further development. These silane complexes may avoid the segregation problems inherent in typical sol-gel processing of multimetallic glasses and ceramics. By the reaction (2.11), a neutral, water-soluble alkoxysilane was obtained.


$$(2.11)$$
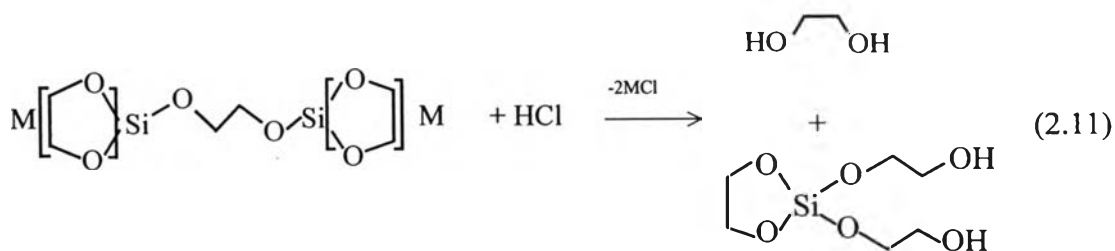
On the other hand, if the group II metal oxide (M = Mg, Ca, Ba) is used, the hexacoordinate dianionic silicate will be obtained by eq (2.12).

$$SiO_2 + M'OH + x's\ HOCH_2CH_2OH \xrightarrow[-3H_2O]{200°C} M'\left[\underset{O}{\overset{O}{\bigcirc}}\right]_3 Si \qquad (2.12)$$
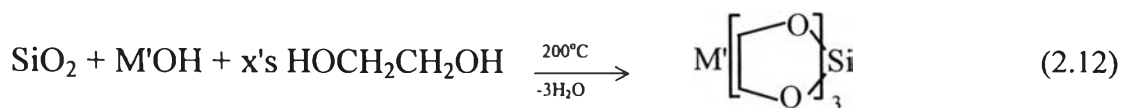
The synthesis of these penta- and hexacoordinate silicates is limited by the need of strong base which is expensive and has low environmental stability. These problems have been resolved by modifying the simple neutral alkoxy silane to reduce hydrolytic reactivity. In 1971, Frye observed that spirosilicate reacted with MeOH and amine bases (eg. Et_3N) at ambient temperatures to form pentacoordinate, anionic silicates with ammonium counterions and that these species were not stable above 100°C (bp. of Et_3N = 88.8°C, MeOH = 65°C), reverting to the tetracoordinate spirosilicate, as shown in eq.(2.13).
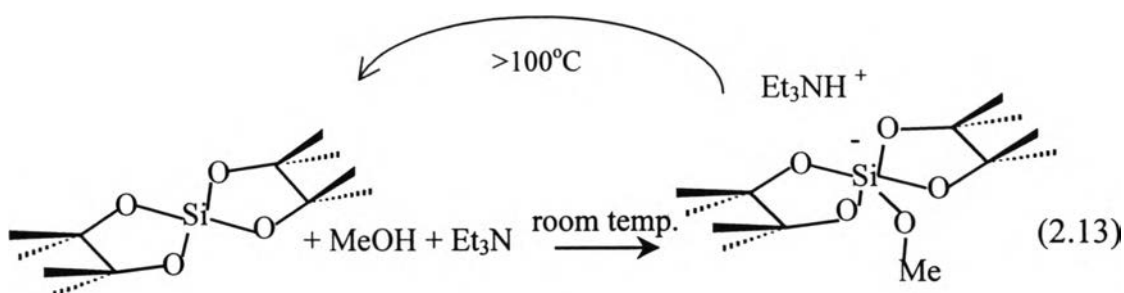

This observation prompted Laine and coworkers to explore the use of high boiling point (b.p. > 200°C) amine bases in place of group I metal hydroxides and group II metal oxide. Triethylene tetramine (b.p. 266°C TETA) and triethylamine [$N(CH_2CH_2OH)_2$, b.p. 270 (15 torr), TEA] can be used either in catalytic or stoichiometric quantities to dissolve SiO_2.

$$SiO_2 \;+\; x\text{'s EG} \quad \xrightarrow[\text{2mol\% TETA}]{200^\circ c \,/\, -H_2O} \quad$$

(2.14)

and/or
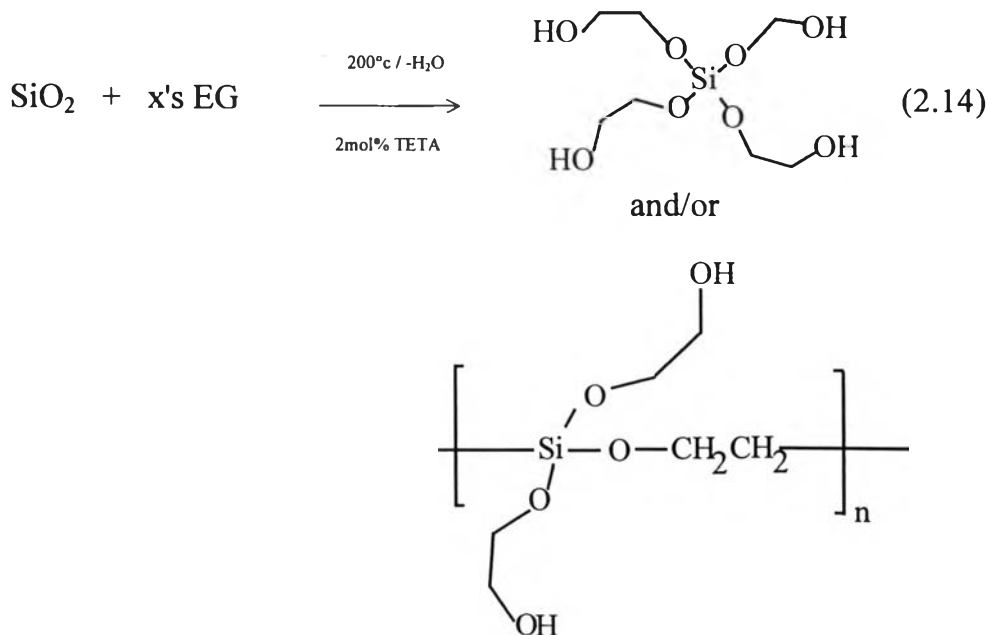
In all instances the products are tractable, neutral alkoxy compounds that provide novel routes to Si containing chemical compounds, polymers, glasses and ceramics.

From ^{29}Si NMR, they found that these products were typical of tetraalkoxy silanes, not pentacoodinate silicon and TETA did not promote the formation of stable ammonium pentacoordinate silicates, which is the reason that the neutral alkoxy silanes can be isolated directly. Similar products were also obtained when small quantities of TEA were used catalytically. However, with increasing TEA content, the products changed considerably up to the molar equivalent of TEA.

$$\text{SiO}_2 + \text{x's EG} + \text{TEA} \xrightarrow[\text{200°C}]{-\text{H}_2\text{O}}$$

(2.15)
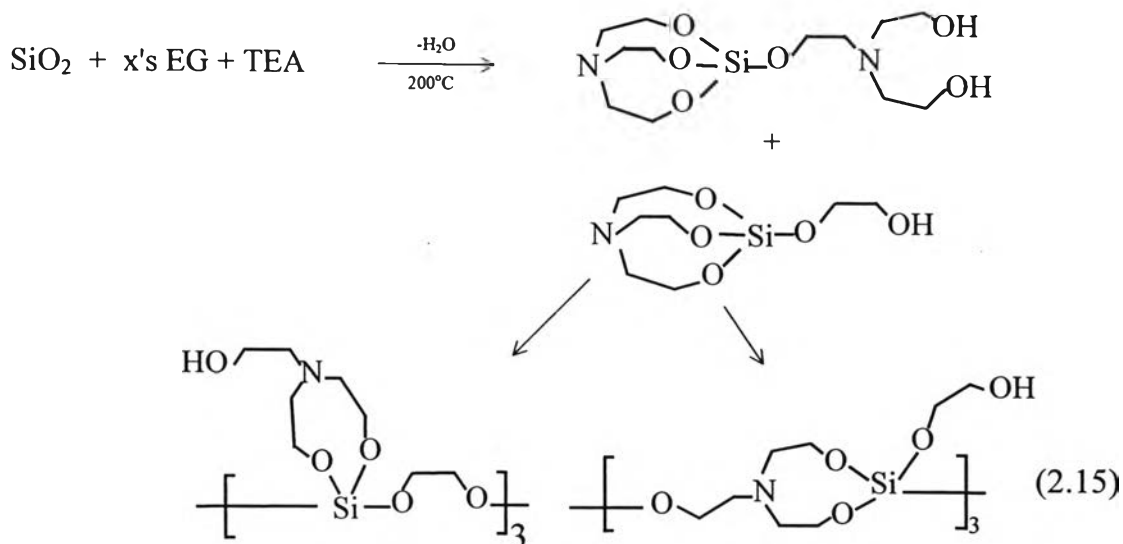
At one equivalent of TEA or less the primary product observed is the ethylene glycoloxysilatrane. After vacuum dried (220°C, 10^{-2} torr) the crosslinked polymer occurred. In 1996, Piboonchaisit, P. synthesized silatranes from SiO_2 and TIS in EG solvent with the presence and absence of TETA. She found that TETA could be used as an accelerator. When TETA was present, the reaction time was twice faster, and the products (with and w/o TETA) gave the same physical properties.

$$\text{SiO}_2 + \text{x's EG} + \text{TIS} \xrightarrow[\text{200°C}]{-\text{H}_2\text{O}}$$

(2.16)
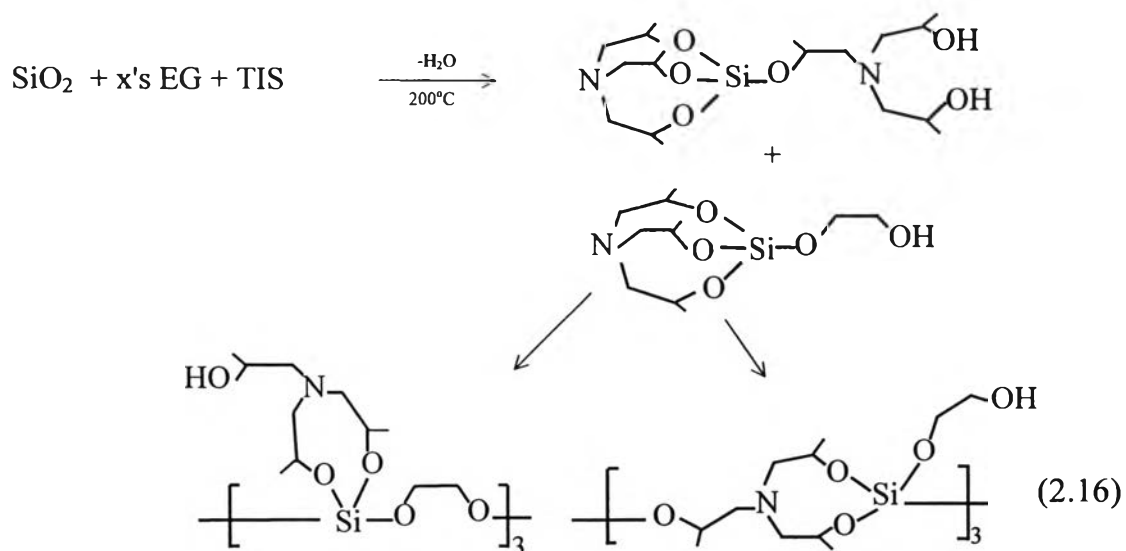
Silatranes are compounds derived from trialkanolamine and have silicon-nitrogen coordination. Generally, these are hydrolytically stable and have unique physiological properties. The first silatrane was found by Finestone in 1960, who suggested Si-N transannular dative bond in the silatrane molecule synthesized.

In 1961, Frye, Vogel, and Hal reported a number of new 1-substituted silatrane (X = H, CH_3, n-$C_{18}H_{37}$,$C_6H_5(CH_3)CH$ and etc.), as shown in *Figure 1.1*
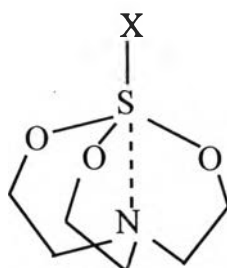
Figure 1.1   Schematic structure of silatrane complexes.

Turley and Boer (1968), using single-crystal x-ray, demonstrated that this transannular bond could exist in silatranes. Other studies on silatranes have shown that the length of this silatrane bond is depended on the substituent bond to the silicon atom. The silicon-nitrogen internuclear distance (r_{Si-N}) was ranged from 2.02 A° for the chloro derivative (X = Cl), 2.89 A° for the transdimethylphenylphosphine platinum derivative and 2.22 A° for the ethyl derivative, (Hencsei, 1985). These radii of 3.5 A° for silicon and nitrogen, yet are longer than a silicon-nitrogen covalent bond length of 1.7-1.8 A° found in tetracoordinate silicon compounds (Turley, 1968). The effect of the substituent on the structure of a silatrane is perhaps most directly seen in r $_{Si-N}$. The more electronegative substituents give a smaller r_{Si-N} than the silatranes with less electronegative substituents. Si-N dative bond results in a negatively charged silicon atom it was anticipated that retarded rates would

be observed for reactions involving nucleophilic displacement on the silatrane silicon center (Frye, 1971). They also found that the silatrane complexes can not formed large molecule by ring opening polymerization since, the bridge head nature of the silicon precludes backside attack, and flank attack is not expected to be particularly facile. Moreover, if silatrane cage is alkyl substituted (TIS) the side group (methyl group) may tend to prevent the attack of an approaching nucleophile. Also, it is well known that alkyl decoration often retards ring-opening reaction. And the other reason is transannular dative bond, 3d orbital of Si are already partially occupied and hence less available to an incoming nucleophile.

Although, the synthesis of silatrane complexes has been developed, but their physical properties have not been studied yet. The molecular weight of silatrane complexes can be determined by GPC. From the small molecules of organosilicon compound, high molecular weight and gel can be obtained by the sol-gel process. The sol-gel transition of polysilatrane can be studied by the change in viscoelastic behavior of the hydrolyzed and condensed silatrane complexes. The viscoelastic functions [$G'(\omega)$, $G''(\omega)$, tan δ and $\eta^*(\omega)$] are observed at this point. As will be described later.

Jamieson *et al.*(1993) studied the viscoelastic properties through the sol-gel transition of gelatin in the concentration range 4-14% w/v as a function of pH and ionic strength. They observed that the formation of the critical gel cluster occurs via a percolation mechanism which was not affected by variation in the solvent conditions (pH, ionic strength, temperature).
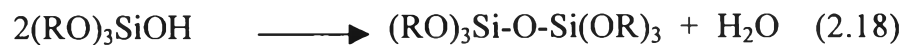
H. H. Winter *et al.* (1994) observed the molecular weight dependence of the critical exponents for the rheology near the gel point. The molecular weight of the precursor materials from which the gels have been made has a large effect on the rheology in general and on the critical exponents in particular.

The feasibility of producing silica glass by the sol-gel process was first proposed in the mid-1800s. The commercial potential of this process was not realized, however, until the 1950s and 1960s [Roy, D. M. and Roy, R. (1954)], when it was demonstrated that the sol-gel technique offered the possibility of producing glasses and ceramic compositions that could not be produced by traditional melting and powder processes.

The chemical steps involved in the sol-gel process are the simultaneous hydrolysis and condensation oligomerization of a metal alkoxide in solution (sol) and the subsequent formation of three-dimensional network to produce a 'gel' before being dehydrated to a glass or ceramic [C. J. Brinker, 1990].

$$Si(OR)_4 + H_2O \longrightarrow (RO)_3SiOH + ROH \quad (2.17)$$

In most cases, condensation polymerization of the silanol groups begins to occur after partial hydrolysis. The condensation reactions may be represented by the following reactions;

$$2(RO)_3SiOH \longrightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O \quad (2.18)$$

$$(RO)_3SiOH + ROSi(RO)_3 \longrightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3 + ROH \quad (2.19)$$

Oligomer hydrolysis and condensation then continue occurring to form polymer;

$$n(RO)_3Si\text{-}O\text{-}Si(OR)_2OH \longrightarrow [(RO)_3Si\text{-}O\text{-}Si(OR)_3]_nOH \quad (2.20)$$

As a result, the chains become more and more branched, and finally a highly swollen gel is formed;

$$
\text{Partial x-linked} \longrightarrow \text{(2.21)} \quad \text{SiO}_2 \text{ network}
$$
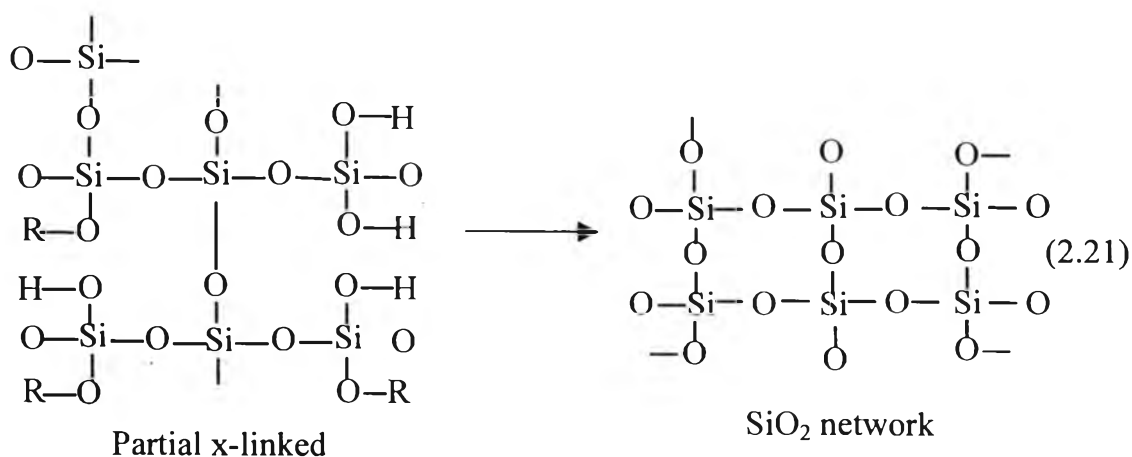
The pH of the solution used for the hydrolysis and condensation reactions affected the hydrolysis and influenced the microstructure of the particles [Arun K. Varshneya, 1993]. At low pH and a low water/ alkoxide ratio, the gel particles are generally about 2-5 nm in size and mostly chain-like linear polymers with few branch-points between cross-links at the gel point. On the other hand, the particles grow to 5-10 nm and are more branching, and hence, more spherical at high pH and large water/alkoxide ratio before gelation, as shown in *Figure 2.1*.

a) b)

Figure 2.1 Schematic representation of microstructures upon gel desiccation: a) acid-catalyzed b) base-catalyzed.

Generally, the organic component can be pyrolyzed at temperatures below the T_g of the inorganic phase so that the (inorganic) gel network will not collapse during the volatilization stage, producing a highly porous material. Saegusa and Chujo (1992) used various organic macromolecular compounds with repeating units containing N-alkyl and N-N'-dialkyl substituted carboxyl amide to produce transparent hybrid gels based on tetralkoxysilanes, aluminium trialkoxides and their mixtures. When heated at temperature between 600°C and 800°C the organic component was volatilized, leaving behind a porous structure with surface area varying between 200 and 800 m^2/g depending on pores of the calcined gel which was found to be the same as the radius of the dendrimer.

Processing conditions for bulk pyrolyses greatly affect powder properties. In particular, the higher surface area was obtained when a sample was placed in a furnace preheated to 500°C (525 m^2/g), than when the sample was ramped at 10°C/min to 500°C (250 m^2/g) [Clint R. Bickmore and Richard M. Laine, 1994]. The advantage of preheating over ramping is that sufficient thermal energy is available to induce both polymerization and decomposition reactions in the material while sufficient ethylene glycol vapor is present to swell the polymer.