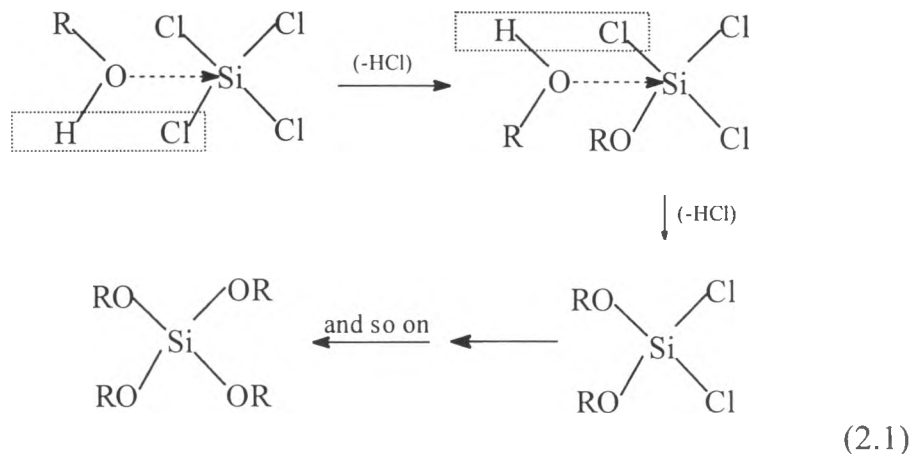


CHAPTER II

LITERATURE SURVEY

The sol-gel technique appears to be the most elegant method for overcoming the disadvantages of the powder metallurgical manufacturing processes. This well-known technique functions from both colloidal solutions and metal-organic combinations. In the case of metal alkoxides, they can be reacted with water to produce a finely distributed sol. This technique was developed mainly for the production of ceramics based on silicon dioxide (Ropp, 1992).

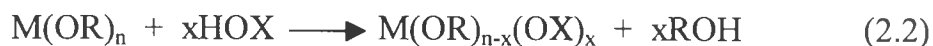
Mchrotra (1989) showed that the first report synthesis of an metal alkoxide was by Ebelman who in 1847 prepared tetraethylorthosilicate (TEOS) by the following reaction (Bradley, 1978):



Soon after the synthesis of TEOS, it was noticed that, on exposure to atmospheric moisture, TEOS was hydrolyzed in a few days to give a transparent glassy gel-like material, from which fibres could be drawn.

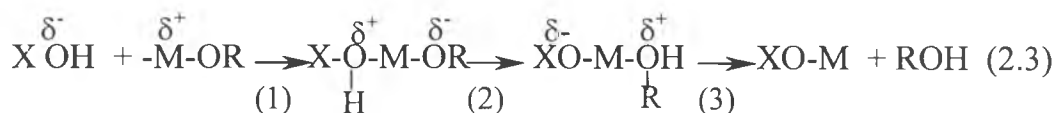
In order to understand the above result, Livage (1989), considered that metal alkoxides are generally very reactive species which may be due to the presence of electronegative alkoxy groups making the metal atoms highly

prone to nucleophilic attack. Their reaction with XOH molecules containing reactive hydroxy groups can be written as follows;



Depending on the chemical nature of X, such a reaction corresponds to hydrolysis (X = H), condensation (X = M). An associative nucleophilic substitution could be described following a 3 step process:

1. Nucleophilic addition of the XOH group onto the positively charged metal atom.
2. Proton transfer, within the transition state $M(OR)_n(XOH)$ from the entering molecule to the leaving alkoxy group.
3. Departure of the positively charged protonated species.



The whole process depends on charge distribution in the alkoxide and the transition state $(HOX)-M-(OR)_n$. Basically, the metal atom M and the leaving group ROH have to be positively charged.

In the study of the reactivity of tetramethylorthosilicate (TMOS) towards gelation, Lippert et al. (1988) were able to assign eight of the Raman bands observed during the gelation of TMOS. Figure 2.1 shows the Raman spectrum with a band at 646 cm^{-1} due to TMOS at early times together with bands at 673 , 696 and 726 cm^{-1} (due to hydrolysis products). A strong broad band due to dimer also appears at early times at 609 cm^{-1} . The bands on the high frequency side of TMOS disappear rapidly and the band at 609 cm^{-1} becomes dominant but with a shoulder at 589 cm^{-1} . At later times these bands give way with sequential growth and conversion of multimetric bands at 525 , 484 and 432 cm^{-1}

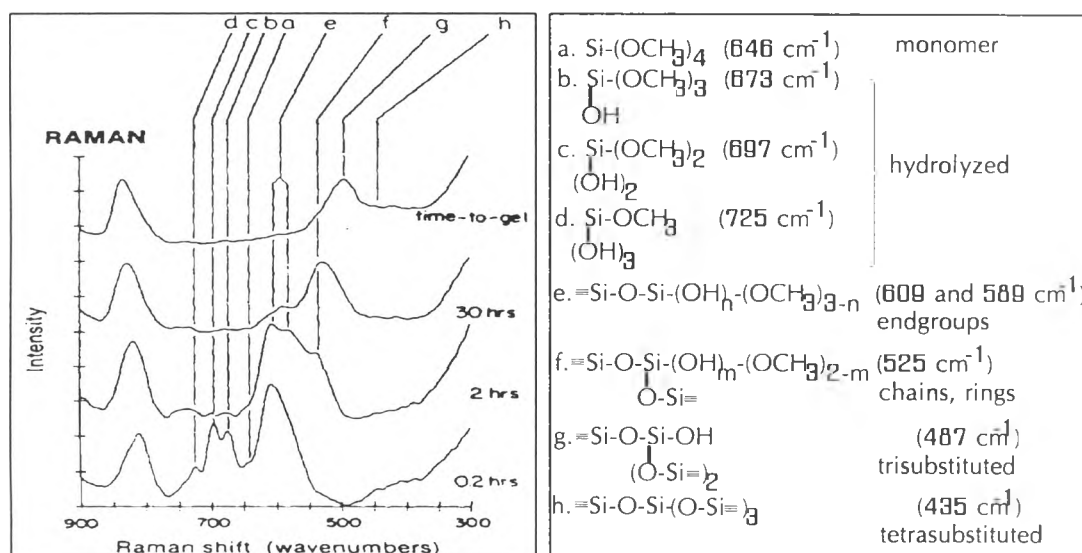
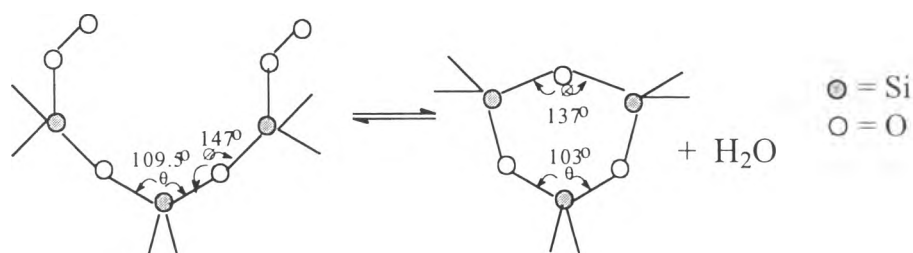


Figure 2.1 Raman spectra obtained at various times during the sol-gel reaction in a solution containing 1:1:0.24(vol) TMOS, MeOH, and 3×10^{-3} M aqueous HCl. From Lippert et al. (1988).

In the same year Brinker et al. (1988) observed that the formation of a cyclic trisiloxane are absent in the as-dried gel. These species form at intermediate temperatures predominantly on the silica surface by the condensation of isolated vicinal silanol groups located on unstrained precursors via the following reaction:



(2.4)

The heat of formation of 3-membered rings according to reaction 2.4 is calculated to be quite endothermic ($\Delta H_f = 23 \text{ kcal/mole}$) due to the strain energy required to reduce the bond formation (\angle) to 136.7° from its

Another important parameter that affects a sol-gel product is the type of precursor. It was found that the size of the alkoxy ligands changes the rates of both hydrolysis and condensation due to steric and inductive effects (David, 1995).

Charles (1994) suggested that by having formed gel, conversion to an inorganic oxide structure is accomplished by heat treatment. The behavior of a gel on heating can be considered in three parts:

1. Drying and pyrolysis of organics
2. Structural rearrangement and densification
- and 3. Crystallization.

Differences in the drying behavior and in the physical properties of gels can be explained in terms of the different structural rearrangements that occur on removal of the solvent. Two extremes of gel structure: linear polymeric chains formed under (say) acidic conditions, and a highly cross-linked colloidal gel formed (for example) in a basic environment are considered. Owing to the low levels of cross-linking in acidic low-water gels, considerable structural rearrangement can occur, resulting in high density, low pore volume gels. With greater water addition, or under basic conditions, structural rearrangements still occur, but due to the already highly cross-linked nature of the gel, less densification is possible, and a larger pore volume results.

Brinker (1988) investigated the formation of gels towards dense glasses and ceramics by thermal treatments, causing a second stage of shrinkage. Owing to the very high surface areas and very small pore dimensions, gels may be completely densified at such low temperatures, as shown in figure 2.3.

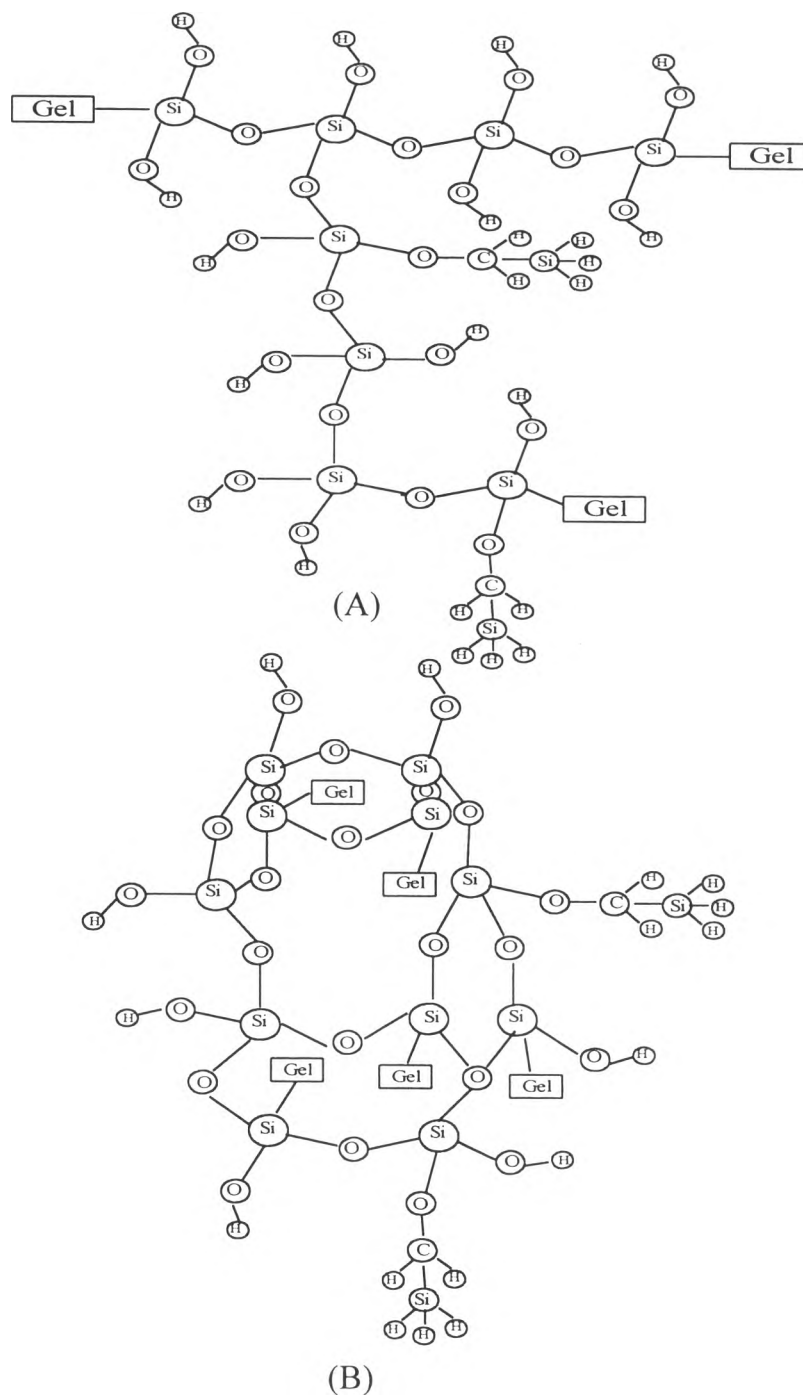


Figure 2.2 Schematics of silica gel network from the hydrolysis and condensation of TEOS; (A) acid and (B) base-catalyzed gel. From David et al. (1995).

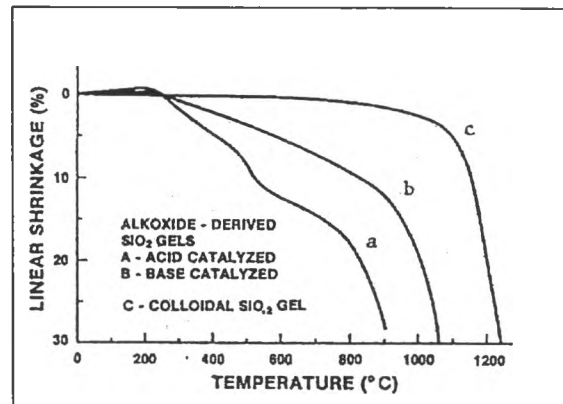


Figure 2.3 Linear shrinkage versus temperature at 1°C/min heating rate for silica gels prepared by three different methods: a) acid hydrolysis, b) base hydrolysis, c) colloidal process. From Brinker et al. (1990).

As a consequence, much effort is devoted to the understanding of the sol-gel transition using a variety of experimental techniques.

Charoenpinijkarn (1999) studied the sol-gel processing of polysilatrane. It was observed that high pH solution accelerates the hydrolysis rate, resulting in fast gelling time. Additionally, after gelation has occurred the reaction continues since the cross-linking is not yet completed in this step, leaving some organic ligand. The pure SiO₂ network is obtained by pyrolyzing the gel to 800°C to remove all organic ligands.

Sun (2000) successfully synthesized spirosilicates from SiO₂ and ethylene glycol, EG, and ethylene glycol derivatives in the presence of triethylene-tetramine, TETA, as a base or catalyst, with/without potassium hydroxide, KOH, as a co-catalyst, as shown in figure 2.4, where R represents as

- i). -CH₂CH₂-
- ii). -CH₂(CH₃)C(NH₂)CH₂-

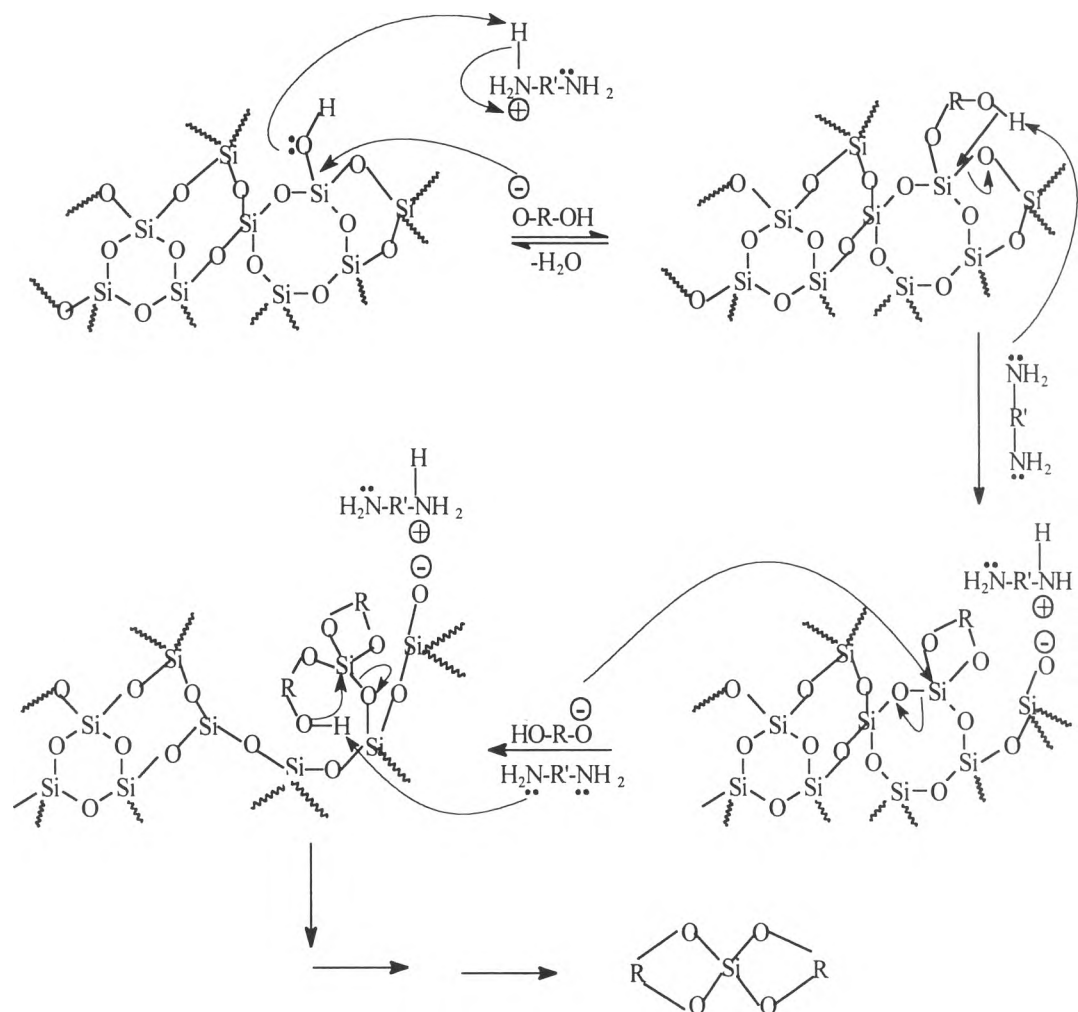


Figure 2.4 Schematic of the synthesis of the tetra-coordinated spiroosilicate and its derivatives.