

HYDROLYSIS AND CONDENSATION OF SILICATES: EFFECTS ON STRUCTURE

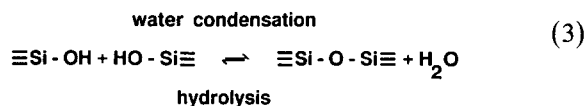
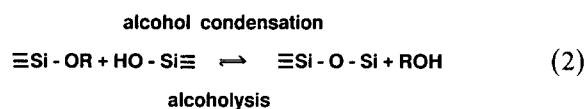
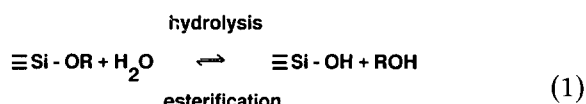
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The hydrolysis and condensation reactions of monomeric alkoxysilanes and organylalkoxysilanes utilized in sol–gel processing are reviewed. Both reactions occur by acid or base-catalyzed bimolecular displacement reactions. The acid-catalyzed mechanisms are preceded by protonation of OH or OR substituents attached to Si, whereas under basic conditions hydroxyl or silanolate anions attack Si directly. Many of the observed structural trends are understood on the basis of the pH and [H₂O] dependence of the hydrolysis, condensation, and dissolution reactions.

1. Introduction

The most common sol–gel process for making glass or glass-ceramics utilizes monomeric alkoxide precursors. In solution, the alkoxides are hydrolyzed and condensed to form polymeric species composed of M–O–M bonds. At the functional group level, three reactions are generally used to describe the sol–gel process as shown below for silicon:



It is evident from eqs. (1)–(3) that the structure of sol–gel glasses evolves sequentially as the product of successive hydrolysis and condensation reactions (and the reverse reactions, esterification and alcoholic or hydrolytic depolymerization). Thus knowledge of the mechanisms and kinetics

of these reactions should provide insight into the structures of gels and gel-derived glasses.

This paper reviews the hydrolysis and condensation reactions of monomeric alkoxysilanes and organylalkoxysilanes utilized in sol–gel processing, especially as they relate to structural evolution. Instead of presenting an historical overview, the rather brief nature of this report requires a selective emphasis on more recent investigations which rely principally on in situ methods of analysis such as NMR, FTIR and SAXS. The hydrolysis and condensation of alkoxides of other network forming elements are not reviewed here but are discussed by several other authors in these Proceedings [1–4].

1.1. General trends

The hydrolysis and condensation of silicates to form silica gels is not new. Silica gels are common in nature (opals and agates), and synthetic silica gels were first reported by Ebelmen in 1844 [5]. More recently, however, it has been demonstrated that by control of the process parameters, e.g., *R*, the H₂O/Si molar ratio, and nature and concentration of catalyst, it is possible to vary the

structure and properties of sol-gel silicates over wide ranges.

For example, Sakka et al. [6] observed that the hydrolysis of TEOS utilizing R values of 1–2 and 0.01 M HCl as a catalyst yields a viscous, spinnable solution when aged in open containers exposed to the atmosphere. Subsequent studies [7] showed that spinnable solutions exhibit a strong concentration dependence of the intrinsic viscosity and a power law dependence of the reduced viscosity on the number averaged molecular weight:

$$[\eta] = kM_n^\alpha. \quad (4)$$

Values of α range from 0.5 to 1.0, which indicates linear or chain molecules [8]. Most recently, Kamiya [9] postulated ladder polymers to account for spinnability.

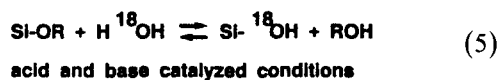
By comparison hydrolyses utilizing R values greater than two and/or base catalysts produced solutions which were not spinnable at equivalent viscosities [6,7]. Values of α in eq. (4) equalled 0.1 to 0.5, indicating spherical or disk-shaped particles. These latter results are consistent with the structures which emerge under the conditions employed in the Stöber process [10] for preparing α -SiO₂ powders. Hydrolysis of TEOS with R values ranging from 7 to 25 and concentrations of ammonia ranging from ~ 1 to 7 molar results in monodisperse, spherical particles.

Based on the results of in situ SAXS investigations, Schaefer, Keefer, and co-workers [11–13] have demonstrated that variations in the hydrolysis and condensation conditions profoundly affect the structures of sol-gel silicates. A two-step hydrolysis procedure (1 H₂O/Si under acidic conditions followed after 90 min by an additional ~ 3 or 4 H₂O/Si under acidic or basic conditions) produced ramified, weakly-branched structures characterized by a mass fractal dimension, D (for mass fractals D relates the polymer mass, M , to its radius, r , according to $M \propto r^D$, where in three dimensions $D \leq 3$). Single step base-catalyzed hydrolysis produced fractally rough particles (surface fractal dimension, D_s , may equal 2 to 3), and base-catalyzed hydrolysis and condensation under aqueous conditions produced smooth colloidal particles (non-fractal).

Thus a consistent trend is apparent: acid-catalyzed hydrolysis with low H₂O/Si ratios produces weakly branched “polymeric” networks, whereas base-catalyzed hydrolysis with large H₂O/Si ratios produces highly branched “colloidal” particles. Intermediate conditions produce structures intermediate to these extremes. Since these structural variations can only result from a different sequence of the basic reactions 1–3, the fundamental questions surrounding hydrolysis and condensation in silicates concern what factors determine the sequence of these reactions. In the following three sections the mechanisms and kinetics of the hydrolysis and condensation reactions (and the reverse reactions, esterification and depolymerization) are discussed with respect to catalytic, steric, inductive, and solvent effects. In the final section, chemistry occurring on short length scales is discussed with respect to macroscopic models of physical growth processes in order to gain physical insight into structural evolution in silicate gels.

2. Hydrolysis

Hydrolysis occurs by the nucleophilic attack of the oxygen contained in water on the silicon atom as evidenced by the reaction of isotopically labeled water with TEOS which produces only unlabeled alcohol both in acidic and basic media [14]:



Tetraalkoxysilanes, organotrialkoxysilanes and diorganodialkoxysilanes hydrolyze upon exposure to water vapor [15]. Hydrolysis is facilitated in the presence of homogenizing agents (alcohols, dioxane, THF, acetone etc.) which are especially beneficial in promoting the hydrolysis of silanes containing bulky organic or alkoxy ligands, such as phenylphenoxysilane, which, when neat, remains unhydrolyzed upon exposure to water vapor [15]. It should be emphasized, however, that the addition of solvents may promote esterification or depolymerization reactions according to the reverse of eqs. (1) and (3) (see discussion of reverse reactions below).

2.1. Effect of catalysts

Hydrolysis is most rapid and complete when catalysts are employed [15]. Although mineral acids or ammonia are most generally used in sol-gel processing, other known catalysts are acetic acid, KOH, amines, KF, HF, titanium alkoxides, and vanadium alkoxides and oxides [15]. Many authors report that mineral acids are more effective catalysts than equivalent amounts of base; however, neither the increasing acidity of silanol groups with the extent of hydrolysis and condensation (acidic silanols may neutralize basic catalysts) nor the generation of unhydrolyzed monomers via base-catalyzed alcoholic or hydrolytic depolymerization processes have generally been taken into account.

McNeil et al. [16] and Pohl and Osterholtz [17] have studied the hydrolysis of alkyltrialkoxysilanes in buffered aqueous solution. These studies do not suffer from complications due to pH excursions, polymerization, or mixed organic-aqueous solvent systems. In aqueous solution (excess water) the pseudo first order rate constants (measured spectrophotometrically or by extraction) were extrapolated to zero buffer concentration to yield the spontaneous first-order rate constants at a particular pH. The rate constants thus obtained by Pohl and Osterholtz for γ -glycidoxypropyl-

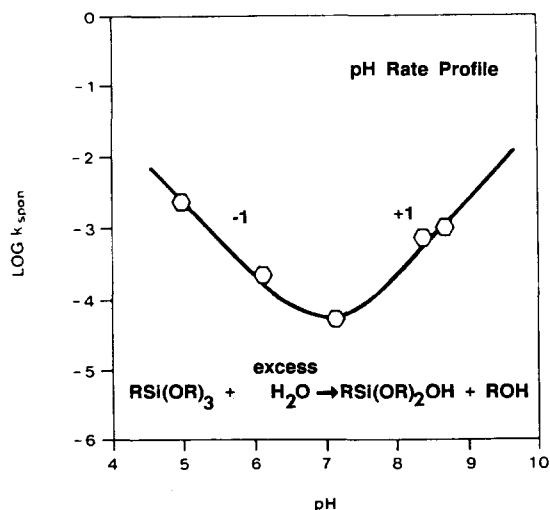


Fig. 1. pH rate profile for the hydrolysis of γ -glycidoxypropyltrialkoxysilane in aqueous solution (after ref. [17]).

Table 1

Effects of catalysts on pH and gel times for TEOS hydrolyzed with 4 equivalents of water (after ref. [18])

Catalyst	Concentration (mol: TEOS)	Initial pH of solution	Gelation time (h)
HF	0.05	1.90	12
HCl	0.05	0.05 ^a	92
HNO	0.05	0.05 ^a	100
H ₂ SO ₄	0.05	0.05 ^a	106
HOAc	0.05	3.70	72
NH ₄ OH	0.05	9.95	107
No catalyst	-	5.00	1000

^a Between 0.01 and 0.05.

yltrialkoxysilane are plotted versus pH in fig. 1. The hydrolysis appears to be both specific acid (hydronium ion) and specific base (hydroxyl ion) catalyzed, because the slopes of the plot above and below the minimum rate around pH 7 are drawn to be +1 and -1, respectively. Similar behavior was observed by McNeil et al. [16] for the hydrolysis of tris-(2-methoxyethoxy)phenylsilane.

The effects of a variety of catalysts on the overall hydrolysis and condensation rates, as judged by the times required for gelation, have been summarized by Pope and Mackenzie [18] for TEOS hydrolyzed with four equivalents of water in ethanol. Their results, listed in table 1, not only show the effects of hydronium ion and hydroxyl ion on the gel times but also the effects of the conjugate base, most notably F⁻. F⁻ is about the same size as OH⁻ and has the ability to increase the coordination of silicon above four, for example in SiF₆²⁻. Many of the properties of HF catalyzed gels are similar to those of base catalyzed gels, which suggests that the roles of OH⁻ and F⁻ are similar. Andrianov [19] proposes that the catalytic effect of F⁻ involves the displacement of an OR⁻ via an S_N2-Si mechanism followed by preferential hydrolysis of the Si-F bond:

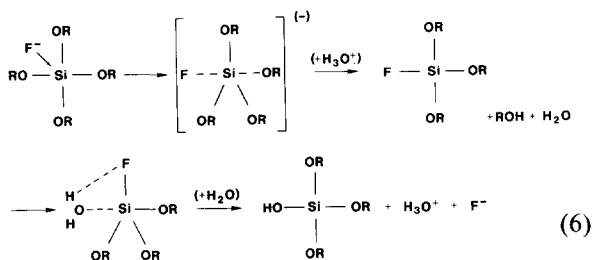


Table 2

Rate constants for acid-catalyzed hydrolysis of alkoxy silanes and mixed alkoxy silanes (after ref. [20])

R	k 10 ² (l mol ⁻¹ s ⁻¹ [H ⁺] ⁻¹)
C ₂ H ₅	5.1
C ₄ H ₉	1.9
C ₆ H ₁₃	0.83
(CH ₃) ₂ CH(CH ₂) ₃ CH(CH ₃)CH ₂	0.30

Rate constants k (10² (l mol⁻¹ s⁻¹ [H⁺]⁻¹)) for acid hydrolysis of alkoxyethoxy silanes (RO)_{4-n}Si(OC₂H₅)_n at 20 °C

n	R	CH ₃ CH(CH ₃)CH ₂ H ₃ C \ CH	CH ₃ (CH ₂) ₅ H ₃ C \ CH	CH ₃ CH(CH ₃)CH ₂ CH ₃ CH(CH ₃)CH ₂ \ CH
0	C ₆ H ₁₃	—	—	0.030
1	0.8	—	—	—
2	1.1	—	—	—
2	5.0	0.15	0.095	0.038
3	5.0	—	—	—

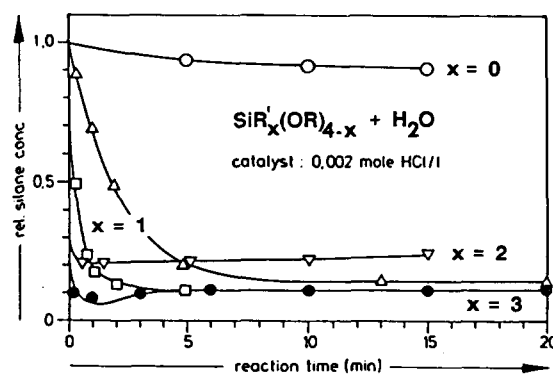
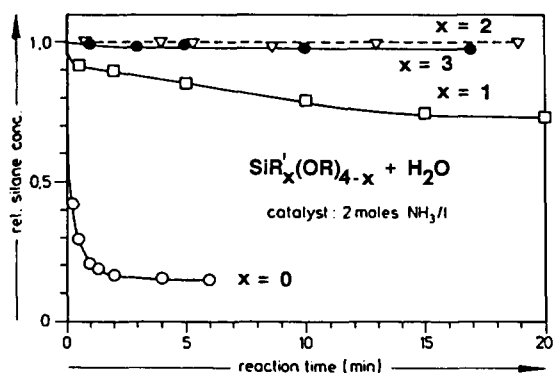


Fig. 2. Acid and base-catalyzed hydrolysis of different silanes in ethanol as solvent (volume ratio 1 : 1). ●, (CH₃)₃SiOC₂H₅; ▽, (CH₃)₂Si(OC₂H₅)₂; □, CH₃Si(OC₂H₅)₃; ○, Si(OC₂H₅)₄; Δ, Si(OCH₃)₄ (after ref. [21]).

2.2. Steric and inductive effects

Steric factors exert the greatest effect on the hydrolytic stability of organoxysilanes [15]. According to Voronkov [15], any complication of the alkoxy group retards the hydrolysis of alkoxy silanes, but the hydrolysis rate is lowered the most by branched alkoxy groups. The effects of alkyl chain length and degree of branching are illustrated in table 2 for the acid hydrolysis of tetraalkoxy silanes [20]. In the case of mixed alkoxides, (RO)_x(R'O)_{4-x}Si where R'O is a higher alkoxy group than RO, if the R'O has a normal structure, its retarding effect on the hydrolysis rate is manifested only when x = 0 or 1. If R'O is

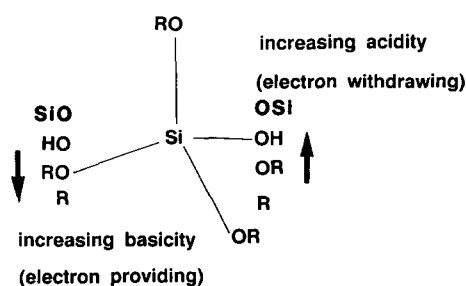


Fig. 3. Inductive effects of substituents attached to silicon, R, OR, OH, or OSi.

branched it has a retarding effect even when $x = 2$. Voronkov [15] discusses steric factors for a wide range of organoxysilanes.

Inductive effects are evident from investigations of the hydrolysis of methylethoxysilanes [21], $(\text{CH}_3)_x(\text{C}_2\text{H}_5\text{O})_{4-x}\text{Si}$ where x varies from 0 to 3 (see fig. 2). Substitution of alkyl groups for alkoxy groups increases the electron providing effect of the ligand, conversely hydrolysis (substitution of OH for OR) or condensation (substitution of OSi for OR or OH) increases the electron withdrawing effect (see fig. 3). Alkyl substitution and hydroxyl substitution should therefore increase the stability of positively and negatively charged transition states, respectively.

Fig. 2 shows that under acidic (HCl) conditions the hydrolysis rate increases with the degree of alkyl substitution, x (electron providing), whereas under basic (NH_3) conditions the reverse trend is clearly observed. Fig. 2 also shows the accelerating effect of methoxide substitution on the hydrolysis rate (TMOS versus TEOS). The consistent acceleration and retardation of hydrolysis with increasing x under acidic and basic conditions, respectively, suggests that the hydrolysis mechanism is subject to inductive effects and (based on the consistent trends) is apparently unaffected by the extent of alkyl substitution. Because increased stability of the transition state will increase the reaction rate, the inductive effects are evidence for positively and negatively charged transition states or intermediates under acidic and basic conditions, respectively. This line of reasoning leads to the hypothesis that under acidic conditions, the hydrolysis rate decreases with each subsequent hydrolysis step, whereas under basic conditions, the increased electron withdrawing capabilities of OH (and OSi) compared to OR may establish a condition in which each subsequent hydrolysis step occurs more quickly as hydrolysis and condensation proceed.

2.3. $\text{H}_2\text{O}/\text{Si}$ ratio, R

As stated in the introduction, the hydrolysis of the alkoxide precursors is achieved with R values varying from ~ 1 to over 25. Pouxviel et al. [22] recently investigated the hydrolysis of TEOS un-

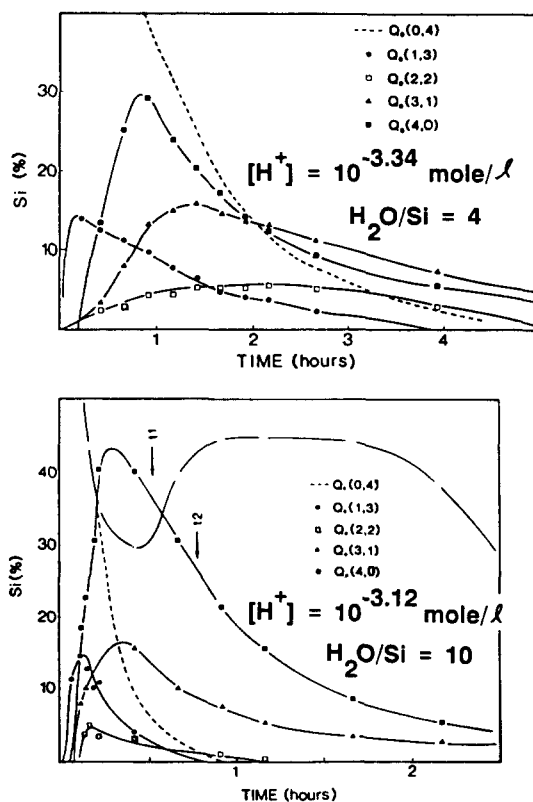


Fig. 4. Temporal evolution of Q^0 silanol species during acid-catalyzed hydrolysis as determined by ^{29}Si NMR: a, $\text{H}_2\text{O}/\text{Si} = 3.8$; b, $\text{H}_2\text{O}/\text{Si} = 10$ (after ref. [22]).

der three different $\text{H}_2\text{O}/\text{Si}$ conditions (low, medium, and high). The most obvious effect of increased $\text{H}_2\text{O}/\text{Si}$ ratios is the promotion of hydrolysis according to eq. (1). This is evident in fig. 4 which shows the temporal evolution of Q^0 species during acid catalyzed hydrolysis of TEOS as determined by ^{29}Si NMR spectroscopy. This result apparently contradicts earlier results which show a retarding effect of increased $\text{H}_2\text{O}/\text{Si}$ on the hydrolysis rate under acidic conditions [23].

Eqs. (2) and (3) suggest two further effects of $\text{H}_2\text{O}/\text{Si}$. With under-stoichiometric additions of water ($R \ll 4$), the alcohol producing condensation mechanism is favored, whereas the water forming condensation reaction is favored when

* In Q terminology: the superscript (0–4) denotes the number of bridging oxygens (–OSi) to which the Si atom is bonded.

$R \gg 4$. Excess water, however, is expected to promote depolymerization according to the reverse of eq. (3), hydrolytic depolymerization.

2.4. Solvent effects

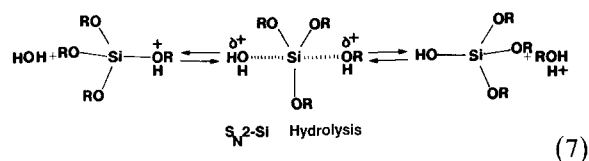
The effects of solvents have been studied primarily in the context of drying control chemical additives (DCCA) used as co-solvents with alcohol in order to facilitate rapid drying of monolithic gels [24]. Two important characteristics of solvents are: (1) polarity, which largely determines the solvating ability for polar or non-polar species, and (2) the availability of labile protons. The latter characteristic determines whether anions or cations are solvated more strongly and whether or not the solvent can participate in dissociative reactions such as alcoholysis of hydrolysis (reverse of eqs. (2) and (3)). Because hydrolysis is both hydroxyl and hydronium ion catalyzed, solvent molecules which hydrogen bond to hydroxyl ions or hydronium ions reduce the catalytic activity under basic and acidic conditions, respectively. Therefore, aprotic solvents, which do not hydrogen bond to hydroxyl ions, have the effect of making hydroxyl ions more nucleophilic, whereas protic solvents make hydronium ions more electrophilic [25].

Jonas [26] and Orcel and Hench [27] have studied the effects of formamide on the hydrolysis of TMOS in methanol under neutral conditions. Although both methanol and formamide can act as donors or acceptors in hydrogen bonding, formamide has a larger dipole moment and is therefore expected to hydrogen bond more strongly to protons and hydroxyls under acidic and basic conditions, respectively. In addition the viscosity of formamide is approximately seven times greater than methanol at 25°C. Presumably, these combined factors cause a reduction in the hydrolysis rate with the addition of formamide [26,27].

2.5. Mechanisms

It is generally argued that hydrolysis proceeds by bimolecular nucleophilic displacement reactions involving pentacoordinate intermediates or transition states (e.g., [16–18]), although by analogy to carbon chemistry siliconium ions, $\text{Si}(\text{OR})_3^+$

have also been suggested as possible intermediates [21]. Under acidic conditions, an alkoxide group is protonated in a rapid first step. Electron density is withdrawn from silicon making it more electrophilic and thus more susceptible to attack by water. Pohl and Osterholz [17] favor a transition state with significant $\text{S}_{\text{N}}2$ -type character. The water molecule attacks from the rear and acquires a partial positive charge. The positive charge of the protonated alkoxide is correspondingly reduced making alcohol a better leaving group. The transition state decays by displacement of alcohol accompanied by the inversion of the silicon tetrahedron:



Consistent with this mechanism, the hydrolysis rate is increased by substituents which reduce steric crowding around silicon (table 2). Electron providing substituents, e.g., alkyl groups, which help stabilize the developing positive charges also should increase the hydrolysis rate (fig. 2) but to a lesser extent, because the silicon acquires little charge in the transition state.

Keefer [28] has discussed possible consequences of inversion with regard to retarding the hydrolysis of silicate species which are contained in polymers. Using optically active monomers $\text{R}'_x\text{Si}^*(\text{OR})_{4-x}$, Sommer and co-workers [29,30] have proven that inversion occurs during hydrolysis of several monomers including $\text{R}_3\text{Si}^*\text{OCH}_3$. As a general rule, inversion occurs in displacement reactions with good leaving groups such as Cl^- or OCOR^- whose conjugate acids have $pK_a < 5$. For poorer leaving groups such as H or OR whose conjugate acids have $pK_a > 5$, retention or inversion may occur depending on the solvent polarity (hydrogen bonding with the leaving group may facilitate inversion) and nature of the catalyst cation. Klemperer et al. [31] have shown that, under neutral conditions, constrained oligomers (cubic octamers) hydrolyze without inversion (see fig. 5). Therefore retention or inversion may also be influenced by specific bonding configurations.

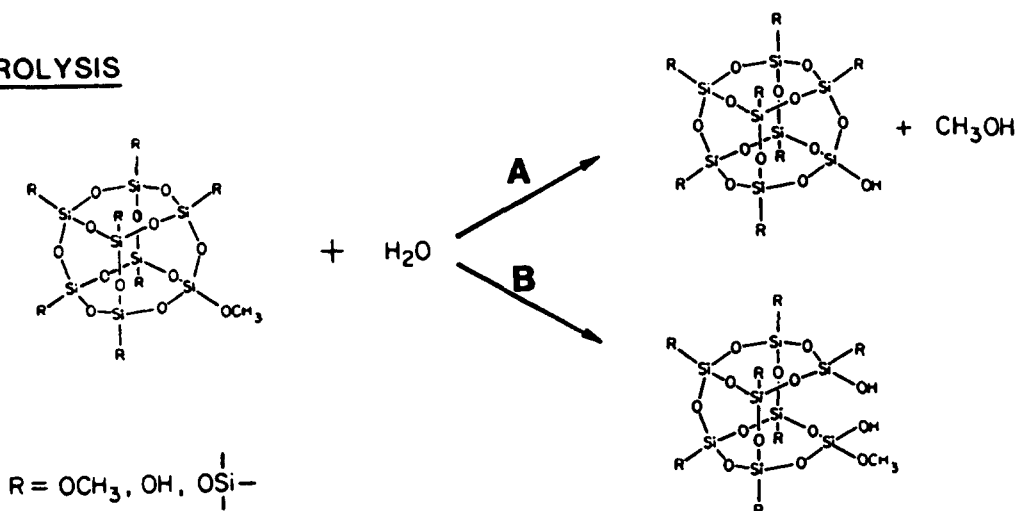
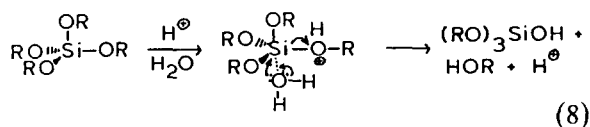
HYDROLYSIS

Fig. 5. Possible pathways for hydrolysis of methoxy terminated Q³ species contained in cubic octamers: (A) with retention of configuration, (B) with siloxane bond hydrolysis (after ref. [31]).

Several investigators have proposed hydrolysis mechanisms involving flank-side attack without inversion of the silicon tetrahedron [28,32]. A possible acid-catalyzed mechanism is the following:

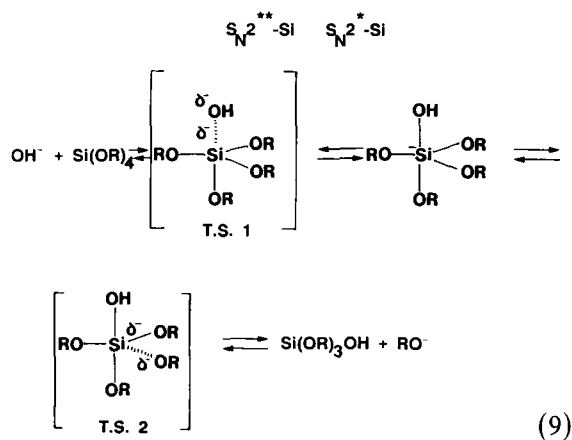


This mechanism should be subject to both steric and inductive effects. Compared to the S_N2 mechanism described above, electron providing substituents should have a greater effect, because the silicon acquires more charge in the transition state.

Several factors argue against mechanisms involving siliconium ion intermediates. McNeil et al. [16] measured the deuterium solvent isotope effect and the activation parameters ΔH^* and ΔS^* . From rate constants measured in hydrochloric acid solutions using the stopped flow method, a $k_{\text{H}_3\text{O}^+}/k_{\text{D}_3\text{O}^+}$ value of 1.24 was obtained. From a plot of $\ln(k_{\text{obsd}}/T)$ vs $1/T$ (where k_{obsd} is the observed first order rate constant at temperature T) the entropy of activation was calculated to be $-39 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The deuterium isotope effect is in accord with an associative A-2 type mechanism as in eq. (8) (rather than a dissociative A-1 type mechanism) in which the silicate mono-

mer is protonated (deuterated) in a rapid first step followed by attack of water and generation of alcohol in subsequent slower steps (rate limiting). The large negative entropy of activation suggests a highly ordered A-2 type transition state with at least one water molecule associated with it. Swain et al. [33] found that the hydrolysis of silyl halides occurs through an intermediate in which silicon is less positively charged than in the original molecule. They concluded that pentacoordinate intermediates are easy pathways for displacements on silicon which are not available for carbon which cannot expand its valence to include more than eight electrons.

Under basic conditions water dissociates to produce nucleophilic hydroxyl anions in a rapid first step. The hydroxyl anion then attacks the silicon atom. Iler [34] and Keefer [28] propose an S_N2-Si mechanism in which OH⁻ displaces OR⁻ with inversion of the silicon tetrahedron. Pohl and Osterholtz [17] favor an S_N2^{**}-Si or S_N2*-Si mechanism involving a stable five coordinated intermediate (see eq. (9)). The intermediate decays through a second transition state in which any of the surrounding ligands can acquire a partial negative charge. Hydrolysis occurs only by displacement of an alkoxide anion, which may be aided by hydrogen bonding of the alkoxide anion



with the solvent. Because the silicon acquires a formal negative charge in the intermediate, this mechanism is quite sensitive to inductive as well as steric effects. Electron withdrawing substituents – OH or – OSi should help stabilize the negative charge on silicon and enhance the hydrolysis rate, whereas electron providing substituents should decrease the rate (in accord with fig. 2). Because inversion of configuration is not required, the hydrolysis rate may increase with the extent of both hydrolysis and condensation.

2.5.1. Transesterification, reesterification, and hydrolysis

The hydrolysis reaction (eq. (1)) may proceed in the reverse direction in which an alcohol (or a protonated alcohol or alkoxide anion under acidic and basic conditions, respectively) displaces a hydroxyl group to produce a water molecule. This reverse process, reesterification, presumably occurs via mechanisms similar to those of the forward reactions, although Voronkov proposes the formation of an active six-membered transition complex that contains two alcohol molecules. Observations of the extent of reesterification of polysiloxanes (e.g., [13]) indicate that it proceeds much further under acidic conditions than under basic conditions. This led Keefer [28] to the conclusion that the base-catalyzed mechanism involves inversion of configuration, whereas the acid-catalyzed mechanism does not.

Reesterification is quite important during drying of gels, because in many solvent systems

(ethanol, propanol, and dioxane) excess water can be completely removed via the azeotrope, which has a higher vapor pressure than the neat solvent or water. Keefer [28] has calculated the number of silanols reesterified for several common gel forming conditions and degrees of condensation. According to these calculations it is easy to understand the common and contradictory observations that although hydrolysis readily goes to completion with slight excesses of water under acidic conditions, the dried gel may be substantially esterified [13,35].

Transesterification, in which an alcohol displaces an alkoxide group to produce an alcohol molecule:



has been extensively studied, because it is the common method of producing various alkoxides of silicon. As discussed by Voronkov et al. [15] a wide range of catalysts have been employed, although information on the relative catalytic activity is sparse. In sol-gel processing transesterification often occurs when alkoxides are hydrolyzed in alcohols containing different alkyl groups. For example, Brinker et al. [13] observed substantial ester exchange during the acid-catalyzed hydrolysis of TEOS in *n*-propanol. Transesterification will also be important in multicomponent systems which employ several alkoxides with differing alkoxide substituents. After transesterification has occurred, subsequent hydrolysis kinetics will depend on the steric and inductive characteristics of the exchanged alkoxide. For example, displacement of ethoxide by *n*-propoxide groups in TEOS was shown to reduce the hydrolysis rate [13].

From studies of optically active organosilicon compounds, it has been established that transesterification can proceed with retention or inversion of configuration depending on the nature of the leaving group, the solvent, and the catalyst [15]. Because alkoxide substituents are poor leaving groups (alcohols have a $pK_a > 10$), Voronkov proposed that only in very polar solvents can there be sufficient separation of charge in the transition state to realize the $\text{S}_{\text{N}}2$ -Si mechanism which proceeds with inversion of configuration [15]. In less polar solvents retention of configuration is gener-

ally observed. In sol-gel systems we expect the retention or inversion of configuration will also depend on the extent of condensation of the silicate species.

Isotopic labeling investigations have also confirmed that silanols can be hydrolyzed. When triethylsilanol is hydrolyzed in oxygen labeled water in the presence of acid or base catalyst or under neutral conditions, the oxygen of the silanol is completely replaced by the water oxygen [15]. This reaction is generally not important in influencing structural development in sol-gel systems; however it does emphasize that all substituents attached to silicon are quite labile and will depend in an equilibrium sense on the changing concentrations of alcohol and water as well as the solvent, nature of the catalyst, and extent of condensation.

3. Condensation

According to eqs. (2) and (3), polymerization to form siloxane bonds occurs by either an alcohol producing condensation reaction (eq. (2)) or a water producing condensation reaction (eq. (3)). The latter reaction has been discussed in detail by Iler [34] with regard to forming silicate polymers and gels in aqueous media. Engelhardt et al. [36] employed ^{29}Si NMR to investigate the condensation of aqueous silicates at high pH. Their results indicate that a typical sequence of condensation products is monomer, dimer, linear trimer, cyclic trimer, cyclic tetramer and higher order rings. The rings form the basic framework for the generation of discrete colloidal particles which are commonly observed in aqueous systems [34]. This sequence of condensation requires both depolymerization (ring opening) and the availability of monomers (species which may be produced by depolymerization). However in alcoholic solutions especially at low pH the depolymerization rate (reverse of eqs. (2) and (3)) is very low. Iler [34] speculates that, under conditions where depolymerization is least likely to occur so that the condensation is irreversible and siloxane bonds cannot be hydrolyzed once they are formed, the condensation process may resemble classical poly-

condensation of polyfunctional organic monomer resulting in a three dimensional molecular network. Owing to the insolubility of silica under these conditions the condensation polymer of siloxane chains cannot undergo rearrangement into particles. In sol-gel systems commonly employed for glass preparation the water/alcohol ratio and pH are widely varied. Thus the importance of the reverse reactions depends on processing conditions, and it is anticipated that condensation may result in a spectrum of structures ranging from molecular networks to colloidal particles.

3.1. Effects of catalysts

Although the condensation of silanols can proceed thermally without involving catalysts, their use especially in organosilanes is often necessary. Numerous catalysts have been employed: generally compounds exhibiting acid or base character but also neutral salts and transition metal alkoxides. In sol-gel systems mineral acids, ammonia, alkali metal hydroxides, and fluoride anions are most commonly used. As discussed in the section on hydrolysis, the understanding of catalytic effects is often complicated by the increasing acidity of silanol groups with the extent of polymerization and the effects of reverse reactions which become increasingly important with greater concentrations of water and base.

Pohl and Osterholtz [17] used ^{13}C and ^{29}Si NMR to investigate the condensation of alkylsilanetriol to bis-alkyltetrahydroxydisiloxane in buffered aqueous solutions as a function of pD. The second order rate constants for the disappearance of the triol are plotted in fig. 6a as a pD rate profile. The slopes of the plot above and below the rate minimum at pD 4.5 are +1 and -1, respectively, indicating that the condensation is specific acid and base catalyzed. It is interesting to compare these results to the pH dependence of the gel time (fig. 6b), which is often used as a measure of the overall condensation kinetics for sol-gel systems (gel time $\propto 1/\text{condensation rate}$). According to fig. 6b the overall condensation rate is maximized at intermediate pH and minimized at pH 2.5. Stable (non-gelling) systems are obtained under more basic conditions. The minimum

at \sim pH 2.5 corresponds to the isoelectric point of silica: surface silanol groups are protonated and deprotonated at lower and higher pH, respectively. Because silanols become more acidic with the extent of condensation of the siloxane network to which they are attached, the shift in the minimum rate from \sim pD 4.5 (condensation of monomers) to pH 2.5 (condensation of polydisperse, higher order polymers) may reflect the increasing acidity of silanols with the degree of condensation, or as discussed below this may reflect an inductive effect. Regardless of the cause, the pH dependence suggests that protonated and deprotonated silanols are involved in the acid and base-catalyzed mechanism. At elevated pH where the gel times are observed to increase (fig. 6b), condensation reactions proceed but gelation does not occur. In this pH regime particles are formed which after reaching a critical size become stable due to mutual repulsion effects. This high pH region represents the conditions in which Stöber silica particles [10] are formed.

In both aqueous and mixed alcohol/water systems traces of HF have a remarkable catalytic effect on the polymerization rate (see table 1). Below pH 2 Iler [34] observed that the polymerization rate is proportional to the concentration of

H^+ and F^- . He proposed that the condensation mechanism may involve a bimolecular intermediate in which fluorine anion temporarily increases the coordination of one silicon from four to five or six just as in the case of the OH^- ion. Rabinovich and Wood [37] proposed a mechanism in which F^- displaces an OH^- , causing localized attractions to other silanol species. Because F^- is a weaker base than OH^- , a more plausible argument is that F^- substitution for OH^- reduces the electron density on Si making it more susceptible to nucleophilic attack.

3.2. Steric and inductive effects

During sol-gel processing condensation can proceed by two different reactions which can occur between substantially different solution species (monomers, oligomers etc.), which have undergone different extents of hydrolysis, therefore steric and inductive effects are not well documented for tetraalkoxides. According to Voronkov et al. [15], the condensation rate of triorganysilanols decreases with increase in the length or branching of the chain of the alkyl radical, or if aromatic groups are present, with increase in their number. Likewise in tetrafunctional alkoxides normally

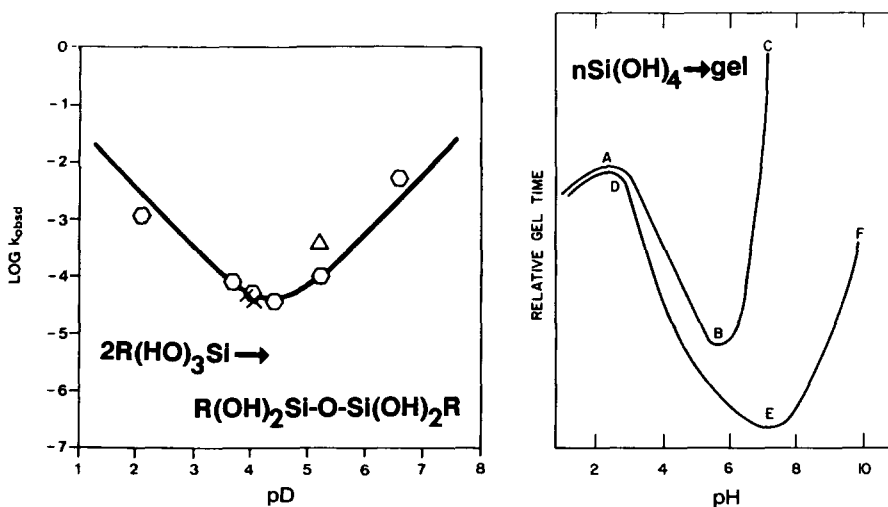


Fig. 6. (a) pD rate profile for the condensation of alkylsilanetriol in buffered aqueous solution (after ref. [17]). (b) Gel time ($\propto 1/\text{condensation rate}$) versus pH for aqueous silicates (after ref. [34]).

employed in sol-gel processing we expect that substituents which increase steric crowding in the transition state will retard condensation. Voronkov and coworkers also state that the condensation rate increases with an increase in the number of silanols on the silicon atom (increasing silanol acidity). As discussed in section 4 this result may be explained on the basis of steric, inductive, or statistical effects.

The previous section indicates that the acid and base catalyzed condensation mechanism involve protonated and deprotonated silanols, respectively. In organosilanes organic substituents may influence the acidity of silanols involved in condensation. Electron providing alkyl groups are expected to reduce the acidity of the corresponding silanol. This should shift the isoelectric point toward higher pH values as observed in fig. 6a, significantly influencing the pH dependence of the condensation mechanism. Voronkov and coworkers state that in acid-catalyzed condensation of dialkylsilanediol steric effects predominate over inductive effects [15], therefore in tetrafunctional alkoxide precursors the inductive effects resulting from longer chain alkyl substituents are probably by comparison even less important. This hypothesis is consistent with studies employing different alkoxide precursors in which little differences in gel structure are observed [38].

3.3. Effects of solvent

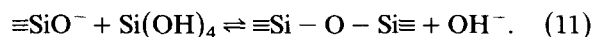
As discussed in the section on hydrolysis, solvents may be either protic or aprotic and may vary in their polarity. Depending on the pH, either protonated or deprotonated silanols are involved in the condensation mechanism. Because protic solvents hydrogen bond to nucleophilic deprotonated silanols and aprotic solvents hydrogen bond to electrophilic protonated silanols, protic solvents are expected to retard base-catalyzed condensation and promote acid-catalyzed condensation. Aprotic solvents would have the reverse effect. Unfortunately few data are available to unambiguously determine the effect of solvent type on the condensation rate. In one study particle growth rates were determined in protic and

aprotic solvent systems using Raman spectroscopy and molybdic acid reagent [39]. At near neutral (unspecified) pH aprotic solvents increased the particle growth rates over protic solvents in agreement with the above hypothesis. Additional work should be performed in buffered solutions as a function of pH.

A second and important effect of the solvent is its ability to promote depolymerization, for example, by the reverse of eqs. (2) and (3). Iler [34] insightfully suggested that under conditions in which depolymerization is suppressed, condensation may lead to molecular networks, whereas conditions in which depolymerization can occur allow restructuring ultimately resulting in colloidal sols. The effects of depolymerization on structural evolution will be discussed further in section 5.

3.4. Mechanisms

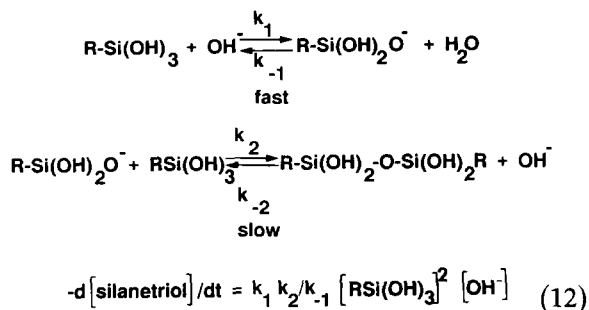
The most widely accepted mechanism for the condensation reaction involves the attack of a nucleophilic deprotonated silanol on a neutral silicate species as proposed by Iler [34] to explain condensation in aqueous silicates systems:



This reaction pertains above the isoelectric point of silica where surface silanols may be deprotonated depending on their acidity. The acidity of a silanol depends on the other substituents on the silicon atom. When basic OR and OH are replaced with OSi, the reduced electron density on Si increases the acidity of the protons on the remaining silanols [25]. Therefore Iler's mechanism favors reactions between larger more highly branched species, which contain acidic silanols, and smaller less highly branched species. The condensation rate is maximized near neutral pH where significant concentrations of both protonated and deprotonated silanols exist. A minimum rate is observed at the isoelectric point (see fig. 6b).

Pohl and Osterholtz [17] and Voronkov et al. [15] propose essentially the same mechanism to account for deuteroxide (hydroxyl) anion and gen-

eral base-catalyzed condensation of alkylsilanetriol and alkylsilanediol, respectively.



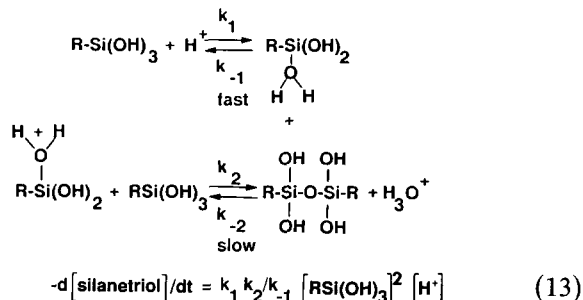
According to Pohl and Osterholtz, deuteroxide (hydroxyl) anion reversibly reacts with silanetriol in a rapid first step leading to an equilibrium concentration of silanolate anion. Silanolate anion reacts with neutral triol in a slower rate determining step resulting in dialkyltetrahydroxydisiloxane and regeneration of deuteroxide (hydroxyl) anion. Consistent with this mechanism the condensation rate is observed to be first order in deuteroxide anion and second order in triol, $-d[\text{silanetriol}]/dt = (k_1 k_2 / k_{-1}) [\text{RSi(OD)}_3]^2 [\text{OD}^-]$. Further condensation of the disiloxane was not observed at short reaction times presumably due to steric effects.

It is generally believed that the base-catalyzed condensation mechanism involves penta- or hexacoordinated silicon intermediates or transition states. For silicic acid polymerization Okkerse [40] proposed a bimolecular intermediate involving one hexacoordinated silicon. Grubbs proposed that the condensation of trimethylsilanol in methanol occurs by an S_N2 -Si mechanism in which the nucleophile approaches the backside of the silicon which subsequently undergoes displacement of its hydroxyl anion. Swain et al. [33] have proposed that silicon forms stable pentacoordinate intermediates: either S_N2^{**} -Si or S_N2^* -Si mechanisms. All of the bimolecular nucleophilic displacement reactions are subject to both steric and inductive effects, but, for the same reasons presented in the hydrolysis section, steric effects are expected to predominate.

Because in aqueous silicate systems gel times are observed to decrease below the isoelectric point of silica (fig. 6b), it is generally believed that the acid catalyzed condensation mechanism involves a

protonated silanol species. Protonation of the silanol makes the silicon more electrophilic and thus more susceptible to nucleophilic attack. The most basic silanol species (silanols contained in monomers or weakly branched oligomers) are the most likely to be protonated, therefore condensation reactions may occur preferentially between neutral species and protonated silanols situated on monomers, end groups of chains etc.

Pohl and Osterholtz [17] proposed that below about pD 4.5 the increased condensation rate of alkylsilanetriol (fig. 6a) also involved a deuterated (or protonated) silanol:



Consistent with this mechanism the condensation rate was observed to be first order in deuterium ion and second order in silanetriol. From these results it is not possible to distinguish between S_N2 -Si, S_N2^{**} -Si, or S_N2^* -Si mechanisms.

As discussed for the hydrolysis reaction, the specific mechanism may be influenced by the local environment of the silicon undergoing condensation, the solvent, and nature of the catalyst. For example, Klemperer et al. proved that two Q^3 silicon species contained in separate cubic octamers undergo condensation under neutral conditions with essentially complete retention of configuration [31], (see fig. 7) whereas condensation reactions between monomers may result in the inversion of one of the silicate tetrahedra.

3.5. Effects of reverse reaction

Alcoholysis and hydrolysis of siloxane bonds (reverse of eqs. (2) and (3)), provide a means for bond breakage and reformation, allowing continual restructuring of the growing polymers. The hydrolysis reaction (dissolution of silica) exhibits a strong pH dependence as shown in fig. 8. Be-

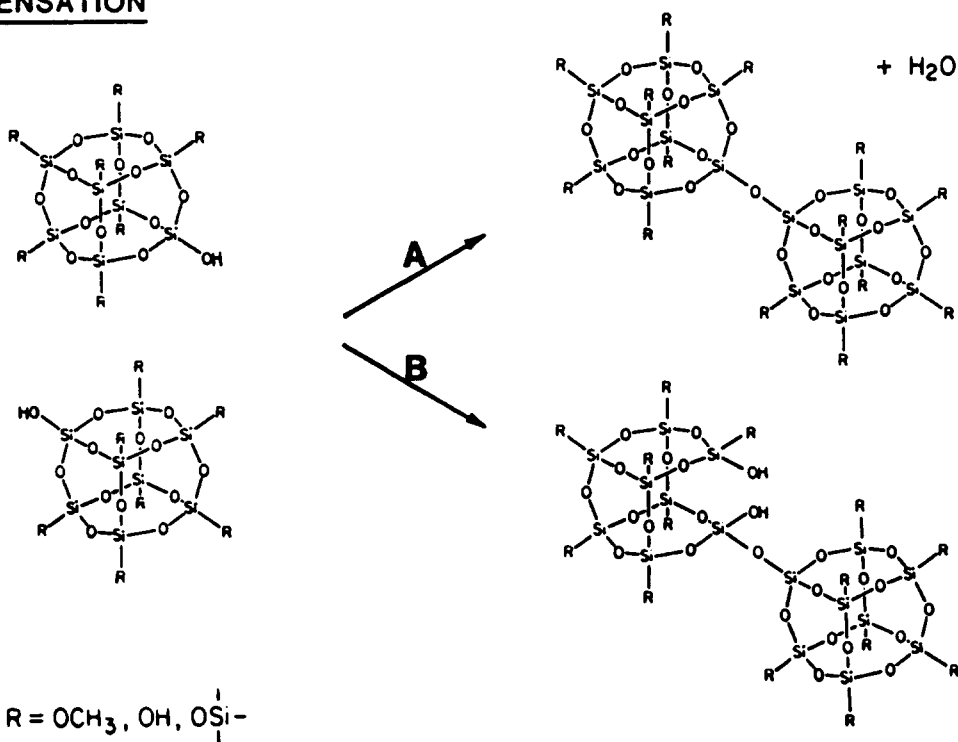
CONDENSATION

Fig. 7. Possible pathways for condensation of Q³ species contained in cubic octamers: (A) with retention of configuration, (B) with siloxane bond hydrolysis (after ref. [31]).

tween about pH 3 and 8 the dissolution rate increases by over three orders of magnitude in aqueous solution. Partial replacement of water (pH 9.5) with methanol decreases the solubility by

over a factor of twenty as shown in table 3. Klemperer [42] and co-workers have proven that alcoholysis occurs under basic conditions, which leads to a redistribution of siloxane bonds:

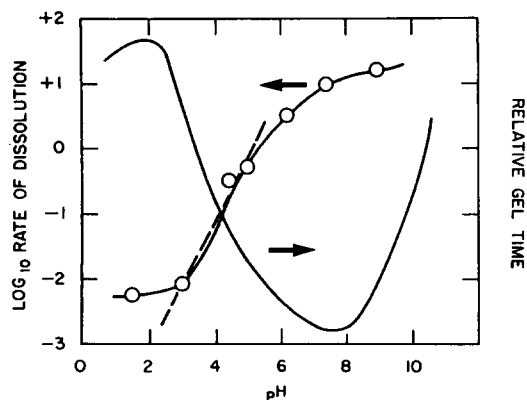
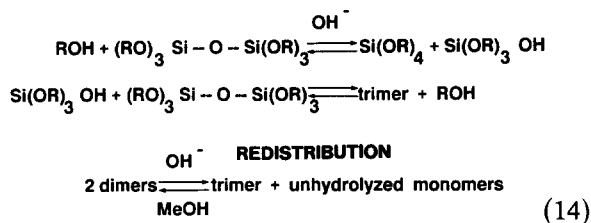


Fig. 8. pH dependence of the dissolution and condensation rates for aqueous silicates (after ref. [34]).



They propose that this reaction accounts for the common observation that under base-catalyzed conditions unhydrolyzed monomers persist past the gel point even with overstoichiometric additions of water (see, e.g., [13]). Based on capillary gas chromatography and ²⁹Si NMR results, Klemperer and co-workers have shown that the redistribution reactions result in an “inverted”

Table 3
Solubility of amorphous silica at 25°C as water (pH 9.5) is replaced with methanol (after ref. [34])

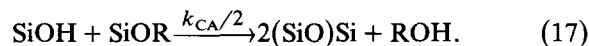
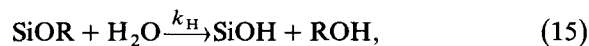
Wt% methanol	Solubility at 25°C (mg l ⁻¹)
0	140
25	75
50	40
75	15
90	5

molecular weight distribution in which high and low molecular weight species are maximized with respect to intermediate molecular weight species. As discussed in section 5 this may be explained on the basis of classic nucleation and growth or ripening theories.

According to Iler [34] the dissolution of amorphous silica above pH 2 is catalyzed by OH⁻ ions which are able to increase the coordination of silicon above four weakening the surrounding siloxane bonds to the network. This general nucleophilic mechanism could presumably occur via S_N2-Si, S_N2**Si or S_N2*-Si transition states or intermediates and could equally well explain alkoxide ion or fluoride ion catalyzed depolymerization mechanisms.

4. Sol-gel kinetics

Thus far we have discussed the hydrolysis and condensation reactions separately at a rudimentary level which ignores how the various functional groups, (OR), (OH), and (OSi), are distributed on the silicon atoms. At this level only three reactions and three rate constants are necessary to describe the functional group kinetics (k_H , $k_{CW/2}$, and $k_{CA/2}$ in eqs. (15)–(17).



In practice hydrolysis and condensation occur concurrently, and at the nearest functional group

level there are fifteen distinguishable local chemical environments. Kay and Assink [43–45] have represented the fifteen silicate species in matrix form as shown in fig. 9, where the ordered triplet (X, Y, Z) represents the number of -OR, -OH, and -OSi functional groups attached to the central silicon: Si(OR)_x(OH)_y(OSi)_z where $x + y + z = 4 =$ coordination of silicon. At this more sophisticated level there are 165 distinguishable rate coefficients: 10 k_H , 55 k_{CW} , and 100 k_{CA} , considering only the forward reactions. At the next-to-nearest functional group level there are 1365 distinct local silicon environments requiring 199 290 rate coefficients!

Using ¹H and ²⁹Si NMR, Assink and Kay [44] determined k_H , k_{CW} , and k_{CA} for acid-catalyzed hydrolysis of TMOS and used these rate coefficients in a statistical model which reduced the number of rate coefficients required to describe the kinetics at the functional group level from 165 to three. Fig. 10 shows the number of methoxy groups attached to silicon (determined by ¹H NMR) as a function of the initial H₂O/TMOS mole ratios, *R*. For *R* values up to 2 the reaction proceeds rapidly to the stoichiometry corresponding to complete hydrolysis without condensation. This indicates that the rate of the hydrolysis reaction is much greater than the sum of the rates of the two condensation reactions. Ad-

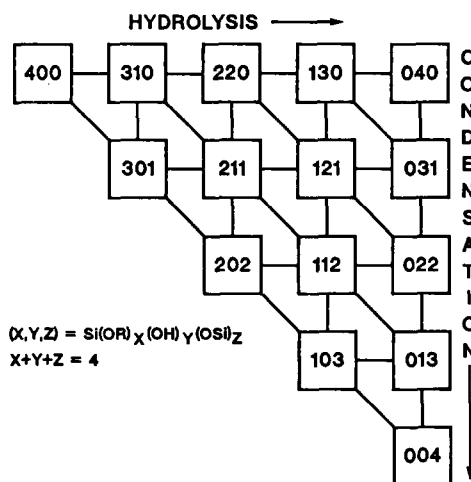


Fig. 9. Chemical speciation at next to nearest neighbor level represented in matrix form after refs. [43] and [45].

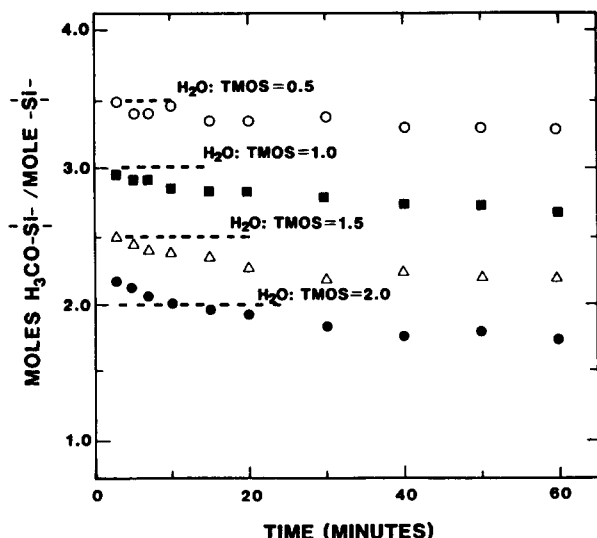


Fig. 10. Mol SiOCH_3 /mol Si versus time for $\text{H}_2\text{O}/\text{Si}$ values ranging from 0.5 to 2.0. Dashed lines are the theoretical values corresponding to complete hydrolysis without condensation (after ref. [44]).

ditional loss of methoxy groups at longer times occurs at a slower rate commensurate with the overall rate of the condensation reactions.

Based on second order hydrolysis kinetics (constant $[\text{H}^+]$) a lower limit for the hydrolysis rate coefficient was established as $0.2 \text{ l}/(\text{mol min})$. From the approximation:

$$\frac{d[(\text{SiO})\text{Si}]/dt}{\langle[\text{SiOH}]\rangle} = (k_{\text{CW}} - k_{\text{CA}})\langle[\text{SiOH}]\rangle + k_{\text{CA}}[\text{SiOMe}]_0 \quad (18)$$

valid at early times when the concentration of Si-O-Si is small compared to the initial methoxy functional group concentration, k_{CW} and k_{CA} were determined from a plot of the initial condensation rate divided by $\langle[\text{SiOH}]\rangle$ versus $\langle[\text{SiOH}]\rangle$. $\langle[\text{SiOH}]\rangle$ is the average value of the silanol group concentration over the measurement window. k_{CW} and k_{CA} determined from the slope and intercept of this plot are 0.006 and $0.001 \text{ l}/(\text{mol min})$, respectively. It is interesting to note that both the hydrolysis and condensation rate coefficients determined for TMOS are significantly greater than corresponding values reported by Pouxviel and coworkers for TEOS. Because

increased electron provision by the alkoxide substituents (OEt versus OMe) would be expected to increase the acid-catalyzed hydrolysis and condensation rate constants if inductive effects were important, this opposite effect suggests that steric rather than inductive factors are more important in determining sol-gel kinetics.

The statistical model of Kay and Assink [45] utilizes two simplifying statistical assumptions: the hydrolysis and condensation rate constants depend only on the functional group reactivity, not the local silicon chemical environment; and the rate coefficient for a particular species undergoing one of the three reactions is simply the product of a statistical factor and the appropriate functional group rate coefficient, k_{H} , k_{CW} , or k_{CA} . For example, the hydrolysis rate coefficient for species (400) is four times the rate coefficient for species (130), and the water forming condensation rate coefficient for species (040) with itself is $4 \times 4 = 16$ times greater than that of species (310) with itself.

Both the temporal and equilibrium distribution of species may be derived from the statistical model. Agreement between theory and experiment is very good as shown in figs. 11 and 12 for the time dependence of Q^0 species and the equilibrium distribution of species, respectively. Because the statistical model implicitly ignores steric and inductive effects, good agreement with experiment suggests that these effects are unimportant for TMOS. However recent ^{29}Si NMR investiga-

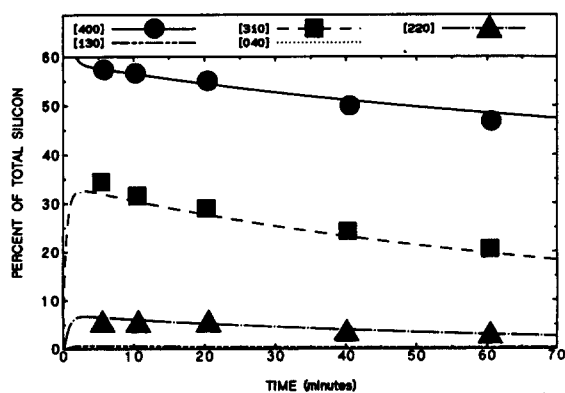


Fig. 11. Temporal distribution of Q^0 species: lines are drawn according to the statistical model; points are experimentally determined by ^{29}Si NMR (after ref. [47]).

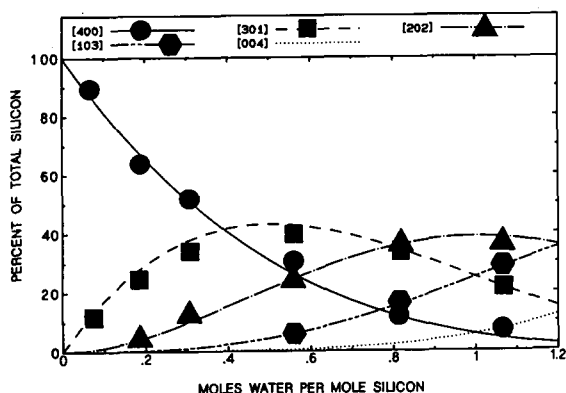


Fig. 12. Equilibrium distribution of species at long times: lines drawn according to statistical model; points determined by ^{29}Si NMR (after ref. [47]).

tions of the hydrolysis and condensation of TEOS reveal inconsistencies with the statistical model. Pouxviel et al. [22] report that the relative hydrolysis rate coefficients are 1:5:12:5 compared to 4:3:2:1 (statistical model) for the species (400), (310), (220), and (130), respectively. Lin and Basil [46] do not observe the dimer, (301)–(301), at early times during acid-catalyzed hydrolysis of TEOS, whereas the statistical model predicts its concentration to be ~23% of the total dimer concentration and ^{29}Si NMR shows that it accounts for ~19% of the dimer concentration at early times during the hydrolysis of TMOS [47]. Based on the results for TEOS we expect that steric factors will become increasingly important as the alkoxide substituents become bulkier. Perhaps a geometric factor could be included in the model to account for steric bulk. However further complications are anticipated with increased concentrations of water and base due to the increasing importance of depolymerization reactions.

5. Structural evolution

In an attempt to explain the general structural features of sol–gel silicates, this section reconsiders silicate chemistry in the context of various physical models which may pertain under specific growth conditions. Any pertinent growth model must start with a random distribution of mono-

mers which become organized into networks, clusters, or particles depending on the specific growth “rules”.

The most generally accepted model to describe silica polymerization in aqueous media is nucleation and growth [34]. At a critical degree of supersaturation nuclei form and subsequently grow by the addition of monomer. The monomer is initially supplied by the supersaturated solution. As the degree of supersaturation diminishes oligomers which have been in solubility equilibrium with the higher monomer concentration depolymerize and add to the growing nuclei. Computer simulations by Keefer [48] have shown that if the probability of a monomer attaching to a nucleus is low with respect to the frequency that it encounters a nucleus, i.e., if condensation is rate limiting, random monomer–cluster growth results in smooth, uniform particles (Eden growth in fig. 13).

From the pH dependence of hydrolysis, condensation, and depolymerization (illustrated somewhat schematically in fig. 14) and the dependence of depolymerization and extent of hydrolysis on R , it is expected that nucleation and

	REACTION-LIMITED	DIFFUSION-LIMITED
MONOMER-CLUSTER	<p>EDEN</p> <p>$D = 3$</p>	<p>WITTEN-SANDER</p> <p>$D = 2.5$</p>
CLUSTER-CLUSTER	<p>RLCA</p> <p>$D = 2.05$</p>	<p>DLCA</p> <p>$D = 1.7$</p>

Fig. 13. Computer simulations of structures formed by monomer–cluster and cluster–cluster aggregation under reaction- and diffusion-limited conditions (courtesy of D.W. Schaefer and K.D. Keefer).

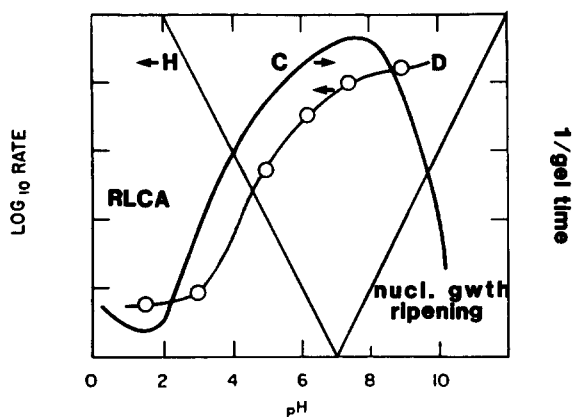


Fig. 14. Schematic representation of the pH dependences of the hydrolysis, condensation, and depolymerization rates.

growth is the dominant growth mechanism under base-catalyzed conditions at sufficiently high values of pH and R , so that depolymerization is facile and hydrolysis is complete. In base-catalyzed condensation, acidic (deprotonated) silanols are the preferred growth sites, therefore basic monomers or dimers tend to condense preferentially with acidic sites on the nucleus surface which bear only one silanol rather than with each other. Depolymerization is essential to the realization of nucleation and growth conditions for several reasons. First it is necessary for the continued supply of monomers. Second repeated depolymerization/repolymerization in essence insures that reaction-limited conditions are achieved. Depolymerization occurs preferentially at less stable sites, e.g. Q^1 sites, therefore repeated depolymerization/repolymerization forms stable configurations at the expense of unstable ones. Individual monomers have the ability to sample many potential growth sites finally "sticking" at the most favored ones rather than the first encountered sites [48]. Depolymerization is also essential to Ostwald ripening in which many smaller particles are reorganized into fewer larger particles with a corresponding reduction in the surface energy [35].

Presumably nucleation and growth followed by ripening account for the smooth, spherical particles produced in the Stöber process ($H_2O/Si =$

7–25 and $[NH_3] = 1–7$ M). Gelation is not observed because after the particles have reached a certain size they are electrostatically stabilized (mutually repulsive). Stabilization prevents particles from condensing with particles but, it does not preclude continued condensation between particles and weakly acidic monomeric species.

At low pH ($< pH$ 3) with reduced H_2O/Si ratios, the depolymerization rate may be decreased by over 4 orders of magnitude (fig. 14 and table 3), and the rate of condensation is low with respect to the rate of hydrolysis (fig. 14). Under these conditions monomers may undergo essentially irreversible condensation in a process similar to reaction-limited cluster-cluster aggregation (RCLA in fig. 13) [49]. In this growth process monomers moving with Brownian trajectories encounter other monomers (or clusters) to which they stick with a certain probability (in our case related to the condensation rate). The resulting cluster moves with a Brownian trajectory, but with a velocity inversely proportional to $\sqrt{\text{mass}}$, encountering and sticking to other monomers or clusters. Because monomers are consumed by condensation but not produced by depolymerization, monomers are eventually depleted leaving only clusters. Due to steric and kinetic constraints clusters are unable to interpenetrate and condense to completely fill space. Computer simulations indicate that this growth process results in rather weakly branched structures characterized by a mass fractal dimension, $D = 2.05$ [50].

The process described assumes that all growth sites are equally probable. However the specified conditions (low pH and low H_2O/Si ratios) probably cause some inequivalence in the reactivity of different sites. Below the isoelectric point the preferred growth sites are the least acidic silanol species (located on monomers, end groups of chains etc.) which are the most likely to be protonated. Condensation may occur preferentially between these species and more acidic silanols located on more highly condensed sites. Because the alcohol forming condensation rate is significantly lower than the water forming condensation rate and condensation of ether (ROR) is not observed, under-stoichiometric additions of water in effect reduce the practical functionality. Based on

simulations by Keefer [48] the latter effect should bias the system toward less highly branched structures, whereas preferential condensation between less and more acidic species may have the reverse effect.

Reaction-limited cluster-cluster growth was probably most closely realized in a two-step hydrolysis procedure [13]. The initial step, 1 H₂O/Si under acidic conditions, produced a distribution of incompletely hydrolyzed oligomers. The second step, ~ 4 additional H₂O/Si after 90 min, completely hydrolyzed the oligomers rendering all potential growth sites approximately equally probable. SAXS investigations during the second hydrolysis step indicated the condensed species to be mass fractals characterized by $D \sim 2$ consistent with RLCA theory.

It is not obvious how a random growth process could result in ladder polymers as recently proposed to account for spinnability [9]. Such rigid, rod-like polymers should exhibit a fractal dimension of 1. ²⁹Si NMR could be used to verify whether or not the polymers are composed of only Q³ species (double chain) or Q³ and Q⁴ species in a molar ratio 2:1 (triple chain). Preliminary SAXS investigations suggest that the spinnable systems are highly polydisperse [51]: no power law region is observed, thus it is impossible to assign a fractal dimension. Earlier SAXS investigations of acid-catalyzed systems showed a strong concentration dependence of the Guinier radius [13]. This indicates that, because the condensation rate is low, the polymers may entangle and interpenetrate one another without gelling. Perhaps polymer entanglement is a sufficient condition for spinnability. Clearly additional work needs to be performed to elucidate the structures responsible for spinnability.

Intermediate values of pH (3–8) and R represent conditions in which a spectrum of transitional structures might be expected. The dissolution and condensation rates smoothly increase with pH, whereas the hydrolysis rate goes through a minimum at approximately neutral pH. Increased H₂O/Si ratios increase the dissolution and hydrolysis rates at any particular pH. Consider as an example neutral pH. With understoichiometric H₂O/Si ratios for complete hydrolysis, the con-

densation reaction initially proceeds between incompletely hydrolyzed species. Hydrolysis is rate limiting therefore the pattern of condensation reflects the pattern of hydrolysis. The depolymerization rate is relatively low. Thus the initial structures are expected to be weakly branched, perhaps similar to structures produced by RLCA. Water produced by condensation causes more complete hydrolysis and enhances the depolymerization rate. This should increase the extent of both branching and restructuring. As the initial H₂O/Si ratio is increased, condensation and restructuring proceed concurrently at more comparable rates and the growth process should more closely resemble nucleation and growth. Keefer [48] has investigated the sensitivity of structure at intermediate pH to the H₂O/Si ratio, R . As R was increased from 1 to 2 the polysilicate structure changed from a mass fractal to a surface fractal. As R was further increased from 2 to 4 the surface became progressively “smoother” (surface fractal dimension, D_s , decreased from 2.71 to 2.45, where $D_s = 2$ is a non-fractal surface). Obviously at sufficiently high R the process is akin to aqueous silicate polymerization, and smooth colloidal particles should form. It should be noted that on larger length scales silicate particles formed at intermediate pH will rapidly aggregate by RLCA, thus when discussing structure it is necessary to specify length scales.

6. Summary

It is generally agreed that both hydrolysis and condensation occur by acid or base-catalyzed bimolecular nucleophilic displacement reactions involving, e.g., S_N2–Si, S_N2**–Si, or S_N2*–Si transition states or intermediates. The acid-catalyzed mechanisms are preceded by rapid protonation of the OR or OH substituents bonded to Si, whereas under basic conditions hydroxyl or silanolate anions attack Si directly. Statistical and steric effects are probably most important in influencing the kinetics, however, inductive effects are certainly evident in the hydrolysis of organyl-alkoxysilanes.

With respect to structural evolution, many of the observed trends, e.g., extent of branching, particle versus polymer gels, occurrence of fractality, spinnability, etc., may be understood by considering the pH and $[H_2O]$ dependence of the hydrolysis, condensation, and dissolution rates. Smooth particle gels (non-fractal) occur only when there is a continued source of fully functional monomers and condensation is reaction limited. Cluster-cluster growth or reduced functionality result in weakly-branched mass or surface fractals.

I am especially indebted to Roger Assink and Bruce Kay at Sandia who kindly supplied me with preprints of refs. [44] and [45] and who provided a review of the manuscript. Discussions with Dan Doughty (Sandia), Walter Klemperer, and Vera Mainz (both of the University of Illinois) are also gratefully acknowledged.

References

- [1] H. Schmidt, these Proceedings (Workshop on Gels '87), p. 51.
- [2] J. Livage, *ibid.*, p. 65.
- [3] M. Guglielmi, *ibid.*, p. 16.
- [4] R.C. Mehrotra, *ibid.*, p. 1.
- [5] M. Ebelmen, *Ann. Chim. Phys.* 16 (1846) 129.
- [6] S. Sakka and K. Kamiya, *J. Non-Cryst. Solids* 48 (1982) 31.
- [7] S. Sakka, in: *Better ceramics through chemistry*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Elsevier-North-Holland, New York, 1984) p. 91.
- [8] H. Tsuchida, *Science of Polymers* (in Japanese), (Baihu-kan, Tokyo, 1975) p. 85.
- [9] K. Kamiya, these Proceedings, p. 195.
- [10] W. Stöber, A. Fink and E. Bohn, *J. Coll. and Int. Sci.* 26 (1968), 62.
- [11] D.W. Schaefer and K.D. Keefer, in: *Better ceramics through chemistry II*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Mat. Res. Soc., Pittsburgh, 1986) p. 277.
- [12] D.W. Schaefer, J.E. Martin, A.J. Hurd and K.D. Keefer, in: *Physics of finely divided matter*, eds. N. Boccara and M. Daoud (Springer, Berlin, 1985) p. 31.
- [13] C.J. Brinker, K.D. Keefer, D.W. Schaefer, R.A. Assink, B.D. Kay and C.S. Ashley, *J. Non-Cryst. Solids* 63 (1984) 45.
- [14] I.G. Khaskin, *Dokl. Akad. Nauk SSSR* 85 (1952) 129.
- [15] M.G. Vorankov, V.P. Mileshevich and Y.A. Yuzhelevski, *The siloxane bond*, (Consultants Bureau, New York, 1978).
- [16] K.J. McNeil, J.A. DiCaprio, D.A. Walsh and R.F. Pratt, *J. Am. Chem. Soc.* 102 (1980) 1859.
- [17] E.R. Pohl and F.D. Osterholtz, in: *Molecular characterization of composite interfaces*, eds. H. Ishida and G. Kumar (Plenum, New York, 1985) p. 157.
- [18] E.J.A. Pope and J.D. Mackenzie, *J. Non-Cryst. Solids* New York 87 (1986) 185.
- [19] K.A. Andrianov, *Metal organic polymers* (Wiley, New York, 1965).
- [20] R. Aelion, A. Loebel and F. Eirich, *J. Am. Chem. Soc.* 72 (1950) 5705.
- [21] H. Schmidt, H. Scholze, and A. Kaiser, *J. Non-Cryst. Solids* 63 (1984) 1.
- [22] J.C. Pouxviel, J.P. Boilot, J.C. Beloeil, and J.Y. Lallemand, *J. Non-Cryst. Solids* 89 (1987) 345.
- [23] H. Schmidt, A. Kaiser, M. Rudolph and A. Lentz, in: *Science of ceramic chemical processing*, eds. L.L. Hench and D.R. Ulrich (Wiley-Interscience, New York, 1986) p. 87.
- [24] L.L. Hench, G. Orcel and J.L. Nogues, in: *Better ceramics through chemistry II*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Mat. Res. Soc., Pittsburgh, 1986) p. 35.
- [25] R.T. Morrison and R.N. Boyd, *Organic chemistry* (Allyn and Bacon, Boston, 1966).
- [26] J. Jonas, in: *Science of ceramic chemical processing*, eds. L.L. Hench and D.R. Ulrich (Wiley-Interscience, New York, 1986) p. 65.
- [27] G. Orcel and L.L. Hench, *J. Non-Cryst. Solids* 79 (1986) 177.
- [28] K.D. Keefer, in: *Better ceramics through chemistry*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Elsevier-North-Holland, New York, 1984) p. 15.
- [29] L.H. Sommer, C.F. Frye, M.C. Muslof, G.A. Parker, P.G. Rodewald, K.W. Michael, Y. Okaya and P. Pepinski, *J. Am. Chem. Soc.* 83 (1961) 2210.
- [30] L.H. Sommer and C.F. Frye, *J. Am. Chem. Soc.* 82 (1960) 3796.
- [31] W.G. Klemperer, V.V. Mainz and D.M. Milar, in: *Better ceramics through chemistry II*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Mat. Res. Soc., Pittsburgh, 1986) p. 3.
- [32] D.R. Uhlmann, B.J.J. Zelinski and G.E. Wnek, in: *Better ceramics through chemistry*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Elsevier-North-Holland, New York, p. 59.
- [33] C.G. Swain, R.M. Esteve and R.H. Jones, *J. Am. Chem. Soc.* 11 (1949) 965.
- [34] R.K. Iler, *The chemistry of silica*, (Wiley, New York, 1979).
- [35] C.J. Brinker, K.D. Keefer, D.W. Schaefer and C.S. Ashley, *J. Non-Cryst. Solids* 48 (1982) 47.
- [36] V.G. Engelhardt, W. Altenburg, D. Hoebbel and W. Weiker, *Z. Anorg. Chem.* 418 (1977) 43.
- [37] E.M. Rabinovich and D.L. Wood, in: *Better ceramics through chemistry II*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Mat. Res. Soc., Pittsburgh, 1986) p. 251.
- [38] I. Hasegawa and S. Sakka, these Proceedings.
- [39] I. Artaki, T.W. Zerda and J. Jonas, *J. Non-Cryst. Solids* 81 (1986) 381.

- [40] C. Okkerse, in: *Physical and chemical aspects of adsorbents and catalysts*, ed. B.G. Linsen (Academic Press, New York, 1970).
- [41] W.T. Grubbs, *J. Am. Chem. Soc.* 76 (1954) 3408.
- [42] W.G. Klemperer, in: *Proceedings of the Am. Chem. Soc. Symp. on Inorganic Polymers*, eds. M. Zeldin and K.J. Wynn (Am. Chem. Soc.) to be published.
- [43] B.D. Kay and R.A. Assink, in: *Better ceramics through chemistry II*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Mat. Res. Soc., Pittsburgh, 1986) p. 157.
- [44] R.A. Assink and B.D. Kay, *J. Non-Cryst. Solids* 99 (1988) 359.
- [45] B.D. Kay and R.A. Assink, *J. Non-Cryst. Solids*, submitted.
- [46] C-C Lin and J.D. Basil, in: *Better ceramics through chemistry II*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Mat. res. Soc., Pittsburgh, 1986) p. 585.
- [47] R.A. Assink and B.D. Kay, unpublished.
- [48] K.D. Keefer, in: *Better ceramics through chemistry II*, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Mat. Res. Soc., Pittsburgh, 1986) p. 295.
- [49] M. Kolb and R. Jullien, *J. Phys. Lett. (ORSAY)* 45 (1984) L977.
- [50] W.B. Brown and R.C. Ball, *J. Phys. A* 18 (1985) L517.
- [51] C.J. Brinker, unpublished.