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Kinetic and thermodynamic issues in the early stages of sol-gel processes using silicon alkoxides

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Abstract

An understanding of the chemical processes that take place in the earliest stages of a sol-gel preparation can provide the potential to better control microstructural evolution of a catalyst. While the desired catalyst properties depend on specific details of a catalytic application, in general one wants at least to control textural and chemical homogeneity. Silica provides an excellent test system for the study of sol-gel processes starting from alkoxide precursors as it can exhibit a wide variety of structure and has been extensively studied. In this review the features of tetraethoxysilane (TEOS) polymerization as observed by ^{29}Si-NMR spectroscopy are summarized. Trends in hydrolysis and condensation with increasing oligomer size are identified. The kinetics and equilibrium of these reactions, metastability and phase separation are reviewed. Finally we suggest a comprehensive reaction engineering picture of TEOS polymerization with special focus on the crossover between gelation and precipitation. Selected comments on other alkoxides, non-alkoxides, and on multicomponent formulations are also offered.

1. Introduction

One of the great promises of sol-gel synthesis is that one might hope to make solid surfaces with new catalytic properties by connecting different dissolved oxide precursors in proportions and with local order chosen at will. We believe this hope is fundamentally well founded. In many instances one might hope for a metastable oxide structure and composition that is quite different from that presented by stable materials so as to create surface reactive sites of desired acid/base reactivity and to manipulate the numbers of such sites. In the extreme case, completely random structures might be sought. To direct such a random and homogeneous assembly, one would ideally like the dissolved oxide components and their assembling networks to remain in solution until solidifying by 'gelation', i.e., by forming an infinite polymeric network, avoiding (to the degree possible) precipitation of the evolving intermediates. On the other hand, if a certain degree of order is required, one would like at least to control phase separation and other ordering processes.

The degree of molecular level randomness and homogeneity should have a profound influ-

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ence on the catalytic properties of a site. It can also have a dramatic effect on aging, energetics and thermal behavior of gels (which, naturally, will also affect catalytic properties). For example, gels prepared from tetraethoxysilane (TEOS) at pH less than 3.5 are microporous and the time to gel and time to syneresis are sensitive functions of the synthesis pH. On the other hand, gels prepared at pH higher than 3.5 are mesoporous with microstructure that is highly pH dependent. These gels do not exhibit syneresis [1]. Ying et al. indicate that the acid-prepared silica gels are energetically more stable, retain much more water and unreacted ethoxy and hydroxy groups and densify at significantly lower temperatures than alkaline-prepared gels [2]. In this review, we will seek kinetic and thermodynamic reasons for the different chemical and textural properties.

Inquiring what causes chemical and structural differences in SiO_2 can serve as an entry into the exploration of homogeneous multicomponent gels containing SiO_2 and can provide a paradigm for understanding the chemistry and structure of non-SiO_2 materials. Recent work in the synthesis of Al_2O_3–SiO_2, ZrO_2–SiO_2, V_2O_5–SiO_2 and TiO_2–SiO_2 gels has demonstrated distinct advantages of sol-gel 'prehydrolysis' techniques in producing a controlled degree of component mixing (e.g., [3–7]). It has been pointed out that the aluminosilicate system is notoriously difficult to process by conventional techniques because of the existence of wide compositional regions prone to phase separate into stable, stoichiometric aluminates, silicates, and aluminosilicates [8]. Yoldas and Partlow have shown that the homogeneity of sol-gel derived aluminosilicates can be vastly superior to sintered colloids [9]. It has been demonstrated that increased homogeneity led to enhanced resistance to low-temperature densification of aluminosilicate gels [10].

This review, however, is limited to early stage aspects of a sol-gel process, i.e., reactions in the synthesis reactor. The restructuring of gels upon aging, drying and sintering is beyond the scope of this review. In practice, of course, the drying of the gel and exposure to catalytically useful conditions will no doubt cause reorganization of the solid to structures more stable than a random assembly, but those structures may well be metastable and can provide at least some catalytically useful sites not ordinarily available unless one had started from a random assembly of high free energy precursors.

This review is also limited to the behavior of SiO_2 systems, particularly those from TEOS. TEOS provides an excellent test system for the study of homogeneous vs. heterogeneous sol-gel processes starting from alkoxide precursors. It is exceptionally easy to force TEOS to evolve into a homogeneous fairly randomly structured gel over a wide range of preparation conditions. In other conditions, though, it can form dense colloidal precipitates; in the presence of templates or cations, TEOS derivatives can even nucleate and grow zeolites [11]. Thus we have the opportunity to learn what kinetics and intermediate structures are required to obtain homogeneous vs. heterogeneous structures. Acquiring a fundamental understanding of TEOS polymerization under a variety of experimental conditions provides important insights into sol-gel processes in general. Moreover, the nuclear magnetic resonance (NMR) properties of the ^{29}Si nucleus are sufficiently favorable and TEOS sol-gel processes can be sufficiently slow that these systems can be quantitatively monitored with now-standard NMR instrumentation. We will note that the kinetic behavior of the TEOS system is simpler than that of other alkoxides.

The behavior of TEOS in water/ethanol solutions results from an interplay of three phenomena typically encountered in sol-gel processes: hydrolysis, condensation and phase separation. TEOS condensation polymerization kinetics are strongly non-ideal (cf. random step polymerization), and this system has even provided a convenient benchmark for testing non-ideal polymer structure development models. TEOS precipitation to colloidal particles has also been studied a great deal, particularly in conditions providing monodispersely sized colloids.

Phase separation during TEOS polymerization is related both to kinetics (and hence structure evolution) and to the solvent quality for hydrolyzed TEOS and its condensation products. Water and ethanol play the role of solvents and, at the same time, the role of reactants (in hydrolysis/reesterification of ethoxy/hydroxy groups and in hydrolysis of siloxane bonds). TEOS hydrolysis and condensation are influenced by concentration and type of acidic or basic catalyst. The kinetics and thermochemistry of these processes vary in a complicated fashion as composition changes, and this gives rise to the intriguing composition dependence of TEOS polymerization/precipitation behavior. We also note that the 'solvent' composition influences solubility of the evolving intermediates, as they bear polar and charged groups. Previous studies have revealed some qualitative kinetic trends, but true materials reaction engineering will require a quantitative understanding of the competing processes. In this paper we identify kinetic and thermodynamic trends of the competing processes involved in TEOS polymerization and we use these trends to deduce reasons responsible for the structure produced (gel vs. precipitate) in various composition regions.

In the first section we summarize the structural features of TEOS polymerization as observed by ^{29}Si-NMR spectroscopy across a range of pH — the single most important composition parameter. In the second section we describe the hydrolysis of TEOS and condensation of partially hydrolyzed monomers to dimers during the earliest stages of TEOS polymerization. These processes can be conveniently and unequivocally followed by ^{29}Si-NMR spectroscopy. We also discuss metastability and phase separation.

In the third section we identify and quantify trends in hydrolysis and condensation (commenting on both kinetics and thermodynamics) with increasing oligomer size during homogeneous polymerization. We also discuss important effects such as cyclization and decreased group mobility that cannot be treated using simple lumping procedures. In the fourth section we pull together the kinetic, thermodynamic and structural trends identified in the previous sections. We suggest a consistent picture of TEOS polymerization across the pH range, with special focus on the crossover between gelation and precipitation.

Sol-gel science up to 1990 was thoroughly reviewed in the book Sol-Gel Science [12], followed by the recent progress reports on sol-gel silica synthesis reaction kinetics (e.g., [13]) and structure development [1]; references contained therein provide a crucial reading list on sol-gel topics. This paper continues from that point.

As this review mostly deals with TEOS polymerization, we do not do justice to much of interesting literature on systems starting from colloids and salt solutions (e.g., sodium silicate or waterglass). However, at times we find it instructive to compare some features of TEOS systems with those of similar overall composition starting from other silicon alkoxides in their parent alcohols (e.g., we will refer to tetramethoxysilane (TMOS) in methanol simply as the TMOS system) and aqueous silica solutions. We are forced to focus on ambient temperature preparations, since few kinetic studies at different temperatures have been made.

This review is also largely limited to single step batch reactors. Silica sol-gel kinetic studies have most frequently been carried out in batch reactors, although this by no means has to be so! In fact, the most successful multicomponent sol-gel processes involve multistep batch processes; semi-continuous and continuous steady state processes are becoming more common, particularly in industrial settings. Even for single component silica synthesis, multistep and continuous coating operations offer advantages in microstructure control. We will focus, though, on single step batch reactors here since most of the reported experimental data correspond to these systems.

2. ^{29}Si-NMR of structural evolution

In the course of a typical SiO_2 sol-gel process, TEOS is introduced to a batch reactor with ethanol, water and 'catalyst' — usually acid (e.g., HCl) or base (e.g., NH_3). Water is necessary to hydrolyze TEOS to allow for polymerization and/or phase separation. Alcohol acts as a common solvent to regulate the miscibility of TEOS, its polymerization products, and water; we will see that it also acts as a reagent. Acids or bases influence the kinetics of various steps in the sol-gel process, can change solubility, and can shift polymerization equilibrium through coupled ionization reactions.

The most important feature of TEOS polymerization is the competition between the ongoing processes of hydrolysis, condensation and phase separation. For example, when TEOS undergoes its first hydrolysis, it may then either: (1) undergo the second hydrolysis, (2) react with another monomer to produce a dimer, and/or (3) precipitate to form a separate phase (generally in the form of colloidal particles). The fate of a single step batch TEOS system is governed by the kinetics and thermodynamics of the competing processes. As we will review shortly, hydroxy (silanol) groups might be barely soluble in an alcohol/water solvent, while ethoxy groups are quite soluble. If silanol groups can condense quickly enough, the polymers might stay in the solution. On the other hand, if the condensation rate is slow, hydrolyzed species might accumulate and phase separate. (Multi-step batch, semi-continuous and continuous processes can be used to manipulate this race!)

We will also review situations where phase separation fails to occur even though the silanol concentration is well above saturation levels. When phase separation does not interfere, TEOS undergoes homogeneous step growth polymerization, although with unusually complex kinetics. Concurrent hydrolysis and condensation of TEOS then leads to an array of oligomers and polymers of various size, architecture and degree of hydrolysis.

^{29}Si-NMR spectroscopy has been an extremely useful tool in sol-gel research because it allows one to monitor concentrations of certain specific silicon sites quantitatively over the course of polymerization without disturbing the evolving system (e.g., [14]). ^{29}Si-NMR spectra show silicon sites with distinct first shell chemical environments (i.e., combinations of groups immediately attached to silicon) [15]. Following nomenclature introduced in 70's [16] these sites can be labeled Q_i^j, where Q denotes the potentially four(quad)-functionality for polymerization, and i and j denote the number of siloxy and hydroxy groups on the given silicon, respectively; the number of ethoxy groups on the silicon is $4-i-j$. Q_0^0 corresponds to TEOS monomer, Q_0^j ($j=1,2,3$) correspond to partially hydrolyzed monomers with j hydroxy groups and $4-j$ ethoxy groups, and Q_0^4 corresponds to fully hydrolyzed monomer, i.e., silicic acid. Q_1^j ($j=0,1,2,3$) correspond to chain end sites, Q_2^j ($j=0,1,2$) correspond to middle sites, and Q_3^j ($j=0,1$) correspond to branching sites. Q_4^0 corresponds to fully condensed silicon sites.

^{29}Si-NMR resonances from fully hydrolyzed silicon sites $Q_i^{j=4-i}$ are well separated into five bands according to their connectivity i, i.e., number of siloxy groups connected to silicon [17]. The presence of ethoxy groups (varying j) substantially enriches the NMR spectra by creating fine structure. In addition, it is a fortunate artifact of ^{29}Si chemical shift sensitivity that it is possible to distinguish Q_2 sites belonging to several specific environments with unusually small siloxane bond angles, such as cyclic trimer and cyclic tetramer (Fig. 1; cf. [18,19]). However, using ordinary single pulse NMR it is difficult to distinguish branched Q_3 sites participating in 3-membered rings due to proximity of their chemical shifts to chain middle sites Q_2.

We have assembled and analyzed a collection of solution ^{29}Si-NMR spectra monitoring the one step batch polymerization of TEOS with a wide range of initial compositions (e.g., [18–28]). This allows us to qualitatively identify accessible reaction trajectories in such systems

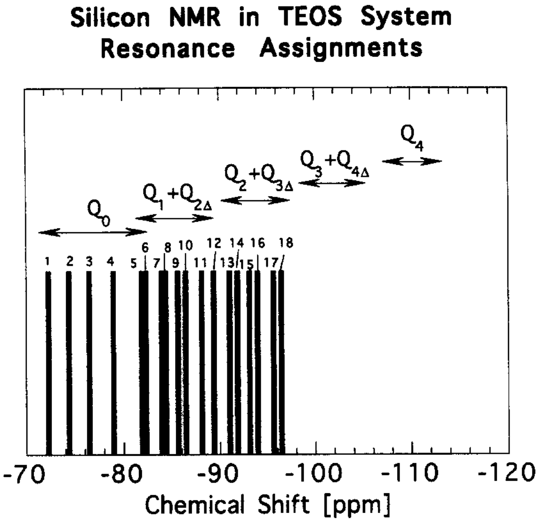

Fig. 1. Peak assignments in ^{29}Si-NMR spectra of TEOS systems (from [18,19]). Peaks are marked by numbers, corresponding to the following silicon sites: 1: Q_0^4, 2: Q_0^3, 3: Q_0^2, 4: Q_0^1, 5: Q_0^0, 6: Q_1^3, 7: $Q_{2\Delta}^2$, 8: Q_1^2, 9: $Q_{2\Delta}^1$, 10: Q_1^1, 11: $Q_{2\Delta}^0$, 12: Q_1^0, 13: $Q_{2\diamond}^2$, 14: Q_2^2, 15: $Q_{2\diamond}^1$, 16: Q_2^1, 17: $Q_{2\diamond}^0$ 18: Q_2^0. Triangles and diamonds designate sites in 3- and 4-membered rings. All chemical shifts are referred to tetramethylsilane.

as shown in Fig. 2. All systems studied were prepared by adding TEOS to a solution of ethanol, water and strong acid (HCl) or base (NaOH) at room temperature.

For $[\mathrm{HCl}] > 1 \times 10^{-3}$ M we typically observe rapid hydrolysis of TEOS to a pseudo-equilibrium state. This process is followed somewhat more slowly by continuous condensation to dimers and higher oligomers that are accompanied by their various hydrolyzed forms. In Fig. 2a, we show a typical plot of time evolution of silicon site concentrations up to the gel point. Q_0 sites disappear quickly; Q_1, Q_2 and Q_3 sites appear in sequence as appropriate to condensation polymerization scheme. Fully condensed Q_4 sites appear later and are visible with ordinary solution NMR, indicating that these sites are still quite mobile, i.e., they are not part of a solid phase which would limit mobility and slow spin-lattice relaxation. In fact, solution ^{29}Si-NMR allows us to follow the silicon site distribution past the gel point without any apparent discontinuity or loss of ^{29}Si-NMR signal [22]. The implication is that, even after gelation, polymer segments are quite mobile as if they are still in a sense 'in solution' — solid-like rheology notwithstanding.

In systems with high water content ($[\mathrm{H_2O}]/[\mathrm{TEOS}] > 8$) hydrolysis can proceed nearly to completion, while in systems with low water content ($[\mathrm{H_2O}]/[\mathrm{TEOS}] < 1$) hydrolysis is still incomplete even when there is essentially no free water left. Moreover, the extent of condensation is stoichiometrically limited by the amount of water available. Inspection of ^{29}Si-NMR spectra shows that the availability of water as a reactant in the course of TEOS polymerization plays an important role in stoichiometrically determining kinetic pathways of gel or particle evolution. High water concentration ($[\mathrm{H_2O}]/[\mathrm{TEOS}] > 8$) allows practically complete hydrolysis of TEOS (cf. TEOS + $4\mathrm{H_2O}$

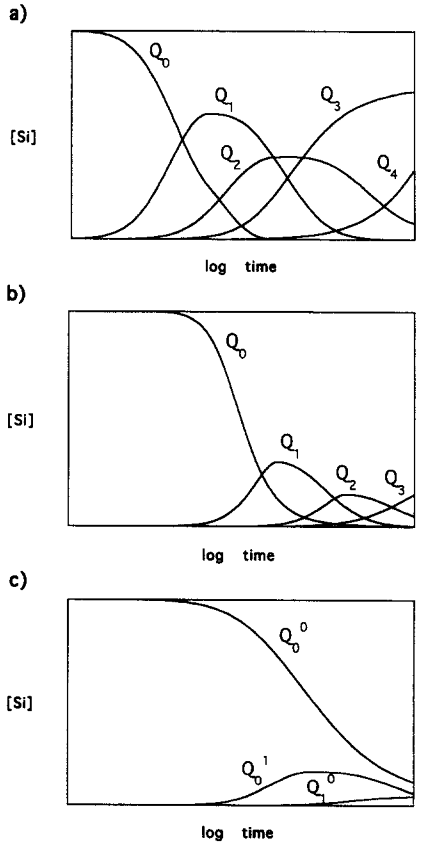

Fig. 2. Schematic depiction of the evolution of silicon site distributions. (a) pH 1 to 3.5, (b) pH 3.5 to 4, (c) pH 4 to 12.

→ $Si(OH)_4 + 4EtOH$) and its condensation products (if phase separation does not interfere). Medium water concentration ($[H_2O]/[TEOS]$ between 2 and 8) allows substantial hydrolysis and (in principle) full condensation to anhydrous silica (cf. $TEOS + 2H_2O \rightarrow SiO_2 + 4EtOH$). Very low water concentration ($[H_2O]/[TEOS] < 1$) allows only limited hydrolysis and condensation, with retardation being more severe as water concentration decreases. In these 'water starved' systems water is the limiting reactant and such systems are ideal for study of kinetics and thermodynamics of early steps in TEOS polymerization [27,29].

For systems with less [HCl] (between 5×10^{-4} and 1×10^{-4} M) we see a gradual disappearance of ^{29}Si-NMR signal over time (Fig. 2b) even though for silicon sites in small oligomers the spin-lattice relaxation times T_1 (in the presence of the relaxation agent) remain substantially unchanged [30]. This indicates that some of the silicon sites accumulate in species that restrict mobility. For systems with even less HCl ($< 1 \times 10^{-4}$ M) or with NaOH we observe only Q_0^0, Q_0^1 sites (i.e., unhydrolyzed TEOS and singly hydrolyzed monomer) with barely detectable signals for dimer or more hydrolyzed monomer. The total intensity of ^{29}Si-NMR signal diminishes even more quickly (Fig. 2c). Similar patterns of signal loss have been observed by others in systems with [HCl] around 1×10^{-4} M [21,31], in systems without any catalyst [32] and in basic systems with $[NH_3] \geq 5 \times 10^{-2}$ M [28,33].

At very high base concentrations ($[NaOH] \geq 0.1$ M), though, the formation of Q_1^0 sites corresponding to the dimer has been detected, but no Q_0^1 sites are detected [23]. Rapid and extensive precipitation and corresponding loss of ^{29}Si-NMR signal are observed. This signal is recovered in Magic Angle Spinning (MAS) NMR experiments, showing typically highly condensed Q_3 and Q_4 sites (e.g., [34]). The rotational mobility of the silicon is $< 10^5$ Hz, which suggests that these sites belong to particles with diameter of at least 200 Å [35]. The water content shows little effect on the solid structure or the ^{29}Si-NMR spectra patterns in neutral and basic systems.

The patterns shown here are not inevitable. Although SiO_2 sol-gel synthesis kinetic studies have been almost exclusively performed in batch reactors, the reactor residence time can be a very useful process variable for controlling sol-gel systems. Multistep procedures have been used to demonstrate that a continuum of silicon site distributions (Q_i^j) can be prepared [19]. Multistep and/or continuous approaches manipulate the reaction routes and dynamics of TEOS polymerization to achieve states (defined by assembly of intermediates) which are not accessible in simple batch reactors. Even so, we will devote our attention through the remainder of this review to explaining the patterns of Fig. 2.

3. Monomer

In this section we will address only the first few reactions that occur after the addition of TEOS to the reaction mixture. The reactions of the monomer can be unequivocally followed by ^{29}Si-NMR spectroscopy in all conditions. Data accumulated by various groups in the last 10 years has allowed identification of the kinetics of TEOS monomer hydrolysis and dimerization. This examination will also set the stage for the next section, where we will discuss trends encountered with polymer growth. Though miscibility is an important issue in the TEOS polymerization (and we will discuss it shortly), let us for now consider only initial compositions that provide homogeneous reaction mixtures at the instant of mixing and before any reaction has taken place (shaded region in Fig. 3).

3.1. Hydrolysis

The first reaction is of course hydrolysis to convert alkoxy groups to condensation-prone hydroxy groups. The monomer hydrolysis reactions are

$$Q_0^j + H_2O \underset{\kappa_{h0}^{-j}}{\overset{\kappa_{h0}^j}{\rightleftharpoons}} Q_0^{j+1} + EtOH$$

Here κ_{h0}^j and κ_{h0}^{-j} are the second order rate constants of the jth monomer hydrolysis and reesterification, respectively, defined with respect to concentrations of silicon sites Q_0^j. Subsequent hydrolysis of monomers ($j = 0$–3) can ultimately lead to the fully hydrolyzed silicic acid Q_0^4. Units are important here. Even if the reactivities of ethoxy groups of differently hydrolyzed monomers were equal, the more hydrolyzed monomers have fewer reactive groups and so the hydrolysis rate constants κ_{h0}^j would decrease in the proportion 4:3:2:1. To avoid the interference of such statistical effects, we will report all rate constants and hydrolysis equilibrium constants defined with respect to concentrations of reacting ethoxy groups or hydroxy groups, e.g.,

$$Q_0^0\text{–OEt} + H_2O \underset{k_{h0}^{-1}}{\overset{k_{h0}^1}{\rightleftharpoons}} Q_0^1\text{–OH} + EtOH$$

and so on for subsequent hydrolysis and reesterification of monomer, where Q_0^0_OEt denotes the ethoxy group attached to the Q_0^0 silicon site. The corresponding functional group hydrolysis equilibrium constant is then $K_{h0}^1 = k_{h0}^1/k_{h0}^{-1}$.

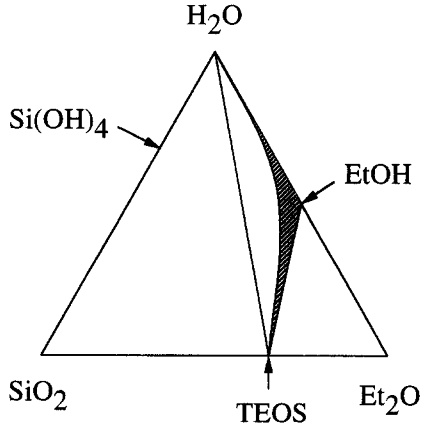

Fig. 3. Miscibility diagram for TEOS/EtOH/H_2O inserted into the oxide composition simplex SiO_2–Et_2O–H_2O (adapted from [36,37]). The shaded area corresponds to initially miscible composition.

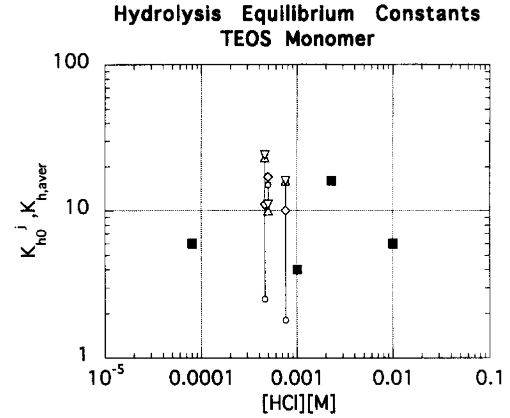

Fig. 4. Hydrolysis equilibrium constants for TEOS-derived monomers. Filled symbols: averaged equilibrium constants $K_{h,aver}$ (data from [26,39]). Open symbols: detailed equilibrium constants K_{h0}^j (data from [24,38]). O: $j = 1$, ◇: $j = 2$, Δ: $j = 3$, ∇: $j = 4$.

In the presence of acid ([HCl] $\approx 1 \times 10^{-3}$ M) the hydrolysis equilibrium constants K_{h0}^j do not change significantly with the extent of hydrolysis [1] [38,24]. We are not aware of any quantitative information on hydrolysis equilibria for other silicon alkoxides, but it seems they are similar to those of TEOS since the observed degrees of hydrolysis of TEOS and TMOS are similar [18]. In Fig. 4 we plot values of individual hydrolysis equilibrium constants K_{h0}^j together with average hydrolysis equilibrium constants $K_{h,\text{ aver}}$ (averaged over all degrees of condensation and hydrolysis of silicon sites) that we have been able to calculate from published experimental data over a broad range of acid concentrations [26,39]. As should be expected for a catalyst, the acid concentration has no apparent influence on hydrolysis equilibrium constants. In principle, at very high acid concentration, protonation of the silanol and formation of siliconium cation may become important and can shift the hydrolysis equilibrium. However,

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[1] Note, however, that hydrolysis equilibrium constants defined on the basis of silicon sites decrease in statistical proportion with the extent of hydrolysis [24].

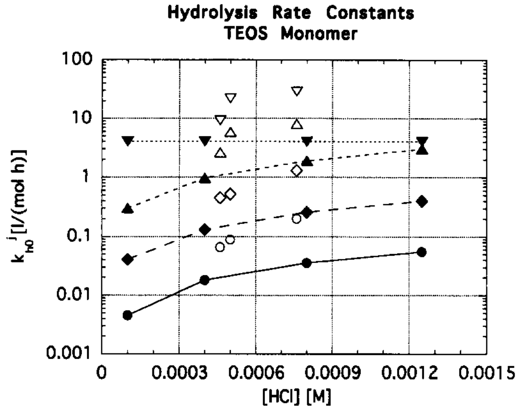

Fig. 5. Hydrolysis rate constants k_{h0}^j for TEOS-derived monomers in the presence of acid. Filled symbols: data from [41]. Open symbols: data from [24,38]. O: $j = 1$, ◇: $j = 2$, Δ: $j = 3$, ∇: $j = 4$.

there is no evidence for significant concentrations of such cations in the presence of moderate acid (up to $[HCl] = 1 \times 10^{-2}$ M; cf. [40]). The enthalpy of hydrolysis is small [24], so hydrolysis equilibrium constants should be fairly insensitive to temperature.

It has been suggested, and then confirmed quantitatively [24,32,38,41], that in the presence of acid ($[HCl] < 3 \times 10^{-3}$ M) the hydrolysis rate constants k_{h0}^j increase with the extent of hydrolysis (i.e., with j) and with acid concentration (Fig. 5). Activation energies for hydrolysis of TEOS in the presence of acid are all 11–16 kcal/mol, and subsequent hydrolyses seem to have a similar activation energy [24,39]. Reported hydrolysis rate constants k_{h0}^1 for silicon alkoxides with larger alkoxides are slightly lower than those for TEOS [42], while those reported for TMOS in water/methanol mixtures are only slightly higher than for TEOS at corresponding acid concentrations [32,43,44]. However, hydrolysis rate constants k_{h0}^j for TMOS do not seem to change with the extent of hydrolysis, j [45].

In the presence of base, the hydrolysis equilibrium seems to be more favorable than in the presence of acid. For instance, hydrolysis with deuterated ethanol at $[NH_3] = 5.6 \times 10^{-1}$ M showed no measurable reesterification [46]. This is in agreement with previous suggestions that, kinetically, the protonation of silanol to $\equiv SiOH_2^+$ is necessary to facilitate its reesterification (cf. [12]). Thermodynamically, though, we would not expect hydrolysis equilibrium constants as defined above to vary with the catalyst (acid or base) concentration. We suspect that the shift in hydrolysis equilibrium distribution in the presence of base can be attributed to the coupled deprotonation reaction equilibria (conversion of silanols to $\equiv SiO^-$). For example, for singly hydrolyzed TEOS we need to consider following equilibria:

$$Si(OEt)_4 + H_2O \rightleftharpoons Si(OEt)_3(OH) + EtOH$$

$$Si(OEt)_3(OH) + OH^- \rightleftharpoons Si(OEt)_3O^- + H_2O$$

The silanols are substantially deprotonated in the presence of base ($pK_a = 9.8$ for Q_0 in aqueous solutions; [40]) and thus the extent of the first reaction increases even at constant K_{h0}^1.

It appears that base is also a very good catalyst for TEOS hydrolysis. The rate of TEOS hydrolysis has been measured in the presence of ammonia (weak base with $pK_a = 9.25$ in water, [47]) in particle producing systems [28,33,46,48–50]. The hydrolysis rate constant k_{h0}^1 increases with increasing base concentration for $[NH_3]$ between 0.05 and 3 M (Fig. 6). In systems with high TEOS concentration (2 M), the buffering action of substantial amount of particle surface silanols tends to decrease pH in

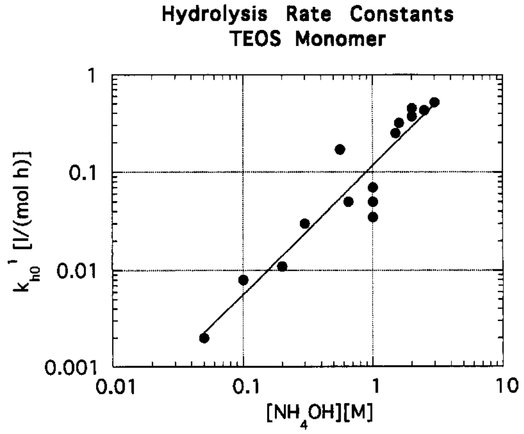

Fig. 6. Hydrolysis rate constants k_{h0}^1 for TEOS monomer in the presence of base. Data from [28,33,46,48–50].

the system due to surface silanol acidity ($\mathrm{p}K_a = 6.8$ for Q_3 vs. $\mathrm{p}K_a = 9.8$ for Q_0 in aqueous solutions; [40]) and thus to lower the hydrolysis rate constant. It is probably the interference by silanol deprotonation that has led to some worry that hydrolysis is non-first order in TEOS or water (e.g., [42]). The activation energy for TEOS hydrolysis in the presence of base was calculated to be 6 kcal/mol [50].

3.2. Dimerization

The next simple reaction of the monomer is the formation of the dimer by condensation of hydroxy (silanol) groups. This reaction can be monitored unambiguously in all conditions; if necessary, multistep and CSTR processing can be used when simple batch processing does not exhibit it readily. Condensation can proceed either between two silanol groups (water producing condensation) or between the silanol and ethoxy groups (alcohol producing condensation):

$$Q_0^j\text{–OH} + Q_0^j\text{–OH}$$
$$\rightarrow Q_1^{j-1}\text{–OSi} + Q_1^{j-1}\text{–OSi} + H_2O$$
$$Q_0^j\text{–OH} + Q_0^j\text{–OEt}$$
$$\rightarrow Q_1^{j-1}\text{–OSi} + Q_1^j\text{–OSi} + \mathrm{EtOH}$$

As suggested by the nomenclature, we again define rate constants in terms of reactive group concentrations and not silicon site concentrations. Although we have written the reactions as irreversible, we will comment below on cases where reversibility becomes a serious consideration. Also, although it is obvious that the two siloxy groups shown as products are members of the same dimer molecule, a mean field functional group kinetic model can not take this into account; in Section 4.2 we will discuss the breakdown of the mean field approach.

Assink and Kay elegantly demonstrated that for TEOS systems the virtually irreversible water producing condensation is dominant in the presence of acid ($[\mathrm{HCl}] = 2 \times 10^{-3}$ M; [29]). TEOS was hydrolyzed with a very restricted amount of water ($[H_2O]/[\mathrm{TEOS}] < 0.5$) so that the equilibrium between partially hydrolyzed monomer species was rapidly achieved and virtually all water was consumed. The initial rate of dimer formation and corresponding concentrations of monomer hydroxy and ethoxy groups were monitored in systems with varying water content and hence varying degree of monomer hydrolysis. It was possible to unequivocally determine the initial rates of water producing and ethanol producing condensation [2]. Most of observed kinetic experimental data for TEOS can be explained by considering just the forward water producing condensation ($[\mathrm{HCl}] = 5 \times 10^{-4}$ to 3×10^{-3} M, [26,38,41]). Reversibility is negligible in all of these experiments.

We should caution, though, that tetramethoxysilane (TMOS) dimerization is not so simple. Condensation of TMOS-derived silanols proceeds by both water and alcohol producing condensation [14] and it is noticeably reversible [45,51,52]. At high acid concentration ($[\mathrm{HCl}] = 5 \times 10^{-2}$ M) where dimerization is fast (see below), the equilibrium between TMOS monomer and dimer is reached rapidly, though at low acid concentration ($[\mathrm{HCl}] = 2 \times 10^{-3}$ M) where dimerization is slower, the dimer breakup is kinetically less significant than the forward condensation to Q_2 silicon sites [45]. Moreover, siloxane hydrolysis of the TMOS derived dimer is observable in the presence of base ($[\mathrm{KOH}] = 0.05$ M, [52]).

We will define the second order rate constant k_{00} for water producing dimerization of TEOS-derived monomers in terms of monomer silanol group concentrations regardless of the degree of hydrolysis of the participating monomers. The available data [26,29,38,41] show that the rate constant k_{00} increases with increasing acid concentration for [HCl] between 1×10^{-4} and 2×10^{-3} M (Fig. 7). This is in agreement with

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[2] Assink and Kay assumed irreversible complete hydrolysis, but their conclusion remains true even for reversible equilibrium hydrolysis.

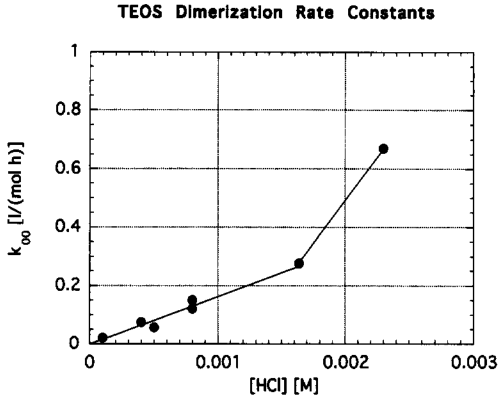

Fig. 7. Dimerization rate constants k_{00} for TEOS-derived monomers in the presence of acid. Data from [38,29,26,41].

observations at varying compositions [27] and at elevated temperature [31]. This also seems consistent with the forward silanol dimerization rates in acidic aqueous/methanol systems [53,54,14,44] and from ion exchanged sodium silicate solutions [51,55] at comparable acid concentrations.

In solutions with very low acid concentration ($[HCl] \leq 10^{-4}$ M) and in basic solutions, it is difficult to observe dimerization of TEOS in a simple batch process since there is now significant interference by precipitation (see below). Dimerization of TEOS appears to be fast again at high base concentration ([NaOH] = 0.1 M, [23]) where dimerization rate constant is similar in magnitude to those observed in highly alkaline aqueous systems ($k_{00} = 10^0$–10^2 1/(mol h), [56]).

Silanol polymerization is clearly reversible in neutral and basic aqueous solutions (e.g., [56,57]). The equilibrium constants K for dimerization of the uncharged silicic acid (the fully hydrolyzed and non-ionized monomer),

$$2\,Si(OH)_4 \rightleftharpoons Si_2O(OH)_6 + H_2O$$

can be calculated from reported concentration data for acidic TMOS systems ($K = 40$) and for a neutral aqueous system ($K = 20$); these values agree qualitatively. Thus the dimerization equilibrium constant as defined by this reaction does not depend significantly on pH, i.e., acid or base are just catalysts. It is important to note, though, that when the silicic acid deprotonates at high pH (pK_a = 9.8 for Q_0 in aqueous solutions, [40] the coupling of deprotonation reactions, e.g.,

$$Si(OH)_4 + OH^- \rightleftharpoons SiO(OH)_3^- + H_2O$$

and so on to more deprotonated monomers,

$$Si_2O(OH)_6 + OH^- \rightleftharpoons Si_2O_2(OH)_5^- + H_2O$$

and so on to more deprotonated dimers),with dimerization can cause the base to influence the extent of dimerization (as for hydrolysis, see above). Thus adding base tends to shift the dimerization equilibrium toward monomer (e.g., [58]). The action of base to shift the polymerization extent is probably best understood as shifting the deprotonation equilibria; this shifts the equilibrium distribution between all variously charged monomers on one hand and all variously charged dimers on the other hand, and the monomer is able to carry more negative charge per silicon than dimer.

Summarizing, we see a pattern similar to that observed for γ-glycidoxypropylsilanetriol dimerization in buffered D_2O solutions [59]. The minimum dimerization rate is at pD 4.5 and the dimerization rate constant increases one order of magnitude for each pD unit to the above and below pD 4.5. To explain this pattern, it was suggested (in agreement with Iler [40]) that for pH values above the isoelectric point, condensation proceeds by a nucleophilic mechanism involving the deprotonated silanol, whereas for pH values below the isoelectric point condensation proceeds by an electrophilic mechanism involving the protonated silanol.

The effect of water concentration on condensation rate constants appears to be weak in the presence of strong acid but the reason remains an open question. However, note that acid–base equilibria in mixed water/ethanol solvents are sensitive to water concentration [47,60,61], with the most pronounced effects for weak acids and bases [62]. Hence, the measurement and interpretation of pH in water/ethanol mixtures requires special care [1].

3.3. Solution metastability

The ternary miscibility diagram of TEOS–EtOH–H_2O [3] (Fig. 3) determines the range of compositions which provides a homogeneous solution immediately after mixing the components and before any reaction takes place [36,2]. It is important to realize, though, that we are even more interested in whether, after reaction, the system will remain a single homogeneous phase. There are situations where the answer does not strictly depend on the equilibrium miscibility of liquid phases or the solubility of a solid phase. For example, although the unhydrolyzed monomer may be perfectly miscible with the solvent, the oligomers produced by hydrolysis and condensation of the monomer may become immiscible. These polymers may phase separate from the solution until their concentration falls to the relatively low SiO_2 solubility limit — this is seen in alkaline systems. On the other hand the oligomers may remain metastable in solution — this is seen in acidic systems. We also see situations where, although TEOS is not miscible, its hydrolyzed and condensed offspring are — this is also seen in acidic systems.

Unfortunately, we are not aware of any explicit solubility or metastability data for partially hydrolyzed TEOS monomers and its oligomers; this would be difficult to obtain but very useful. We can, however, easily study the miscibility of the fully hydrolyzed monomer (silicic acid) in water/ethanol mixtures. Silicic acid is commonly observed at high concentrations in acidic water/ethanol mixtures ([26]; and references therein) and it is well known that in the presence of acid ([HCl] $\geq 5 \times 10^{-4}$ M) in both alcoholic and aqueous solutions silicic acid undergoes homogeneous polymerization without precipitation, even though the equilibrium solubility of silica in such mixtures is very low (about 2 mM; [40])! Such systems are clearly metastable against silica precipitation. However, in basic and neutral solutions, the miscibility of aqueous silicic acid solutions with ethanol is very limited [63] and precipitation of silica particles occurs readily until the dissolved silica concentration falls to the equilibrium solubility of SiO_2.

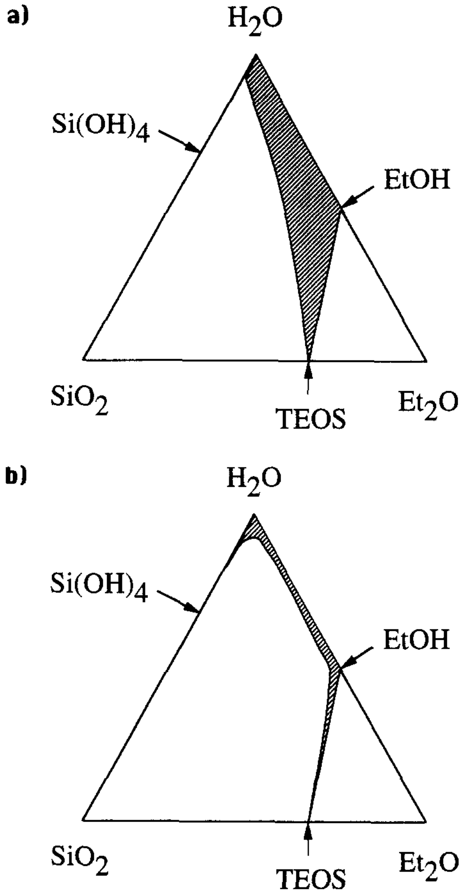

Fig. 8. Schematic metastability diagrams of SiO_2–Et_2O–H_2O system. (a) Low pH (e.g., 2), (b) high pH (e.g., 12). Shaded areas correspond to metastable solutions.

We illustrate this situation by drawing quali-

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[3] We show the miscibility diagram embedded in the oxide composition simplex SiO_2–Et_2O–H_2O. Our choice of the composition simplex is dictated by the desire to include aqueous silica systems, so that we could graphically describe any molar combination of $Si(OH)_4$, TEOS, EtOH and H_2O. The minimum simplex satisfying this requirement is SiO_2–Et_2O–H_2O. Note that we do not consider the possibility of diethylether formation, so that the triangle TEOS–EtOH–Et_2O is not accessible.

tative metastability diagrams of silica–ethanol–water systems in their oxide composition simplex SiO_2–Et_2O–H_2O (Fig. 8). The practically accessible composition region (to maintain a single liquid phase) is larger at low pH and smaller at high pH than is implied by the TEOS–EtOH–H_2O miscibility diagram (Fig. 4). Hydrolyzed and condensed TEOS derivatives are soluble at low pH, but they precipitate at high pH. At this stage of discussion it is still not clear whether precipitation in alkaline solutions might be the indirect result of polymerization kinetics. It has been shown that certain condensation kinetics can lead to precipitation-like high density aggregates [64]. We will address these points shortly.

4. Oligomers

As we account for reactions involving a larger number of silicon sites, it becomes necessary to consider kinetic lumping procedures, where lumping means that the kinetic model regards certain collections of sites as kinetically identical. Several different lumping procedures have been employed, each with a specific set of assumptions about hydrolysis and/or condensation reactions. The simplest approach is based on the random branching polymerization concept [15], whereby it is assumed that each functional group is equally reactive regardless of its chemical environment. In TEOS systems, then, this lumping procedure would recognize only two reactions, with no distinction of what kind of silicon sites participate in the reactions:

$$Q\text{–OEt} + H_2O \rightleftharpoons {\equiv}Q\text{–OH} + \text{EtOH}$$

$$Q\text{–OH} + Q\text{–OH} \rightarrow Q\text{–OSi} + Q\text{–OSi} + H_2O$$

Although this simple model can adequately describe TEOS polymerization at very early times, it fails in systems with extensive condensation [14,45]. For example, the apparent condensation rate constant sharply decreases with conversion during TEOS polymerization in the presence of acid ([HCl] ≈ 10^{-3} M) and excess water [27]. Clearly the Q–OH reactivity decreases as the reaction proceeds. It can be hypothesized that a more appropriate lumping procedure is to allow the reactivities for different Q_i–OH and Q_i–OH to change as the silicon site connectivities, i and i, increase — this is known as a first shell substitution effect on the condensation rate constant caused by conversion of a neighboring ethoxy or hydroxy group to a siloxy group. We will abbreviate this as a FSSE as ≡SiOEt → ≡SiOSi≡ for condensation. There is little indication to date as to whether the effect of ≡SiOH → ≡SiOSi≡ substitution is much different than ≡SiOEt → ≡SiOSi≡, but coupling among these substitution effects is inevitable due to hydrolysis reversibility in the presence of acid [24].

An approach allowing such substitution effects [14] distinguishes 15 silicon sites Q_i^j according to their first shell chemical environment (cf. Section 2). Within this framework one can speak of the first shell substitution effect FSSE for the hydrolysis reaction rates

$$Q_i^j\text{–OEt} + H_2O \underset{k_{hi}^{-j}}{\overset{k_{hi}^j}{\rightleftharpoons}} Q_i^{j+1}\text{–OSi} + \text{EtOH}$$

and condensation reaction rates

$$Q_i^j\text{–}OH + Q_i^j - OH \rightarrow {}^{k_{ii}} Q_{i+1}^{j-1} - OSi + H_2O.$$

For example, a positive FSSE for hydrolysis rate constants as ≡SiOEt → ≡SiOH means that as ethoxy groups are substituted by hydroxy groups on the silicon site, hydrolysis of ethoxy groups on the site becomes progressively faster. We can also speak of FSSE for hydrolysis equilibrium constants

$$K_{hi}^j = \frac{k_{hi}^j}{k_{hi}^{-j}}$$

As before, condensation rate constants are easily measured only as average for differently hydrolyzed silicon sites (cf. k_{00} in Section 3.2). We will refer as k_{ii} to the second order rate constant of the condensation between silanol groups at silicon sites Q_i and $Q_{i'}$ with connec-

Table 1
Average degrees of hydrolysis and condensation rate constants at $[\mathrm{HCl}] = 2.3 \times 10^{-3}$ M [a]

i	0	1	2
$\langle j \rangle$ for Q_i	1.3	1.0	0.76
k_{i0} [l/(mol h)]	0.67	0.57	0.48
k_{i1} [l/(mol h)]	0.57	0.080	0.058
k_{i2} [l/(mol h)]	0.48	0.058	0.0013

[a] Data from [26].

tivities i and i', respectively, averaged over actual degrees of hydrolysis j and j' of these sites.

4.1. First shell substitution effects (FSSE)

Both hydrolysis and condensation rate constants depend on the first shell chemical environment of silicon. In the presence of acid, the hydrolysis rate constants of the dimer follow the same trends as for the monomers, still exhibiting the positive FSSE (as ≡SiOEt → ≡SiOH) for hydrolysis and with similar values of the rate constants. Q_2 sites hydrolyze somewhat more slowly than Q_0 and Q_1 sites [24,25,65]. Moreover, hydrolysis equilibrium constants are only weakly dependent on the extent of condensation [26].

In the presence of acid, hydrolysis seems so much faster than condensation that, unless precipitation interferes (i.e., for $[\mathrm{HCl}] > 1 \times 10^{-3}$ M, see below), hydrolysis equilibrium is established before the hydrolyzed silicon sites undergo any substantial condensation.

At high acid concentrations the condensation rate constants in TEOS polymerization decrease strongly with increasing connectivity of the sites of the hydroxy groups entering condensation. In Table 1, we list average degrees of hydrolysis $\langle j \rangle$ for silicon sites and a selection of condensation rate constants determined at $[\mathrm{HCl}] = 2.3 \times 10^{-3}$ M [26]. The magnitude of the rate constants seems to be governed by the connectivity of the least connected site entering the condensation, since rate constants k_{ij} are similar to k_{i0}.

In the case of nearly complete hydrolysis ($[\mathrm{H_2O}]/[\mathrm{TEOS}] > 8$ and $[\mathrm{HCl}] > 1 \times 10^{-3}$) one can observe the evolution of exclusively fully hydrolyzed Q_i silicon sites. The negative FSSE (as ≡SiOEt → ≡SiOSi≡) for condensation is indicated by the delayed appearance of more condensed sites (Q_3, Q_4) than in the random polymerization model [22]. The negative FSSE (as ≡SiOEt → ≡SiOSi≡) for condensation persists for other solvent systems, including methanol/water [18], or just water [55]. At lower acid concentrations ($[\mathrm{HCl}] = 5 \times 10^{-4}$ to 8×10^{-4} M), however, there seems to be only a much weaker dependence of condensation rate constants on the site connectivity [27,38]. A negative FSSE for TMOS condensation has also been quantitatively evaluated in the presence of acid ($[\mathrm{HCl}] = 1.6 \times 10^{-3}$ M); it appears to be more severe for water producing condensation than for methanol producing condensation [66].

Table 2 summarizes the first shell substitution effects for the hydrolysis and condensation caused by the two relevant first shell substitutions in the presence of acid. Little is known yet about substitution effects for condensation rate constants in the presence of base. Even less is known about substitution effects for condensation equilibrium constants in general. However, as noted in the section on the monomer dimerization, in the presence of base it appears that condensation equilibrium is shifted toward

Table 2
Summary of first shell substitution effects in the presence of acid

	≡SiOEt → ≡SiOH	≡SiOEt → ≡SiOSi≡
Hydrolysis rate constants	Strong positive	Negative ($Q_1 \to Q_2$)
Hydrolysis equilibrium constants	None	Weak
Condensation rate constants	Weak	Negative, strong with high acid

smaller species because of coupling with silanol deprotonation equilibria.

4.2. Cyclization and non-mean field kinetics

The mean field functional group kinetics formalism with FSSE lumping provides an adequate description of TEOS polymerization when there is no extensive formation of small rings [26]. Although it is tempting to assume that branching polymerization with appropriate FSSE for condensation can be applied throughout the TEOS polymerization up to the gelation point, we are not provided with this luxury. Even with the most severe negative FSSE for condensation with mean field kinetics, random branching of a tetrafunctional monomer could achieve at most 50% conversion at the gelation point [67]. However, the observed gel point conversion for TEOS polymerization in the presence of acid ($[\mathrm{HCl}] = 5 \times 10^{-4}$ to 5×10^{-1} M) falls into a remarkably narrow range 80–85%, regardless of composition ($[\mathrm{TEOS}] = 1$–3 M, $[\mathrm{H_2O}]/[\mathrm{TEOS}] = 2$–$10$) and temperature (25–80°C) [68].

This unusually high gel point conversion is consistent with the preferential formation of small cage-like intermediates and their subsequent assembly into the gel [22,68]. Three- and four-member rings are indeed commonly observed intermediates during TEOS polymerization in the presence of acid (only 4-membered rings are common in TMOS systems; [18]). Cyclization is also common in aqueous systems both with acids [55] and with bases [58]. The formation of three member rings by intramolecular cyclization of the linear TEOS trimer is kinetically preferred against intermolecular condensation in the presence of acid ($[\mathrm{HCl}] = 5 \times 10^{-4}$ M) [25]. Ring formation, however, cannot be accounted for with mean field branching kinetics, so these approaches becomes less successful as the preference for ring formation becomes stronger, such as in highly acidic TEOS [27] or TMOS [44] systems.

The evidence for extensive cyclization during TEOS polymerization naturally raises concern about the validity of the condensation rate constants for branching discussed in the previous section since these rate constants were calculated using a mean field approximation for silicon sites. Cyclization, when detected, was erroneously treated as bimolecular reaction of two silicon sites entering condensation. However, we can remain confident in the trends shown in Table 1 since the error introduced by any cyclization would lead one to underestimate the importance of FSSE for condensation. If we could correctly account for non-mean field cyclization, we would still see an even stronger negative FSSE for 'true' bimolecular rate constants. Moreover, simulations show that even with substantial extent of ring formation, 'true' bimolecular condensation rate constants are only up to 50% lower than lumped rate constants calculated from crude mean field approximation. Current progress is being made in the correct, non-mean field evaluation of cyclization rates [27].

4.3. Are heterogeneous gels and particles due to a positive FSSE for condensation?

Polymerization of TEOS, at least in the presence of acids, commonly has been thought of as a homogeneous polymerization process, although certainly complicated by strong substitution effects and extensive cyclization. At pH 3.5–4 (as measured in the solution), though, gels become mesoporous and gel structure is no longer homogeneous [1]. It has been shown [64] that heterogeneous, dense polymer gels with high fractal dimension might result from condensation with strongly positive FSSE. Because gel times for TEOS polymerization decrease with increasing nominal pH between 2 and 4, it has in fact been speculated that condensation becomes faster with increasing pH and that there is a positive FSSE (as $\equiv\mathrm{SiOEt} \rightarrow \equiv\mathrm{SiOSi}\equiv$) for condensation [40]. This has been rationalized by a nucleophilic condensation mechanism, suggesting that the preferred condensation reaction is between the least ionized silanol (thought to be on the least condensed, Q_0, site) and the most ionized silanol (thought to be on the most condensed, Q_3, site) [12]. We are led to ask, then, whether transition in gel structure is due to a positive FSSE for k_0^i as i increases.

The experimental evidence discussed above suggests that the answer is either no or that the picture is more complicated. First, the rate of TEOS-derived monomer dimerization *decreases* with increasing nominal pH between 2.5 and 3.5. Second, there is no strong FSSE (as $\equiv$SiOEt → $\equiv$SiOSi$\equiv$) for condensation of monomer hydroxy groups with those of differently connected silicon sites up to a nominal pH of 3.5. In fact, the monomer condensation rate in general does not correlate with the time required to gel [53]. Even in very basic particle producing systems, Bogush and Zukoski demonstrated that condensation reactions between monomer and the particle surface do not govern particle growth or gelation [49].

We conclude that gelation rates do not correspond to monomer condensation rate constants k_{0i}. What then is governing gelation kinetics up to nominal pH of 3.5? Spectroscopic and kinetic evidence suggests that by the time required for gelation the less condensed silanols Q_0 and Q_1 have long vanished. In fact, only more condensed Q_2 and Q_3 silanols are present for most of the reaction period (e.g., [22]). Thus, if gelation is due to homogeneous polymerization, then gelation kinetics are governed largely by the higher condensation rate constants k_{22}, k_{23}, k_{33} and corresponding cyclization rate constants.

The question becomes whether the transition in gel structure might be due to a positive FSSE for $k_{ii'}$ as i,i' increase and whether $k_{ii'}$ $(i,i' \geq 2)$ increase with pH. There is the strong negative FSSE (as $\equiv$SiOEt → $\equiv$SiOSi$\equiv$) for condensation at nominal pH < 3. While there seems to be only a weaker negative FSSE for condensation at pH between 3 and 3.5, it seems unlikely that at the transition from homogeneous to heterogeneous gels there is suddenly a strong positive FSSE. One the other hand, we do acknowledge that the rate constant k_{33} might be expected to increase with pH between 2 and 4, since for Q_3 the isoelectric point in aqueous solutions is at pH ≈ 2 [40].

It is important to note that in later stages of TEOS polymerization, when conversion is high ($> 60\%$) and the system is approaching the gel point, unusually slow condensation kinetics has been observed [22]. This effect does not appear to be caused by decrease of molecular diffusion coefficients (the viscosity remains fairly low up to the gel time; cf. [12]), but rather by the decrease of segmental diffusion. This is caused by the trapping of highly condensed silicon sites upon entanglement and segregation. This situation of course leads to the breakdown of the mean field approach to gelation. It remains to be seen how significant this breakdown is in eroding our ability to relate kinetic and structural features of gelation to underlying condensation kinetics.

5. Precipitation

An alternative to the positive FSSE condensation rationale for particle formation is that oligomers simply become able to precipitate. The possibility of straightforward phase separation in sol-gel systems has been discussed before [69,70] and it was early recognized in basic systems where colloidal particles obviously form [71].

The miscibility of a polymer with a particular solvent system depends on temperature, polymer size, functional groups and charge. The last two factors have been often overlooked in alcoholic silicate systems. Let us summarize the known features of the crossover between gelation and precipitation in TEOS polymerization and consider whether precipitation might simply be a true phase separation of low molecular weight intermediates rather than the growth of dense polymers.

It is instructive to review purely aqueous systems. Iler suggested a mechanism of gel formation in aqueous silicate systems postulating formation of primary particles as small as 1 nm aggregating to extended networks and gelling for $pH < 7$ or further growing to colloidal dimensions at $pH > 7$ [40]. The formation of primary particles in aqueous solutions has been supported experimentally by SAXS [72] and by monitoring soluble silica [73,74]. At pH 4 the size of primary particles is less than 1 nm [72] and so they correspond to silicate oligomers with not more than 10–12 silicon atoms [75]. For $pH > 5$ though nucleation of larger silica particles has been observed [73,74] in aqueous solutions.

It may be that Iler's view is essentially correct even for the TEOS alcoholic systems, only in this case there is a sharp demarcation between homogeneous and heterogeneous gels with transition at about pH 3.5. SAXS investigation of TEOS systems with $pH < 3$ suggest only the formation of oligomers with diameter 0.5–1 nm and their subsequent aggregation to fractal clusters with fractal dimension D between 1.75 and 2.1 for systems with high water content ($[H_2O]/[TEOS] > 4$) and $D = 1.38$ for a water starved system ($[H_2O]/[TEOS] = 1$) [76,22]. However, at pH 4 and $[H_2O]/[TEOS] = 4$, 'particles' with radius of gyration $R_g = 4$ nm are observed after 48 h at 25°C. In a basic system ($[NH_4OH] > 0.001$ M) with $[H_2O]/[TEOS] > 1$, dense particles with $R_g = 6$ nm are observed after 48 hours at 25°C [77,78].

These SAXS results are consistent with the observed microstructure of resulting gels [1]. Gels prepared from TEOS at pH (as measured in the solution) between 1 and 3.5 are homogeneously microporous (meaning no dense regions) regardless of substantial variation in their gel time. However, gels prepared at pH (as measured in the solution) above 3.5 are mesoporous, their microstructure is affected by solution pH, with gel times relatively insensitive to pH. These gels are apparently formed from primary particles of colloidal dimensions. The SAXS results are also consistent with NMR observations. The disappearance of peaks corresponding to oligomer species, the decrease in overall signal intensity with time in ^{29}Si-NMR spectra at $pH > 3.5$, and the qualitative similarity of spectra for systems with pH between 4 and 12 are all consistent with the concept of rapid formation of colloidal size particles.

How are these colloidal size particles formed? Though we have already ruled out strong positive FSSE for TEOS condensation at $pH < 4$, it is harder to assess condensation kinetics at higher pH because heterogeneous gels or precipitates are rapidly formed in simple batch polymerization processes. Nevertheless, we can conclude that for $pH < 3$ the size of primary particles corresponds to small oligomeric cages, while for $pH > 4$ primary particles have colloidal dimensions. ^{29}Si-NMR and gel microstructure studies indicate a rather sharp transition between oligomeric and colloidal size primary particles around pH 3.5.

We stress that in multistep processes it is well known that polymers might be formed in acid conditions and then subjected to basic conditions and gels of low fractal dimensions might be formed rather than dense spherical colloids familiar from simple batch base catalyzed systems. Such processes (e.g., [12]) are excellent examples of the microstructure engineering that might be accomplished as we come to understand the underlying kinetics and equilibria.

6. Conclusions and implications

Based on the reviewed information, we suggest the following scenario for TEOS polymerization in batch systems. Different primary structures are formed in different composition regimes because we are in different kinetic regimes. At $pH < 3$, condensation leads to small, cage-like units, and at $pH > 3.5$, phase separation of low molecular weight intermediates leads to larger particles. This is largely related to nucleation rates in these systems. Below pH 3.5, the solution kinetics allow particularly metastable oligomers to form; these oligomer have difficulty in nucleating a dense solid phase because the activation energy of nucleation is high, so the solution remains metastable until gelation. Above pH 3.5, though, the kinetic regime is changed so as to disfavor the construction of metastable oligomers, so the activation energy for nucleation is lowered and phase separation proceeds at the timescale comparable to or faster than the timescales of hydrolysis and condensation.

In accord with Iler's model, primary structures aggregate either in a Smoluchowski fashion to form gels or they can aggregate in a phase separation fashion to form discrete colloid particles. The only enhancement to this picture offered here is in outlining the polymerization kinetic reasons of crossover from metastability to phase separation as a function of pH. We have identified kinetic reasons for establishing metastable species and conditions leading to insoluble species. Metastability and formation of homogeneous random gels is associated with highly negative FSSE for condensation, favorable cyclization and fast, reversible hydrolysis.

The mechanism of nucleation of particles remains unclear; the roles played by positive FSSE and by loss of metastability of low molecular weight intermediates may well vary with pH and other processing parameters. The engineering of particulate gels will be enhanced by multistep kinetic studies that discern these roles. Moreover, the quantitative evaluation of kinetic and thermodynamic trends for hydrolysis and condensation of TEOS in the homogeneous polymerization regime ($pH < 3$) can allow the design and optimization (by mimicry) of homogeneous systems with *different* compositions, perhaps using multistep [19] methods.

There has in fact already been a good deal of progress on the front of using multistep methods to synthesize homogeneous multicomponent gels. Exploration of 'prehydrolysis' methods leading to clear alumino–silicate, vanado–silicate and titano–silicate gels revealed critical importance of tailoring specific degrees of condensation and hydrolysis of silicon alkoxide precursors before the addition of aluminum, vanadium or titanium alkoxides in order to maintain solubility of the non-silicate component [5,7,79–81]. It has been also shown that solvent effects related to reesterification and solubility of polymerization intermediates are important in these systems, so that manipulation of solvent quality by varying solvents and temperature to maintain solution metastability provides a route to homogeneous multicomponent gels.

For example, when TEOS, water and aluminum sec-butoxide were combined in several stages of a 'prehydrolysis' technique, reaction intermediates at each stage were examined by means of both liquid and solid NMR of ^{13}C, ^{29}Si, ^{17}O, and ^{27}Al nuclei [81]. When aluminum sec-butoxide is added to an appropriately prehydrolyzed TEOS solution, the aluminum becomes coordinated by silicate ligands. When further water is then added, gelation can proceed by the formation of new siloxane linkages. When too much aluminum alkoxide is added, though, there appear to be too few silanols to fully coordinate the aluminum, the remaining aluminum alkoxide groups can undergo transesterification with the solvent. The choice of isopropanol as solvent is helpful in alleviating this constraint. Al–OPr moieties formed by this transesterification in isopropanol are attacked by the H_2O added in the third step, but slowly enough as to allow Si–OR groups to hydrolyze and either condense with themselves or attack Al, expanding its coordination to octahedral.

Much more work is necessary to truly design gelling systems of arbitrary composition and homogeneity. This review of recent work on SiO_2 and our comments on multicomponent systems show role of kinetics of hydrolysis, condensation, precipitation and transesterification. Moreover, it demonstrates the crucial need for correlation between inorganic polymer structure and chemistry on one hand and solubility and metastability on the other.

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