SAND96-1230 C
CONF-960401--31

[illegible]

CROSS-CONDENSATION KINETICS OF ORGANICALLY MODIFIED SILICA SOLS+

S. PRABAKAR* and R.A. ASSINK, **

*Advanced Materials Laboratory, 1001 University Blvd., SE., #100, Albuquerque, NM 87106.
**Sandia National Laboratories, Albuquerque, NM 87185-1407.

ABSTRACT

The hydrolysis and self- and cross-condensation kinetics of the hybrid sol tetraethoxysilane and ethyltriethoxysilane were investigated by high resolution ^{29}Si NMR spectroscopy. A kinetic model in which hydrolysis is reversible and condensation is irreversible was developed. We found excellent agreement between the product distributions measured by ^{29}Si NMR spectroscopy and calculated by the model. The cross-condensation rates for each of the sols were intermediate to the condensation rates of the individual components. Calculations show that for these sols, the concentration of cross-condensed species is a weak function of the relative rates of self-condensation.

INTRODUCTION

Sol-gel techniques provide a convenient method for the production of high purity, homogeneous materials [1]. The properties of sol-gel derived materials can be tailored by combining an organic component with the conventional inorganic components. Hybrid materials can be prepared from either a single monomer or a mixture of two or more monomers. These hybrid silicate materials are being widely investigated because of their potential application in optical devices, fibers and thin films [2,3]. Some of the factors controlling the homogeneity of multiple component hybrid sol-gels are pH and water to silicon ratio. These factors affect the relative hydrolysis rates and the extent of competition between self- and cross-condensation reactions.

When an inorganic precursor such as tetraethoxysilane (TEOS) and an organically modified triethoxysilane such as ethyltriethoxysilane (ETES) are reacted with water in the presence of an acid the following hydrolysis reactions take place:

$$\mathrm{TOR} + \mathrm{H_2O} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{TOH} + \mathrm{ROH} \tag{1}$$

$$\mathrm{QOR} + \mathrm{H_2O} \underset{k'_r}{\overset{k'_f}{\rightleftharpoons}} \mathrm{QOH} + \mathrm{ROH} \tag{2}$$

+ This work was supported by the United States Department of Energy under contract DE-AC04-94AL8500.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

where T represents the trifunctional silicon in ETES and Q represents the tetrafunctional silicon in TEOS . The forward rate constants are denoted k_f and k'_f while the reverse rate constants are denoted k_r and k'_r for the T and Q silicons respectively. Our results will show that reversible reactions are significant. The hydrolyzed species condense by three routes, two due to self-condensation, (3), (5), and one due to cross-condensation, (4), as follows:

$$\mathrm{TOH} + \mathrm{TOH} \xrightarrow{k_{TT}} \mathrm{TOT} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{TOH} + \mathrm{QOH} \xrightarrow{2\,k_{TQ}} \mathrm{TOQ} + \mathrm{H_2O} \tag{4}$$

$$\mathrm{QOH} + \mathrm{QOH} \xrightarrow{k_{QQ}} \mathrm{QOQ} + \mathrm{H_2O} \tag{5}$$

where TOT is the dimer formed by the condensation of two T silanols, QOQ is the dimer formed by the condensation of two Q silanols and TOQ is the dimer formed by the condensation of one T and one Q silanol. k_{TT} is the rate constant associated with the condensation of two TOH species, k_{QQ} is the rate constant for the condensation of two QOH species and $2k_{TQ}$ is the rate constant associated with the condensation of one TOH and one QOH species. A factor of two is associated with the formation of the cross-condensed product because statistically, this species is twice as likely to be formed as either self-condensed species.

^{29}Si NMR spectroscopy is a widely employed technique to study the chemical kinetics of silica sol-gels [1]. The sensitivity of ^{29}Si NMR to nearest neighbors, next-nearest neighbors and cyclic species makes it a convenient probe to study the hydrolyzed and condensed species. In a previous publication [4], we identified the resonances corresponding to hydrolyzed and self- and cross-condensed species in TEOS/ETES hybrid sol-gels. In this work we have investigated the hydrolysis and condensation kinetics of the hybrid sol-gel TEOS/ETES by ^{29}Si NMR and developed a kinetic model for the hydrolysis and condensation reactions.

EXPERIMENTAL

Reagent grade tetraethoxysilane (TEOS) and ethyltriethoxysilane (ETES) were used as received from Hüls America. All the sols were prepared by HCl-catalyzed hydrolysis of an equimolar mixture of TEOS and ETES in ethanol. The total silicon concentration was 2.2M. Two sols were prepared one with water-to-silicon ratio of 0.15 at a pH of 2.2 (designated as TEOS/ETES(I)) and the other with water-to-silicon ratio of 0.3 at a pH of 1.7 (designated as TEOS/ETES(II)). 5 mM chromium acetylacetonate (CrAcAc) was added to reduce the ^{29}Si spin relaxation time. Previous studies have found no effect of CrAcAc on the initial reaction rates of sol-gels [5,6].

The ^{29}Si NMR spectra were recorded at 39.6 MHz (magnetic field 4.7 Tesla) on a Chemagnetics spectrometer described previously [5]. Line widths were typically 0.3 Hz. The spectra were referenced with respect to an external standard tetramethylsilane (0 ppm). The resonances of the observed species were well resolved and could be integrated quantitatively.

RESULTS AND DISCUSSION

When TEOS/ETES in ethanol is reacted with water, the monomers first undergo hydrolysis reactions, eqs. (1) and (2), to give silanol functional groups represented by TOH and QOH. We carried out several experiments to determine if the OH groups in TOH and QOH exchange with each other. This exchange would be transparent when the sol has reached equilibrium because the net exchange between silanols would exactly cancel each other. The exchange can be observed, however, when the sol is in a nonequilibrium state. The nonequilibrium state was prepared by hydrolyzing TEOS and then adding ETES to the hydrolyzed solution. Immediately after mixing, ETES hydrolysis species were observed and the extent of hydrolysis of the TEOS was reduced. This clearly shows that the OH groups are exchanging between TEOS and ETES. Experiments conducted in the reverse order ie. hydrolyzing the ETES and then adding TEOS also showed hydrolyzed species of TEOS. The distribution of hydrolyzed species was calculated from the equation

$$\frac{[\mathrm{TOH}]}{[\mathrm{QOH}]} = K_R \frac{[\mathrm{TOR}]}{[\mathrm{QOR}]} \qquad (6)$$

where K_R is defined from the appropriate forward and reverse hydrolysis rates [7]. Analogous experiments in which the first monomer was fully condensed and then the second monomer added, showed that the condensation reactions are irreversible on a timescale of 24 h.

Equation (6) enables K_R to be determined during the first 3-5 minutes of the reaction before significant condensation products have formed. The initial distributions of hydrolyzed species and the calculated K_R are shown in Table I for each of the sols. Since the T and Q monomers are equimolar, we expect that the ratio of hydrolyzed species would be 0.75 and K_R = 1.0 if each alkoxy group were equally likely to be hydrolyzed. The concentration of hydrolyzed T silicons for the TEOS/ETES sol is less than that predicted by statistical arguments.

Table I *Initial distributions and equilibrium constants of hydrolyzed species*

Sol	Initial TOH/QOH	K_R
TEOS/ETES	0.61	0.81
TEOS/ETES	0.54	0.76

Since limited amounts of water are used, and since the early stages of the process are being investigated, the primary condensation reactions observed are those between two monomeric species to form a dimeric species given by equations 3-5. We assume alcohol producing condensation is negligible compared to water producing condensation. Although alcohol producing condensation can be important in tetramethoxysilane sol-gels [6], it was found to be very low in TEOS sol-gel systems [8]. For second order condensation reactions, the three rate equations can be written as:

$$d\,[TOT] / dt = k_{TT}\,[TOH]\,[TOH] \qquad (7)$$

$$d\,[TOQ] / dt = 2\,k_{TQ}\,[TOH]\,[QOH] \qquad (8)$$

$$d\,[QOQ] / dt = k_{QQ}\,[QOH]\,[QOH] \qquad (9)$$

The time evolution for each of the self- and cross-condensed species was calculated by numerically integrating eqs. (7)-(9). The initial values for the concentrations of TOH and QOH were determined from spectra recorded 3 to 5 minutes after the solutions were prepared. When the first spectra were recorded, the water had already been consumed by hydrolysis, and the concentration of hydrolyzed species had reached a state of quasi-equilibrium. During the longer condensation period, the concentrations of TOH and QOH species decrease as the silanols undergo condensation reactions. The condensation reactions yield additional water which immediately participates in hydrolysis reactions to form silanols.

Figs 1(a) and 1(b) show the experimental and calculated time dependencies for the concentrations of TOT, TOQ and QOQ species in the TEOS/ETES(I) and TEOS/ETES(II) sols respectively. The concentrations of TOT, TOQ and QOQ species increase rapidly for the first 300 minutes followed by a slight increase over the next 13 h. We see excellent agreement between the calculated (full curve) and experimental values (symbols). The absolute values of the condensation rate constants depend on fitting the initial slope and are subject to some error because of the difficulty of rapidly recording accurate spectra. The relative values of the condensation rate constants depend on the concentration of dimer species at long times and are quite accurate. The absolute and relative rate constants for the three condensation reactions and the final product distribution for these sols are shown in Table II.

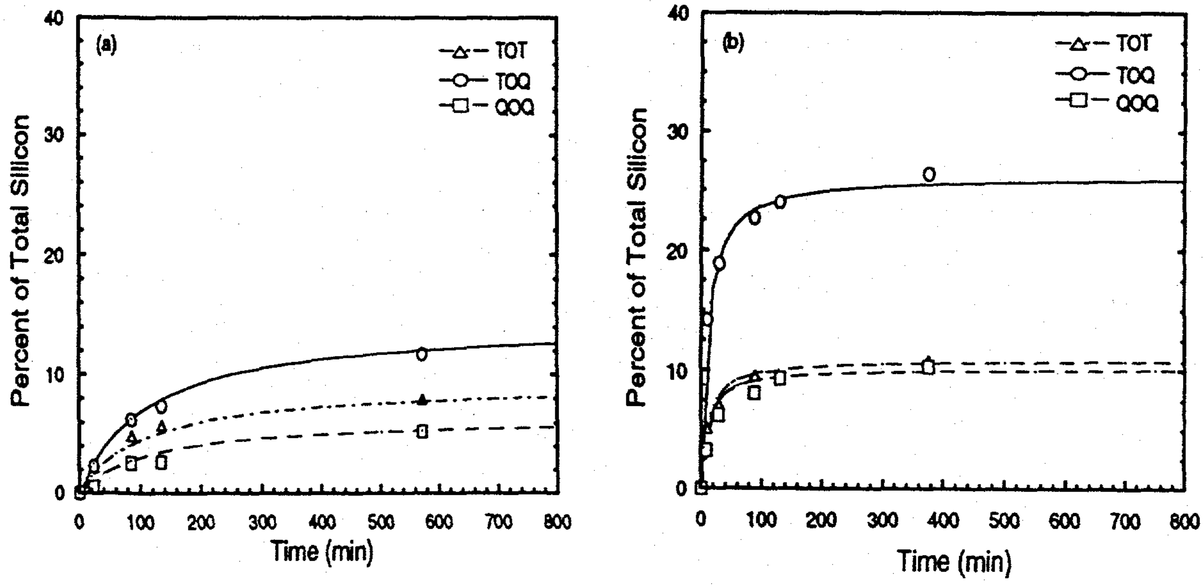
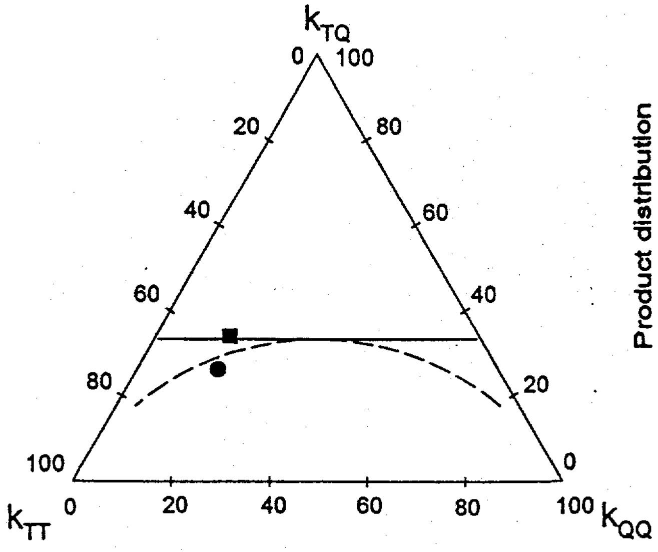


Fig 1 Calculated and experimental distributions of condensed silicon species in (a) ETES/TEOS (I) (b) ETES/TEOS (II) as a function of time.

Table II Absolute and relative condensation rates and final product distributions

Sol	AbsoluteRates $k_{TT} : k_{TQ} : k_{QQ}$ x (l/m) s^{-1} 10^{-4}	Relative Rates $k_{TT}: k_{TQ}: k_{QQ}$	Relative Concentrations TT : TQ : QQ (after 24h)
TEOS/ETES(I)	14 : 6.4 : 3.4	0.59: 0.27 : 0.14	31 : 48 : 21
TEOS/ETES(II)	54 : 36: 16	0.51: 0.34: 0.15	22 : 55 : 23

For each of the TEOS/ETES sols investigated, we found that the self-condensation rate of the organically modified monomer was greater than the cross-condensation rate which in turn was greater than the self-condensation rate of TEOS, $k_{TT} > k_{TQ} > k_{QQ}$. The relative rates for the two sols are comparable, demonstrating the utility of the model. We expect that the rates for sol(II) would be 3.2 times as large as the rates for sol(I) assuming that the condensation rates are proportional to the hydrogen ion concentrations for these acid catalyzed sols. The experimentally derived rates average 4.7 times as large. Although this difference is larger than we expected, the overall trends are reasonable.



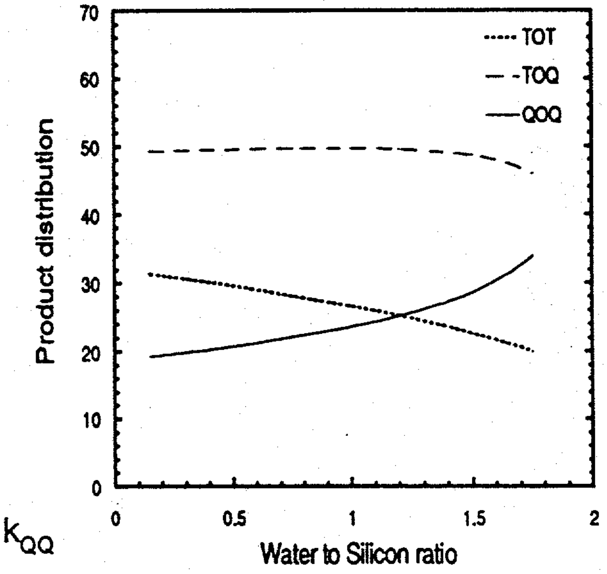


Fig 2. Ternary diagram of rate constants. The solid line represents $k_{TQ} = 1/2\ (k_{TT} + k_{QQ})$ and the broken line represents $k_{TQ} = (k_{TT}\ k_{QQ})^{1/2}$.
● - TEOS/ETES (I) ■ - TEOS/ETES (II)

Fig 3. Product distribution as a function of water to silicon ratio (r)

The cross condensation rate constants calculated for the two sols are shown in the form of a ternary diagram (Fig 2). Each of the vertices represents the domination of one of the condensation rates. The calculated ratios of rate constants for the two sols are represented by symbols. The solid line corresponds to a cross-condensation rate equal to the arithmetic mean of the self-condensation rates, $k_{TQ} = 1/2\ (k_{TT} + k_{QQ})$. The broken line corresponds a cross-condensation rate equal to their geometric means, $k_{TQ} = (k_{TT}\,k_{QQ})^{1/2}$. The range of rate constants for these sols is too limited to provide an accurate assessment of the relative merits of the two simple models.

In Fig 3 we have plotted the product distribution of the various silicon-oxygen-silicon condensation bonds as function of water-to-silicon ratio. The product distributions were calculated assuming $K_R = 1$. We find that approximately 50% of the bonds formed are TOQ bonds, independent of water-to-silicon ratio. The relative amounts of TOT vs. QOQ bonds formed are a function of water-to-silicon ratio. For low ratios, more of the TOT bonds form because these silicons compete more successfully for the limited amount of water present. As the water-to-silicon ratio reaches 1.75, sufficient water is present for the reaction to go to completion. Both silicon species react fully and stoichiometric amounts of bonds are formed.

CONCLUSIONS

We have developed a kinetic model for the hydrolysis and self and cross condensation of the hybrid sol TEOS/ETES. The model treated hydrolysis as reversible and condensation as irreversible reactions. The final product distributions for these sols are a function of both the equilibrium between T and Q silanols and the relative rates for the various self- and cross-condsation reactions. The concentrations of the self- and cross-condensed species as a function of reaction time predicted by this model are in good agreement with the concentrations measured by ^{29}Si NMR.

REFERENCES

1 C.J. Brinker and G.W. Scherer, Sol-gel Science: The Physics and Chemistry of Sol-Gel Processing (Academic, San Diego, 1990) p. 166, 840.

2 C. Sanchez and F. Ribot, New J. Chem. **18**, 1007 (1994).

3 F. Babonneau, New J. Chem. **18**, 1065 (1994).

4 S. Prabakar, R.A. Assink, N.K. Raman, S.A. Myers and C.J. Brinker J. Non-Cryst. Solids (In Press).

5 S. Prabakar, R.A. Assink, N.K. Raman and C.J. Brinker. Mat. Res. Symp. Proc. **346**, 979 (1994).

6 R.A. Assink and B.D. Kay, J. Non-Cryst. Solids **99**, 359. (1988)

7 S. Prabakar and R.A. Assink, J. Non-Cryst. Solids (Submitted)

8 R.A. Assink and B.D. Kay, Colloids and Surfaces A: Physicochemical and Engineering Aspects **74**, 1 (1993).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.