Study of the Solution in the Synthesis of a Sol−Gel Composite Used as a Chromatographic Phase

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Tetraethoxysilane (TEOS) and octyltriethoxysilane (C_8-TEOS) were used in the synthesis of an organic−inorganic hybrid glass composite by the sol−gel process. This composite was used as the stationary phase for chromatographic and electrophoretic separations when cast onto the inner walls of capillary columns. To investigate the reactions leading to the final chromatographic material, the hydrolysis and initial condensation reactions of TEOS, C_8-TEOS, and the C_8-TEOS/TEOS hybrid mixture were studied by ^{29}Si and ^{1}H NMR spectroscopy. The reaction of methyltriethoxysilane (C_1-TEOS) and ethyltriethoxysilane (C_2-TEOS) were also followed for comparison purposes. The formation of the various silicon species and the degree of substitution on the Si atom in the reactions revealed that TEOS hydrolyzes faster than C_8-TEOS when each precursor reacts individually. However, the rate of hydrolysis for C_8-TEOS increases when reacting in a C_8-TEOS/TEOS (1:1 mole ratio) mixture, driven by the condensation of hydrolyzed TEOS species with those of C_8-TEOS. The rate of hydrolysis for alkyl-monosubstituted alkoxysilanes and TEOS followed the trend C_1-TEOS > C_2-TEOS > TEOS > C_8-TEOS. The maximum degree of condensation in the C_8-TEOS/TEOS reaction mixture was observed after 7 h of reaction. The maximum chromatographic retention on the columns fabricated with the C_8-TEOS/TEOS sol−gel composite correlates with the maximum degree of condensation and with a C_8-TEOS/TEOS mole ratio of 1:1.

Introduction

The development and study of new stationary phases for chromatography are areas of continuous interest among separation scientists. Recently, our laboratory reported on the use of the sol−gel process as a means to synthesize organically modified silica (ORMOSIL) materials that can act as the stationary phase in open tubular liquid chromatography (OTLC) and open tubular capillary electrochromatography (OT-CEC).[1−3] The high permeability of the open tubular format makes it possible to use longer columns, hence achieving high theoretical plates in a reasonable analysis time, as compared to conventional packed columns.[4−6] Others have also followed this approach to fabricate stationary phases for OT-CEC and other chromatographic techniques.[7,8] The use of the sol−gel process to fabricate stationary phases offers several advantages over conventional methods. First, the preparation procedure is simplified by incorporating the stationary phase and the formation of a porous glass network in one step. The sol−gel technology produces a glass matrix with a large surface area, resulting in a high chromatographic phase ratio. This provides efficient separations and an increased mass loadability. Stationary phases prepared by this method also offer good hydrolytic stability with superior retentive characteristics.

In general, the sol−gel process is a low-temperature glass formation method that consists of hydrolysis and condensation reactions (see Scheme 1) of a metal alkoxide, such as tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS).[9] In the process, hydrolysis of the metal alkoxide produces reactive monomers which through polycondensation reactions promotes cross-linking, leading to a three-dimensional matrix. Hydrolysis can be acid- or base-catalyzed, and it is known to proceed faster at a pH between 2 and 4. The rate of condensation, however, proceeds faster at higher pH conditions (6−9).[9] In our approach to fabricate chromatographic phases via the sol−gel process, the stationary phase is incorporated as an integral part of a glass matrix during the glass fabrication process. This is accomplished by synthesizing a sol−gel-processed glass composite using TEOS and another organosilane compound as a co-precursor, for example, *n*-octyltriethoxysilane (C_8-

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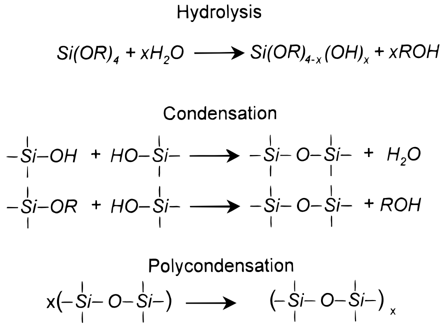
Scheme 1. Representation of the Sol−Gel Process



TEOS). While in its liquidlike stage, the polymerizing mixture is used to coat the inner walls of fused silica capillaries, producing a layer of the composite inside the column. During this process, the organic moiety (i.e., octyl group) becomes an integral part of the bulk glass producing an ORMOSIL. The octyl groups are accessible as the stationary phase for chromatographic interactions.[1−3] The chromatographic performance of a capillary column coated with a sol−gel-processed composite will depend on the characteristics of the gelling solution used to coat the capillary column.

In our approach, the hydrolysis and condensation of the precursors take place in an acidic medium. Very little is known about the reactivities of the C_8-TEOS and C_8-TEOS/TEOS sol−gel-processed systems. It is important to understand these systems in order to fabricate materials with desired characteristics. It has been postulated that the rate of hydrolysis for alkyl-substituted trialkoxysilanes proceeds faster than their corresponding tetraalkoxysilanes.[9−11] Such postulations, however, were drawn from NMR studies of relatively low chain alkyl-substituted trialkoxysilanes (e.g., methyltriethoxysilane (C_1-TEOS) and ethyltriethoxysilane (C_2-TEOS)). In these experiments, species evolving during hydrolysis were identified. The species present in our sol−gel solution (i.e., C_8-TEOS/TEOS) at the time of column coating are not well-known, since different chemical reactivity of the precursors used in our reaction can be expected. To produce homogeneous gels in hybrid mixtures, the monomers should hydrolyze at similar rates; otherwise, the precursor that hydrolyzes faster will tend to self-condense, producing a heterogeneous material.[12] In the case of monomers that hydrolyze at different rates, the problem can be alleviated by hydrolyzing first the monomer that hydrolyzes slower in the reaction and then the faster reacting monomer is introduced. To control our fabrication procedure, it is extremely important that we understand the kinetics of each precursor and the composition of the sol−gel solution used to coat the chromatographic columns. Knowledge of the hydrolysis and condensation reactions will allow us to manipulate the processing parameters to tailor the sol−gel-derived stationary phase with desired and/or improved chromatographic characteristics. Such knowledge can also aid in the fabrication of other sol−gel-derived materials using precursors similar to ours. In this paper, therefore, we present the study of the C_8-TEOS/TEOS sol−gel solution used to fabricate a sol−gel-derived stationary phase. We used NMR techniques to follow the reactions of our systems. In addition, a correlation was established between chromatographic retention and the characteristics of the sol−gel solution used in the fabrication of the ORMOSIL film composite.

Experimental Section

Materials and Chemicals. Tetraethoxysilane (TEOS) was purchased from United Chemicals Technologies, Inc. (Horsham, PA). *N*-Octyltriethoxysilane (C_8-TEOS), methyltriethoxysilane (C_1-TEOS), ethyltriethoxysilane (C_2-TEOS), tetramethylsilane (TMS), ethanol-d^1, chromium acetylacetonate (Cr(acac)$_3$), and polycyclic aromatic hydrocarbons (PAHs) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Fused silica capillaries (10−12 μm i.d., 350 μm o.d.) were purchased from Polymicro Technologies (Pheonix, AZ). Hydrochloric acid, sodium borate, sodium phosphate (NaH_2PO_4 and Na_2HPO_4), toluene, and HPLC grade methanol, acetonitrile, and ethanol were purchased from Fisher Scientific (Pittsburgh, PA). Ethanol (200 proof) from Pharmco (Brookfield, CT) was used as the solvent for the sol−gel reactions. Deuterium oxide was obtained from Isotec (Miamisburg, OH). The stock solution of the compounds used to test the chromatographic columns was prepared in HPLC grade ethanol and diluted with the mobile phase prior to use. Water was purified using a Milli-Q UV Plus water purification system fed from a Milli-RO 10 Plus reversed-osmosis system (Millipore, Bedford, MA). The mobile phase consisted of a mixture of HPLC grade methanol and sodium phosphate aqueous solution (pH ∼ 7) or a mixture of HPLC grade acetonitrile and borate aqueous solution (pH ∼ 9), which were filtered through 0.45 μm nylon filters (Nalgene, Rochester, NY) and degassed by sonication prior to use. The electroosmotic flow (EOF) in the electrochromatographic experiments was measured by adding a small amount of ethanol (5%) to the sample mixture, which served as the unretained neutral marker.

NMR Experiments. Sol−gel solutions of single and/or multiple components for ^1H and ^{29}Si NMR spectroscopy were prepared by the acid-catalyzed hydrolysis of the respective alkoxides in ethanol-d/D_2O. The C_8-TEOS/TEOS molar ratios studied were 0.5:1, 1:1, and 2:1 for the hybrid mixtures. The HCl/Si mole ratio was kept constant at 7.6×10^{-4}. The D_2O/Si mole ratio corresponded to the stoichiometric amount of ethoxy groups in the precursors for all systems studied. The EtOD/Si mole ratio was 3. Cr(acac)$_3$ was added to reduce the ^{29}Si spin−lattice relaxation time. Previous studies have reported no effect of the Cr(acac)$_3$ on the sol−gel reaction.[13−16] The Si/Cr(acac)$_3$ mole ratio was 85. The ^{29}Si NMR spectra were acquired at 79.45 MHz on a Unity Varian NMR-Inova 400 spectrometer (Varian, Palo Alto, CA). Data were acquired using a 30° pulse width with a relaxation delay of 0.1 s. Spectra were accumulated with a 5 mm probe at 18.8 ± 0.2 °C and the number of scans ranged from 32 to 192, using a higher number of scans for the slower reacting precursors. A fast acquisition sequence was necessary to follow the hydrolysis of the fast-reacting precursors (i.e., C_1-TEOS and C_2-TEOS). Other studies have indicated that the integration of the various silanol species under a fast NMR sequence is similar to the one where the Si nuclei are allowed to relax completely.[17,18] The data were processed using the Varian software. The

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intensity of the fully hydrolyzed TEOS oxo-bridged species (Q_3^1, −81.3 ppm) and TEOS ($Q_0(0,4)$, −81.5 ppm) were estimated by deconvolution analysis of overlapping peaks. Spectra were externally referenced to TMS at 0 ppm. The ^1H NMR spectra were acquired at 399.94 MHz on the Unity Varian NMR-Inova 400 system using a 5 mm probe. Spectra were recorded with a pulse delay of 2 s for a total of 8−16 scans. The resonance line width was 0.7 Hz and spectra were externally referenced to ethanol-d^1.

Column Preparation. The preparation of capillary columns coated with the sol−gel-derived stationary phases involves three steps. First, the capillary is pretreated with 1 M NaOH solution for 1 h to expose the maximum number of silanol groups at the silica surface. After the pretreatment, the capillary is rinsed with water for another hour and dried overnight at ~180 °C under a flow of nitrogen gas. The second step is the preparation of the acid-catalyzed sol−gel solution. The precursors were handled under nitrogen and filtered through a 0.45 μm nylon filter prior to use. As an example, a C_8-TEOS/TEOS molar ratio of one was prepared by mixing 0.107 mL of TEOS, 0.150 mL of C_8-TEOS, 0.168 mL of ethanol, and 0.060 mL of 12 mM HCl/H_2O (D_2O for the NMR experiments) for 6−7 h at room temperature in a closed glass vial. HCl is used as the catalyst. The third step is the coating of the capillary with the sol−gel solution. The coating assembly consists of a pressure tube with a nylon cap that contains a ferrule through which the capillary is inserted.[19] Nitrogen, at 200 psi, is used to force the sol−gel solution through the capillary for 10 min. After this time, the capillary is quickly withdrawn from the solution and a pressure of 200 psi is applied to force the excess sol−gel solution out of the column. The coated capillary is then dried overnight at 120 °C under a nitrogen flow, at 200 psi. The prepared capillary is further washed with acetone for 1 h followed by HPLC grade methanol for another hour. The column is equilibrated with the mobile phase prior to use.

Chromatographic Experiments. All chromatographic experiments were performed using the OT-CEC technique in a system constructed in our laboratory.[1−3] The electric field was supplied with a high-voltage power supply (Whitehouse Station, NJ). Two platinum electrodes, located at each end of the capillary column, were used to connect the power supply with the buffer reservoirs. The injection end (anodic end) was contained in a Plexiglas box for operator's safety. Sample injection was performed by the electromigration technique. Column detection was made at the cathodic end with an Isco UV detector, model CV^4 (ISCO, Lincoln, NE) at 214 nm.

Results and Discussion

Figure 1 shows the chromatographic separation of three test compounds in capillary columns coated with (A) TEOS and (B) C_8-TEOS/TEOS sol−gel-derived composites. No separation was obtained with the column coated with the TEOS solution, whereas the three compounds were baseline-separated in the column containing the C_8-TEOS/TEOS material. This indicates that alkyl groups (i.e., C_8) are exposed to function as the stationary phase, interacting with the solutes during the chromatographic process. It is clear that separation can be achieved using this sol−gel-processed composite. However, we raise the questions of which species are present in solution at the time of column coating and at what point in time should the columns be coated.

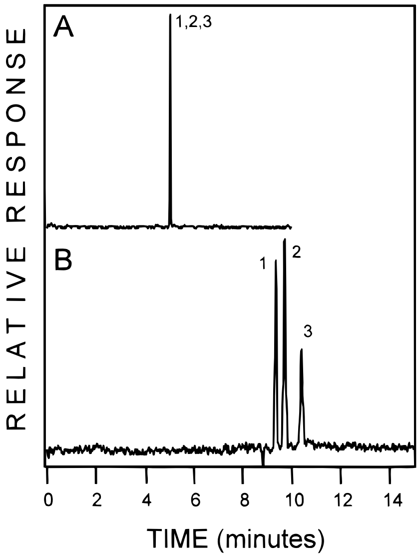

Figure 1. Electrochromatograms obtained in columns coated with sol−gel composites: (A) TEOS and (B) C_8-TEOS/TEOS. The test mixture contains (1) toluene, (2) naphthalene, and (3) biphenyl. Separation conditions: fused silica capillary, 12 μm i.d. × 60 cm total length (40 cm injection to detector); mobile phase, methanol/1 mM phosphate buffer (60/40); separation voltage, 30 kV; electrokinetic injection, 5 s at 6 kV; UV detection at 214 nm.

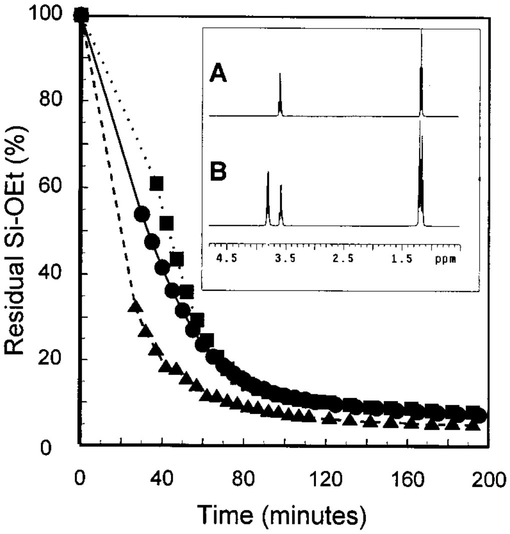

Figure 2. Plot of residual −OEt groups as a function of time. For all systems: $CH_3CH_2OD/Si = 3$; $D_2O/{-OEt} = 1$; $HCl/Si = 7.6 \times 10^{-4}$. Sol−gel system: (■) C_8-TEOS, (▲) TEOS, and (●) C_8-TEOS/TEOS hybrid (1:1 molar ratio). Insert: ^1H NMR of (A) d-ethanol and (B) TEOS in d-ethanol.

To develop an understanding of the solution chemistry prior to column coating, ^1H NMR was used to follow the hydrolysis reaction of TEOS, C_8-TEOS, and the C_8-TEOS/TEOS (1:1) hybrid mixture under acid-catalyzed conditions. The chemical shift of the methylene protons ($-CH_2-$) of d-ethanol (around 3.55 ppm) is different from those bonded to Si atoms (around 3.78 ppm), as shown in the insert of Figure 2. The amount of residual ethoxy (−OEt) groups attached to the Si atom can be determined from the relative intensity of the appropriate methylene peaks in the ^1H NMR spectra. A plot of residual −OEt groups as a function of time is shown in Figure 2. This plot indicates that hydrolysis reactions proceed mostly during the first hour for all three systems studied. Sixty minutes after the addition of acidic D_2O, the amount of residual Si−OEt groups is 13% for TEOS, 20% for C_8-TEOS, and 20% for C_8-TEOS/TEOS (1:1 hybrid mixture). After 1 h, the consumption of these groups slows down considerably. These results

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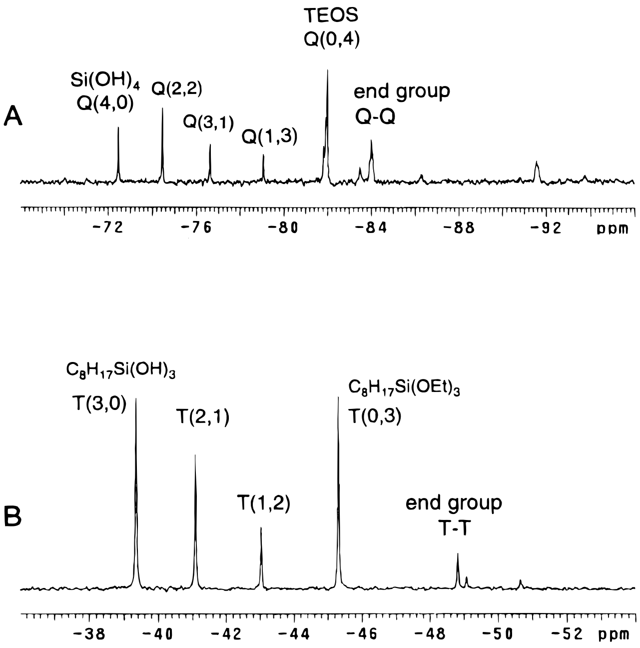

Figure 3. ^{29}Si NMR spectrum of (A) TEOS and (B) C_8-TEOS. Labels indicate peak assignment for hydrolyzed and condensed species.

indicate that the overall hydrolysis reactions for C_8-TEOS proceeds at a lower rate than that for TEOS. In the hybrid mixture, the residual amount of −OEt groups falls between those of the individual precursors during the first hour of reaction.

The different hydrolyzed species for TEOS, C_1-TEOS, C_2-TEOS, and other alkoxysilanes have been identified by ^{29}Si NMR.[16,20−29] We also used this technique to follow the reaction of our sol−gel system. The nomenclature for the different silicon environments formed during the reaction of TEOS is represented by Q_0(n,p) for hydrolyzed species and Q_n^m for condensed species, where $m = 0-4$ and represents the number of Si−O−Si bonds surrounding the silicon atom, n represents the number of hydroxy groups, and p represents the number of ethoxy groups, being TEOS denoted as $Q_0(0,4)$.[16,21−22] The nomenclature for monosubstituted alkoxysilanes (e.g., C_8-TEOS) is similar to that for TEOS. In these systems, however, the different species are identified by $T_0(n,p)$ for hydrolyzed species and T_n^m for condensed species, where $m = 0-3$. Herein, we followed the formation of the different hydrolyzed species and the initial condensation reactions for TEOS, C_8-TEOS, and C_8-TEOS/TEOS systems under the conditions used to prepare the sol−gel material for chromatographic separations.

Figure 3 shows typical ^{29}Si NMR spectra for TEOS (A) and C_8-TEOS (B). The different Q and T units for hydrolyzed and condensed species are identified. The assignment of the different silicon species were made by using values reported in the literature for TEOS and C_1-TEOS,[16,22−24] and by following the ^{29}Si δ trends. The chemical shifts for Si atoms lie in the range of −120 to −30 ppm, −81.5 ppm for TEOS, and −45.3 ppm for C_8-TEOS. The downfield shift for C_8-TEOS, compared to TEOS, is due to the inductive effect of the alkyl group which leads to a lowering of the positive charge at the silicon atom.[16,24] As the number of oxygen atoms on Si increases, there is a greater shielding of the Si nucleus and upfield shifts are observed. For both systems, TEOS and C_8-TEOS, the replacement of an ethoxy group by a hydroxyl during the hydrolysis, weakens the effective oxygen electronegativity because of the more ionic −OH bond character and promotes a downfield shift. The opposite is observed when an −OH group is replaced by a siloxane bridge during condensation. The upfield shift observed is caused by the increase of the effective oxygen electronegativity, from the −OH bond to the covalent O−Si bond.

To follow the hydrolysis and condensation reactions, ^{29}Si NMR spectra were recorded for the TEOS, C_8-TEOS, and C_8-TEOS/TEOS systems for a period of 15 h. The different regions were integrated to follow the evolution of the various species present. The time-dependent ^{29}Si NMR spectra for the copolymerization reaction of a 1:1 molar ratio C_8-TEOS/TEOS hybrid mixture is shown in Figure 4. After approximately 1 h of reaction, some of the original precursors remained unreacted; hydrolyzed and condensed species for each precursor can also be identified. After 5.5 h, small amounts of T^0 species still remained and most of the mixture consisted of condensed species. In C_8-TEOS/TEOS hybrid mixtures, three kinds of condensed species

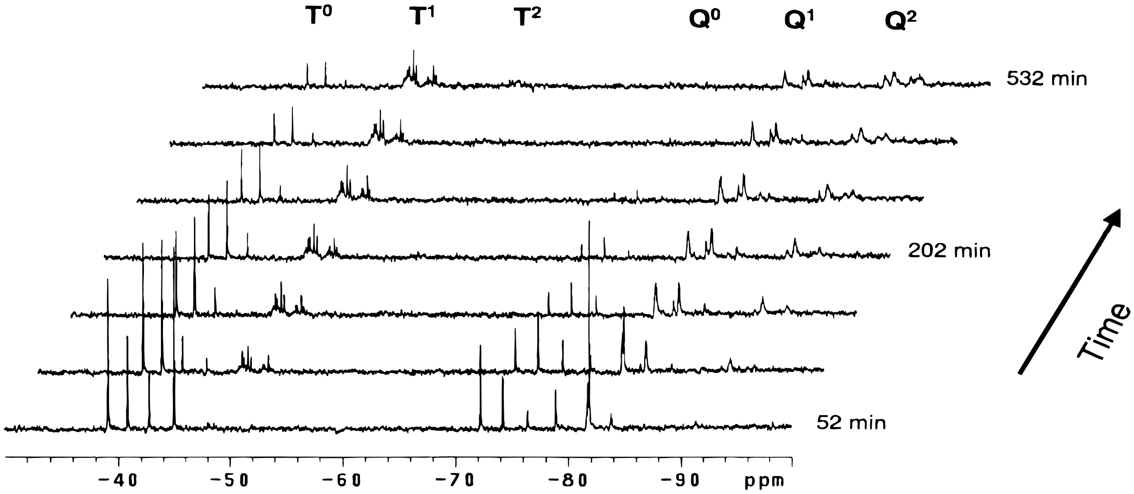

Figure 4. Time dependence ^{29}Si NMR spectra for the copolymerization of C_8-TEOS and TEOS. Reaction conditions are the same as those in Figure 2.

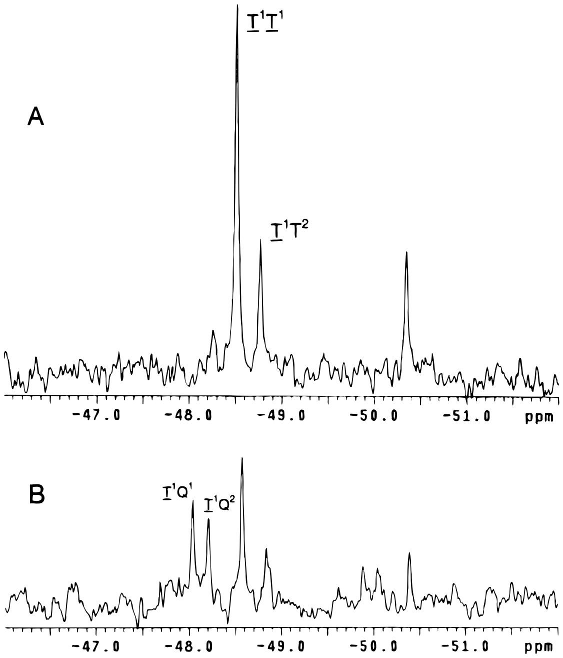

Figure 5. ^{29}Si NMR spectra of the T^1 region of (A) pure C_8-TEOS and (B) C_8-TEOS/TEOS (1:1 molar ratio) at 80 min after initiating the reaction.

are possible, two due to self-condensation (*TT* and *QQ*) and one due to cross-condensation (*TQ*).[22] Figure 5 shows an expanded section of the T^1 region for C_8-TEOS in the homopolymerized and the copolymerized (1:1 molar ratio) reaction mixtures after 80 min of reaction. For the hybrid mixture (B), the broadening of the peaks corresponding to *T* units and the splitting of peaks in the T^1 region are evident. The new bands at about −48.0 and −48.2 ppm are indicative of species formed by cross-condensation reactions (T^1Q^1 and T^1Q^2 units, respectively).

The progress of the reactions as a function of time for pure C_8-TEOS (A) and TEOS (B) is presented in Figure 6. The evolution and disappearance of the different silane species can be observed, as shown by the *T* and *Q* units. It is evident that the sol−gel solution for the C_8-TEOS system is composed of mostly hydrolyzed species at about 100 min, with about 30% of C_8-TEOS unreacted. After 2 h of reaction, there is less than 10% of C_8-TEOS in solution. In the TEOS system, however, the maximum amounts of hydrolyzed species are observed at about 30 min. At this time, there is about 50% of TEOS still in solution. After 90 min, there is less than 20% TEOS in solution and falls under 10% after 2 h of reaction. The disappearance of the hydrolyzed species in solution after 30 min is indicative of condensation reactions taking place. The hydrolyzed TEOS species are highly reactive and start condensation even when there is still most of the precursor available to undergo hydrolysis. This is in contrast with the C_8-TEOS system, where the disappearance of the hydrolyzed species, which indicates condensation, occurs after most of the precursor has been hydrolyzed.

The TEOS hydrolyzes faster than C_8-TEOS; only 40% of TEOS remained unreacted after 45 min while 65% of C_8-TEOS remained to react at this time. The general hydrolysis rate, k_H, has been calculated using the method by Pouxviel et al.[30] An overall rate constant of $2.8 \pm 0.4 \times 10^{-2}$ L mol^{-1} min^{-1} was obtained for TEOS compared to $6.2 \pm 0.4 \times 10^{-3}$ L mol^{-1} min^{-1} for the C_8-TEOS system. The hydrolysis of TEOS proceeds at a rate almost 5 times faster than C_8-TEOS. These findings are in disagreement with the generalization that the hydrolysis of alkyl-substituted alkoxysilanes proceeds at a higher rate than that of their corresponding tetraalkoxysilanes, because of the inductive effect of the alkyl groups on the Si atom.[9−11] Previous reports have based this generalization on studies conducted with lower alkyl chain substituted alkoxysilanes. We followed the reaction of C_1-TEOS and C_2-TEOS, two short-chain alkyl-substituted alkoxysilanes used by others in previous reports, under the same conditions as those for the C_8-TEOS system. The results, depicted in Figure 7, show that the rate of hydrolysis for the different alkoxysilanes follows the trend C_1-TEOS > C_2-TEOS > TEOS > C_8-TEOS. The longer the alkyl-chain substituent, the slower these precursors react, with the rate of hydrolysis for TEOS being faster than C_8-TEOS. The inductive effect of the alkyl groups on the silicon atom promotes a downfield shift, δ, for alkyl-substituted ethoxysilanes compared to that of TEOS. Downfield chemical shifts, relative to TEOS, follow the same trend as reactivity with δ in the following order: −43.7 (C_1-TEOS) > −45.0 (C_2-TEOS) > −45.3 (C_8-TEOS). The present study shows that C_1-TEOS and C_2-TEOS hydrolyzes faster than TEOS while C_8-TEOS reacts slower and inductive effects do not account solely for this behavior.

In addition to inductive effects, steric factors should be taken into consideration in the evaluation of the hydrolysis of the C_8-TEOS monomers. An increase of the steric bulky alkyl groups hinders the access of the water molecule to the reactive site. Similar effects have been observed for alkyl substituents on the alkoxy groups,[17,31] showing that methoxysilanes react faster than the corresponding ethoxysilanes. A similar behavior is to be expected with sterically bulky alkyl groups. In our studies, the acid/silane molar ratio was kept constant. Therefore, for the substituted ethoxysilane the hydrolysis is favored by the larger HCl/ethoxy groups ratio relative to TEOS. Variation of the acid/silanol ratio has a lesser effect on condensation relative to hydrolysis.[31] The inductive effect caused by the octyl group in C_8-TEOS can lower the positive charge on the silicon

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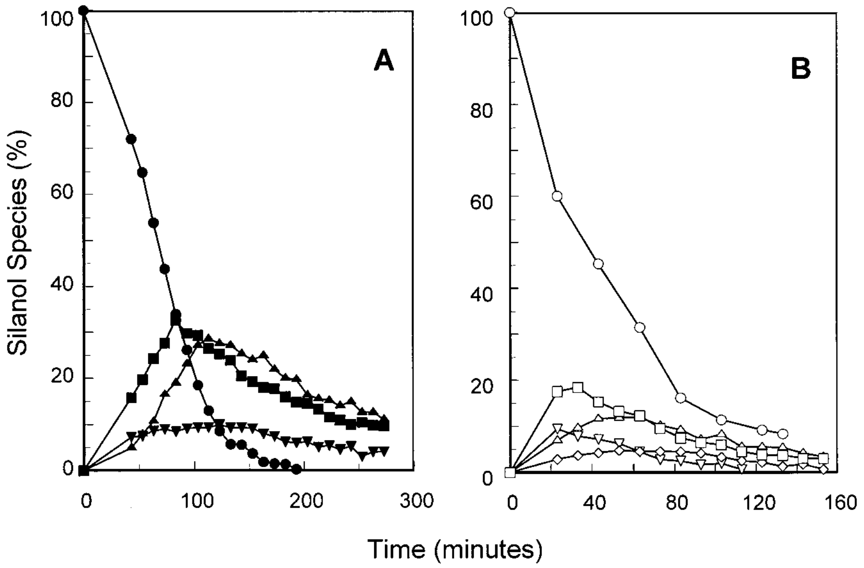

Figure 6. Progress of the hydrolysis reactions of (A) C_8-TEOS and (B) TEOS followed by ^{29}Si NMR. Reaction conditions are the same as those in Figure 2. Silane species: (●) C_8-TEOS (T_0 (0,3)), (▼) T_0 (1,2), (▲) T_0 (2,1), (■) T_0 (3,0), (○) TEOS (Q_0(0,4)), (▽) Q_0 (1,3), (◇) Q_0 (2,2), (△) Q_0 (3,1), and (□) Q_0 (4,0).

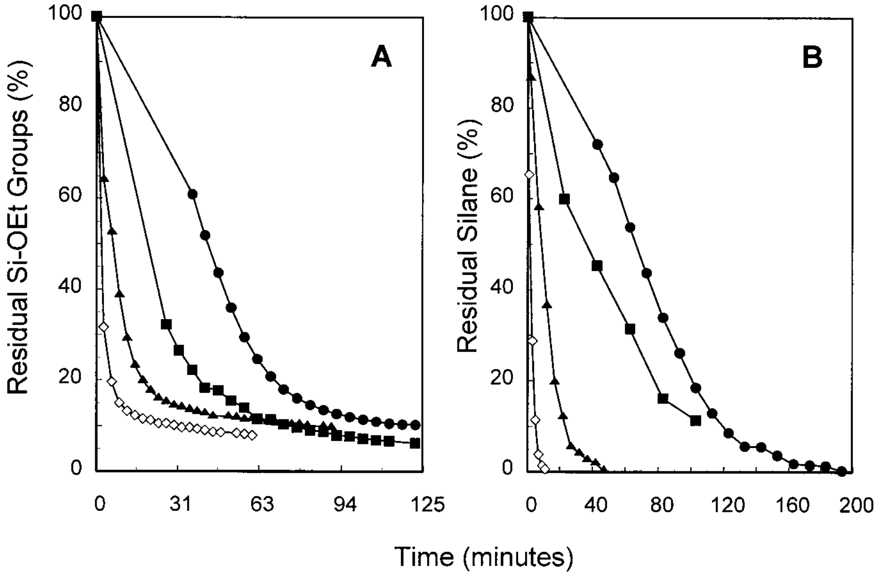

Figure 7. Rate of hydrolysis of alkyl-substituted alkoxysilanes. Reaction conditions are the same as those in Figure 2. Reactions were followed by (A) ^{1}H NMR and (B) ^{29}Si NMR. Monomers: (●) C_8-TEOS, (■) TEOS, (▲) C_2-TEOS, and (◇) C_1-TEOS.

nucleus when compared to TEOS. However, the slower hydrolysis rate observed for C_8-TEOS indicates that the steric effect of this hydrophobic group influences the access of water to the reactive site. This effect is critical in the reactivity of C_8-TEOS.

The different hydrolysis rates of TEOS and C_8-TEOS give rise to questions about the homogeneity of the materials fabricated by mixing these two species. Heterogeneous materials with rich TEOS-derived blocks may be formed upon the self-condensation of the fast-hydrolyzing species.[12] To address this issue, the disappearance of each precursor was followed in a 1:1 C_8-TEOS/TEOS hybrid mixture (Figure 8). Contrary to what was observed in the single-component reactions, the rate at which both precursors are consumed in the hybrid mixture is similar. The initial distribution of hydrolyzed species was calculated according to the following equations:[32]

$$\frac{[\mathrm{TOH}]}{[\mathrm{QOH}]} = K_\mathrm{R}\frac{[\mathrm{TOR}]}{[\mathrm{QOR}]} \tag{1}$$

$$K_\mathrm{R} = \frac{k_{\mathrm{f(C_8TEOS)}}k_{\mathrm{r(TEOS)}}}{k_{\mathrm{f(TEOS)}}k_{\mathrm{r(C_8TEOS)}}} \tag{2}$$

where k_f and k_r are the corresponding foward and reverse rate constants for C_8-TEOS and TEOS. [TOH] and [QOH] represent the concentration of silanol groups and [TOR] and [QOR] represent the concentration of alkoxy groups. The calculated ratio of hydrolyzed species ([TOH]/[QOH]) is 0.76 and K_R = 1.01. This indicates that the alkoxy groups in both monomers are being hydrolyzed at a similar rate when both are present in

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(32) Prabakar, S.; Assink, R. A. *J. Non-Cryst. Solids* **1997**, *211*, 39.

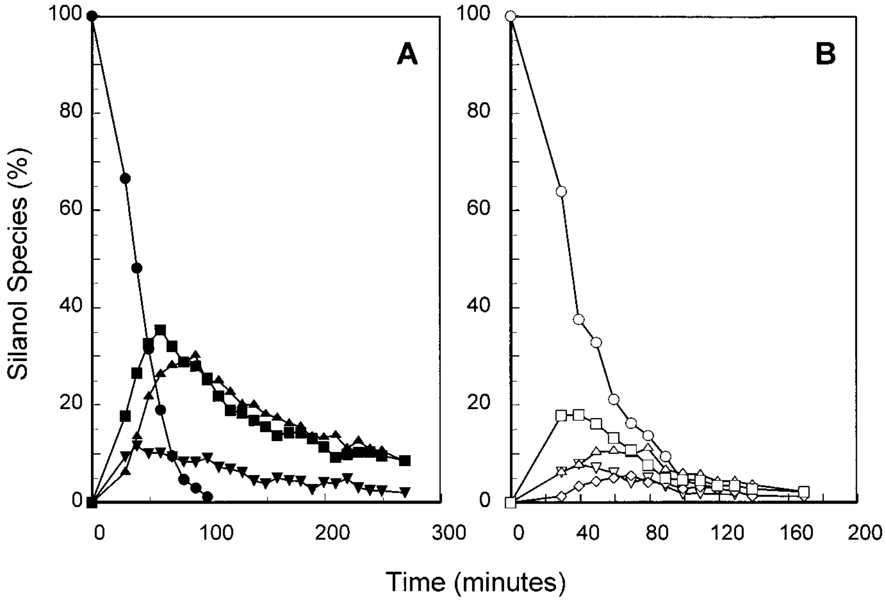

Figure 8. Rate of hydrolysis of silane precursors in the 1:1 molar ratio C_8-TEOS/TEOS mixture. Reaction conditions are the same as those in Figure 2. Silane species: (●) C_8-TEOS (T_0 (0,3)), (▼) T_0 (1,2), (▲) T_0 (2,1), (■) T_0 (3,0), (○) TEOS (Q_0(0,4)), (▽) Q_0 (1,3), (◇) Q_0 (2,2), (△) Q_0 (3,1), and (□) Q_0 (4,0).

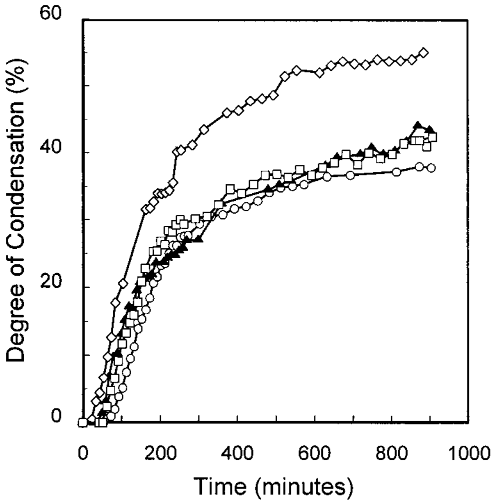

Figure 9. Effect of TEOS on the degree of condensation of C_8-TEOS. Reaction conditions are the same as those in Figure 2. Sol−gel system: (◇) TEOS, (○) C_8-TEOS, (▲) C_8-TEOS in C_8-TEOS/TEOS (1:1 molar ratio), and (□) C_8-TEOS in C_8-TEOS/TEOS (2:1 molar ratio).

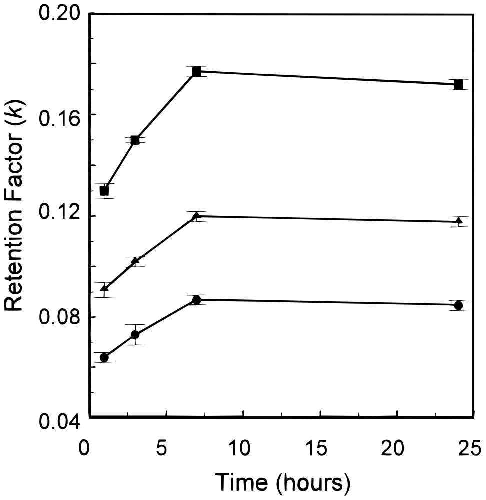

Figure 10. Effect of sol−gel reaction time on retention factors for three test compounds. Column coated with C_8-TEOS/TEOS (1:1 molar ratio) sol−gel composite. Mobile phase: 50/50, acetonitrile/water in 4 mM borate (pH ~ 9.3). Test compounds: (●) Toluene, (▲) naphthalene, and (■) biphenyl.

the reaction mixture. This similarity in the rate of hydrolysis can be rationalized as follows. The highly reactive hydrolyzed species from TEOS (Figure 8B) can start condensation reactions with hydrolyzed C_8-TEOS (Figure 8A) before most C_8-TEOS is hydrolyzed. After 1 h of reaction, there is about 20% of each initial precursor in the 1:1 mixture. C_8-TEOS in the mixture decreases rapidly as the hydrolyzed species are consumed in condensation reactions with the hydrolyzed TEOS, driving the hydrolysis of C_8-TEOS. As depicted in Figure 8, the time at which the hydrolyzed C_8-TEOS species are at maximum approaches that of TEOS, when both precursors react together. At the same time, the hydrolyzed TEOS species reach a maximum at a slightly later time than when TEOS is reacting alone. Such behavior eliminates the need of a prehydrolyzation step of the C_8-TEOS, before mixing the precursors, to promote the formation of cross-condensed species (shown in Figure 5).

Other studies on multicomponent sols have been performed using low concentrations of water (i.e., water-to-silane ratio of 0.3).[32] The low concentration of water in the system facilitates the estimation of the condensed species; one type of hydrolyzed species is predominantly available for condensation at a given time. It is not until condensation occurs that water is available for further hydrolysis, which offers more control on the hydrolysis and condensation reactions. In our hybrid system, an equimolar amount of H_2O to −OEt groups has been used. This promotes the formation of all hydrolyzed species possible, which in turn increases the species formed by the condensation process. Thus, the process becomes more complicated for the quantitation of the different condensed products. Nevertheless, we estimated the distribution of condensed products at differ-

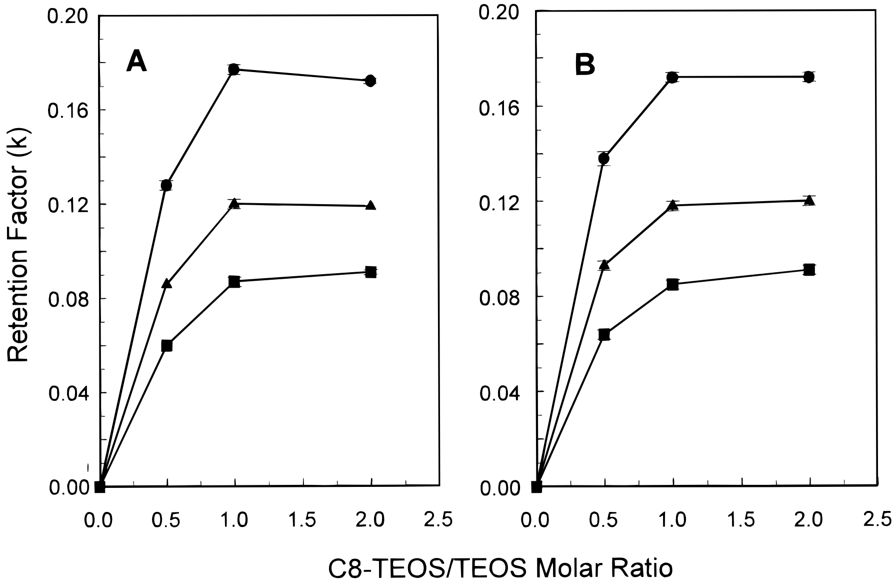

Figure 11. Effect of C_8-TEOS/TEOS molar ratio on retention factors for three test compounds. Columns were coated at 7 (A) and 24 (B) h for all molar ratios studied. Mobile phase: 50/50, acetonitrile/water in 4 mM borate (pH ∼ 9.3). Test compounds: (■) toluene, (▲) naphthalene, and (●) biphenyl.

Table 1. Relative Concentration of Condensed Products for a 1:1 Molar Ratio C_8-TEOS/TEOS Sol

	relative concentration, %		
reaction time (h)	*TT*	*TQ*	*QQ*
1	10	14	76
3	17	36	47
6	23	42	35
8	27	40	33

ent reaction times from the NMR experiments and the results are shown in Table 1. At 1 h, the concentration of *QQ* species predominates. After 6 h, the relative concentration of cross-condensation is substantial and has reached a maximum. These results agree with those previously reported for the cross-condensation product of a two-component sol.[32]

The above experiments do not provide a clear indication on the degree of cross-condensation in the multicomponent sol−gel composite. We studied the degree of condensation, in a period of 15 h, for C_8-TEOS, TEOS, and different molar ratios of the C_8-TEOS/TEOS system (1:1 and 2:1). The degree of condensation (*c*) of the system is defined as[23,24]

$$c = \frac{\sum_i iq_i}{f} \tag{3}$$

where q_i represents the relative concentration of the Q^i or T^i species, and *f* represents the connectivity of the monomer, determined by the number of reactive ethoxy sites ($f = 3$ for C_8-TEOS and $f = 4$ for TEOS). As shown in Figure 9, after 6 h of reaction the degree of condensation for all the systems studied reaches a maximum. The highest degree of condensation was observed for TEOS alone. The long alkyl groups in C_8-TEOS lower the formation of bridged species and affect the rate and degree of condensation. In the hybrid systems, the overall degree of condensation was similar. In the same period of time, the 1:1 and 2:1 hybrid systems reached the same degree of condensation.

To correlate the results of the NMR experiments to chromatographic performance, columns were prepared with the 1:1 sol−gel hybrid mixture at the following reaction times: 1, 3, 7, and 24 h. These columns were evaluated using toluene, naphthalene, and biphenyl as test compounds and the mobile phase used consisted of 4 mM borate buffer (pH 9.3) in 50% acetonitrile and 50% H_2O. Figure 10 shows the retention factor (*k*) for the test compounds on these columns as a function of reaction time. The lowest retention was obtained on the column prepared with the solution that was allowed to react for 1 h. At such times, the NMR experiments showed that the largest amount of hydrolyzed species (T^0 and Q^0) are present in the reaction mixture (see Figures 6 and 8). The stronger chromatographic retention was observed on the columns coated with the sol−gel solution that was allowed to react for 7 h. At this time the degree of condensation for all systems has reached a maximum (see Figure 9). The column coated at 24 h of reaction gave retention behavior similar to the one coated at 7 h. These results indicate that higher retentive characteristics are obtained by coating the columns when the highest degree of condensation in the sol−gel solution has been reached.

The effect of the C_8-TEOS/TEOS molar ratio on the retention factor was studied for columns coated at 7 and 24 h of reaction (Figure 11). The retention factors reached a plateau for all test compounds at a C_8-TEOS/TEOS molar ratio of 1. This indicates that partition with the stationary phase (C_8H_{17} groups) accessible for chromatographic interaction has reached a maximum at this point. Such a behavior suggests that a maximum surface coverage for chromatographic interactions has been achieved. Similar results were obtained for columns coated after 24 h of starting the sol−gel reaction.

Conclusions

Our studies indicate that in the hydrolysis of C_8-TEOS steric effects of the octyl group are considerably higher than the inductive effect, leading to a slower rate of hydrolysis than TEOS alone. Kinetics studies for C_1-TEOS and C_2-TEOS sol−gel systems showed that the hydrolysis rate for these alkyl-substituted alkoxysilanes is faster than that for the TEOS system under acidic conditions. The rate of hydrolysis for C_8-TEOS and TEOS shows to be similar when reacting together, because of condensation reactions between hydrolyzed species of TEOS and C_8-TEOS, which drives the hydrolysis of C_8-TEOS. In the hybrid mixture, the difference in peak shape of *T* units is attributed to the formation of cross-condensed species. Higher chromatographic retention factors are obtained when columns are coated after the sol−gel solution has reacted for at least 7 h; this corresponds to the point where the degree of condensation for these species has reached a maximum. Maximum chromatographic retention is obtained when using a C_8-TEOS/TEOS hybrid mixture with a molar ratio above 1.

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