

Silica Gels Made by Bicontinuous Microemulsion Polymerization

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Microporous silica gels can be made by polymerizing partially hydrolyzed tetra-methoxysilane sols present in the aqueous phase of bicontinuous microemulsions stabilized with didodecyldimethylammonium bromide. When vacuum-dried, the gels made in microemulsions have about twice the specific surface area of conventional vacuum-dried silica gels. They have 70% of the specific area of supercritically dried gels. Small-angle X-ray scattering measurements in these gels show two characteristic sizes. One size, around 24 Å, in the original microemulsion is retained during polymerization, but lost when the detergent is extracted. The second size grows with the square root of time during the polymerization, suggesting diffusion-controlled gelation.

Introduction

Silica gels are microporous materials, with specific surface areas around 800 m²/g (Brinker and Scherer, 1990). Their void fraction is about 0.4, and their pores typically have radii around 100 Å. These properties make silica gels commercially valuable as catalyst supports, adsorbents, and dessicants. Gels with still higher surface areas can be made by drying the hydrogels with supercritical solvents (Fricke, 1985). While effective, this supercritical drying can be slow, expensive, and difficult to carry out on a large scale.

This article explores the synthesis of silica gels in the aqueous phase of a bicontinuous microemulsion. The hope is that the gels obtained will have very large specific areas, comparable with those obtained by supercritical drying, but without the complexities of supercritical drying. By using a bicontinuous microemulsion, we are choosing a structure in which both oil and water are continuous (Lindman et al., 1989; Olsson and Lindman, 1990). While such structures may initially seem strange, they are not uncommon. A piece of toasted bread is bicontinuous: it has both a continuous structure of crumbs and continuous channels of air. A basket of apples is bicontinuous: a gnat could fly through the air spaces to cross the basket and a worm could bore through the apples to cross the basket.

We plan to make our silica gel in the aqueous phase of this microemulsion and thus use the emulsion as a template for the microporous structure. As such, it is another effort to exploit

the self-assembly characteristic of these systems (Anderson, 1986; Anderson and Ström, 1989; Friberg et al., 1989; Qutubuddin et al., 1989; Kresge et al., 1992; Ström and Anderson, 1992). Our synthesis can be idealized as four steps:

1. Making the microemulsion with a silica sol in the aqueous phase
2. Polymerizing the sol while retaining the microemulsion structure
3. Extracting the detergent
4. Drying the microporous polymer.

This sequence is an oversimplification, because the four steps are not completely sequential. For example, the polymerization in step 2 is already under way while the microemulsion is being formed in step 1. Still, this idealized sequence is an easy way to think about this problem.

This article describes the chemical synthesis of these silica gels whose surface areas are about twice those in conventionally prepared materials, though about 30% less than those made by supercritical drying. We track the structural changes in the silica gels by small-angle X-ray scattering. We also discuss why these changes may occur and suggest new routes by which materials with still higher surface areas might be synthesized.

Experimental Studies

Our experiments emphasized bicontinuous microemulsions containing didodecyldimethylammonium bromide (DDAB). This well-studied detergent gives an unusually large region of bicontinuous microemulsions which have been largely identi-

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fied by electrical conductivity (Chen 1985; Chen et al., 1984, 1986). It does not require a cosurfactant; it is only sparingly soluble both in water and oil; and it has diffusion coefficients which are relatively constant with concentration. Most importantly, it has been successfully used for other emulsion-based syntheses (Friberg et al., 1992a,b; Ström and Anderson, 1992; Burban et al., 1995). The reagent-grade materials used as received in our experiments are sulfuric acid (J.T. Baker), hydrofluoric acid (J.T. Baker), sodium hydroxide (Mallinckrodt), decane (Aldrich), ethanol (Eastman), didodecyldimethylammonium bromide (Eastman), tetramethoxysilane (Aldrich), methyltrimethoxysilane (Petrarch Systems), cyclohexane (Fisher), and tertiary butanol (Fisher). Distilled, deionized water was used in all synthesis.

Since a broad variety of syntheses are detailed by Burban (1993), only one typical example is described here. The bicontinuous microemulsion formation usually begins with the preparation of an aqueous tetramethoxysilane sol. In conventional silica solgel systems, a sol is produced by adding the nonpolar silicon alkoxide and the polar water to alcohol. The alcohol acts as a cosolvent, solubilizing otherwise immiscible reactants. Avnir and Kaufman (1987), however, showed that methanol is unnecessary in the tetramethoxysilane systems. They found that the methanol released during the hydrolysis was sufficient to convert the immiscible system to a homogeneous one. We adapt this method for achieving miscibility by using an acid solution as one of the reactants instead of pure water. Using an acid solution increases the hydrolysis rate and thus the miscibility rate of the silane and water.

Specifically, sulfuric acid is added to distilled, deionized water to make a 0.25-M H_2SO_4 solution. Next, the silica sol is made by slowly adding 2 g of tetramethoxysilane to 1 g of the 0.25-M H_2SO_4 while vigorously stirring. This ratio, corresponding to four moles of water per mole of silane, is sufficient for the complete hydrolysis of the silane. The sol is then slowly added to a stirred mixture of the surfactant and decane. When the bicontinuous microemulsion forms, the mixture becomes transparent. In our example, additional sol is then added until the resulting bicontinuous microemulsion had the composition, by weight, of 48.7% DDAB, 19.5% decane, and 31.8% aqueous silica sol. To accelerate the reaction rate, 0.10 g of 10 wt. % aqueous hydrofluoric acid is then added to the microemulsion under vigorous stirring. For this example, the amount of HF solution is 0.0387 times the mass of sol in the microemulsion. Reaction times, about 12 hours at this catalyst level and at room temperature, can be decreased by increasing the amount of catalyst or by heating the microemulsion.

During the polymerization, the initially clear bicontinuous microemulsion is transformed into a transparent solid material. No phase separation occurs. The volume of transparent solid material formed is essentially the same as the volume of the initial bicontinuous microemulsion. Because the initial microemulsion is a liquid of modest viscosity, we can make microemulsion-based silica gels in a variety of shapes and sizes. Most commonly, we use a Teflon block with a 5-cm disc cut out as our mold.

The microemulsion-based silica gel is then placed in an absolute ethanol bath to extract the surfactant, decane, and unreacted monomer. The ethanol in the bath is replaced several times until no traces of surfactant remained in the bath ethanol. A quick test for traces of surfactant which we find reliable is

placing 25 cm³ of the extract in a flask with an equal volume of water. We then vigorously shake the stoppered flask and note if bubbles are formed. When very few bubbles appear, we expect that essentially all of the surfactant has been removed. We have confirmed these findings by looking for residual surfactant and counterion using energy dispersive spectrometry on the Jeol Scanning Electron Microscope. In making this measurement, we are presuming that the ionic surfactant is nonvolatile. We commonly use 100 times the volume of ethanol per microemulsion-based silicon gel, allow a day for extraction, and replace the ethanol bath four times. These times depend on the smallest characteristic dimension of the piece of microemulsion-based silica gel, that is, the thickness for a disk. They can be reduced greatly with reductions in the characteristic size.

The remaining step in this synthesis of a microemulsion-based silica gel is drying. This removes the ethanol from the pores of the gel. We have used three drying techniques. First, we frequently vacuum-dry our gels. This method shrinks and fractures the material, although to a less extent than the shrinkage and fracture in ordinary silica gels produced without microemulsions. Second, we freeze-dry the gels. To do so, we first place the ethanol-wet gel in a large bath of cyclohexane to replace the ethanol in the pores. Cyclohexane is used because it has a convenient freezing point (6.5°C) and a high sublimation rate, and so a good choice for the freeze drying (in a Model 10-010 Automatic Freeze Dryer, Virtis, Gardiner, NJ). Freeze drying also results in gel shrinkage and fracture which do not differ much from vacuum drying. Third, we used supercritical drying with carbon dioxide (in a Samdri-780 critical point dryer, Tousimis Research, Rockville, MD). In this method, the microemulsion-based silica gel is placed in the high-pressure chamber of the dryer with enough additional absolute ethanol to cover the sample. The pressure chamber was sealed and cooled to 5°C. The gel was then purged with carbon dioxide at 800 psig (5.5 MPa) for 2.5 h to replace all the ethanol, which is miscible with liquid carbon dioxide. Next, the sealed pressure chamber is electrically heated to 35°C, above the critical temperature of carbon dioxide (31°C). As the pressure vessel is heated, pressure rises past the critical pressure of 1,100 psig (7.6 MPa) to 1,200 psig (8.3 MPa). After an hour, the carbon dioxide is slowly bled from the pressure chamber at 2 psi/min (14 kPa/min), while staying above the critical temperature. Under supercritical drying, the microemulsion-based silica gels and the conventional silica gels remain intact and transparent, but they do shrink significantly. All silica gels are stored under dry nitrogen.

The silica gels made in this way are characterized by nitrogen adsorption and desorption and by mercury porosimetry, following the same methods (Burban, 1993; Burban et al., 1995). The small-angle X-ray scattering also followed the same procedures described by Bohlen (1990).

Results and Discussion

The purpose of this research is to make a microporous silica by polymerization in a bicontinuous microemulsion. This process depends on four steps: making the microemulsion, polymerizing a silica sol in the microemulsion's aqueous phase, extracting the detergent responsible for the microemulsion, and drying the resulting material. A similar process can be suc-

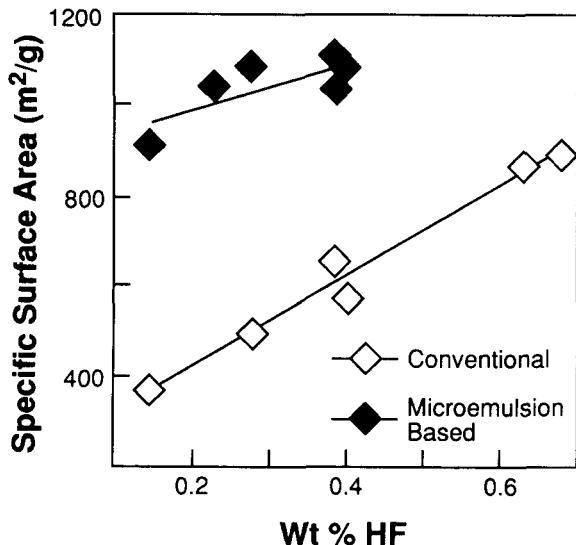


Figure 1. Surface areas in vacuum dried silica gels.

Gels made in bicontinuous microemulsions containing didodecyltrimethylammonium bromide have about twice the area of gels made without this surfactant.

cessfully used to make microporous organic materials (Burban et al., 1995).

The idealization of this process as four steps hides major approximations, even more than in the case of organic materials made in bicontinuous microemulsions. For example, the microemulsion generation and the polymerization occur simultaneously. As described above, we make the microemulsion out of a reacting, partially hydrolyzed tetraalkoxy silane. This system can continue reacting during the extraction. The drying step can be done under vacuum or using supercritical carbon dioxide. Thus, organizing our results around this four-step process seems difficult.

As an alternative, we begin by discussing the dried, finished materials made by vacuum drying and then compare those made by supercritical drying. This comparison includes measurements of pore size distributions. We then examine the evolution of these structures by small angle X-ray scattering. We explore this evolution further by a Guinier analysis, showing a diffusion-limited process in the first few hours and more complex structures in materials aged for weeks.

We begin by comparing materials made by vacuum drying in Figure 1. The microemulsion-based silica gels have roughly twice the specific surface area as conventional gels. These conventional samples were prepared at the same aqueous concentrations, the same catalyst concentrations, and the same temperature history as the microemulsion-based materials. Thus, we are successful in our primary goal of making higher areas without resorting to supercritical drying. The specific area is increased in both cases by higher HF catalyst concentration and hence faster polymerization. The increase for microemulsion-based gels is about half that of conventional gels. We should stress that in both cases, vacuum drying ruptures the original silica gel into many small pieces, typically on the order of 100 μm . The pieces of dried gel seemed three to five times larger for a microemulsion-based material than for a conventional silica gel, but we made no effort to quantify this. While the clear inference is that the detergent reduces stress

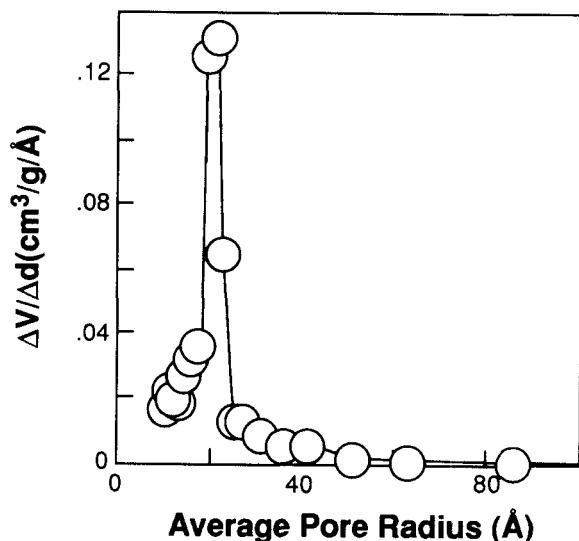


Figure 2. Pore size distribution in vacuum-dried microemulsion-based silica gels.

The gel shows a pore size distribution with a single characteristic radius around 20 \AA .

in drying, we have no proof of this. The pores in the vacuum-dried microemulsion-based gel are monodisperse, as shown in Figure 2, which shows that these gels have primarily 20- \AA -radius pores.

We are not sure why the microemulsion-based materials have a higher surface area than the conventional ones. The most obvious hypothesis is that the effect is an experimental artifact, a consequence of different densities of the two materials. Consistent with this hypothesis, the density of the microemulsion-based material is about half that of the conventional, and the surface area per gram is about twice as big. Thus, the surface area per gel volume is about the same for both materials. The trouble with this hypothesis is that the vacuum-dried microemulsion-based material shows no larger pores in Figure 2 which could account for this extra volume, and the macroscopic void fractions of the two samples are about the same. This simplest hypothesis remains unproven.

A second hypothesis is that the microemulsion generates extra structure which protects the silica structure. In this explanation, the microemulsion-based silica gel contains large pores generated by surfactant. These large pores empty first when the gel is dried. As the microemulsion-generated pores empty, they absorb the capillary forces of drying and collapse, thereby preserving the smaller pores of the silicon backbone. By sacrificing the larger pores, the microemulsion-based silica gels retain their higher surface area. In contrast, the small, high surface area pores in the conventional silica gels collapse when these gels dry because they are the only small pores present within the gel. The trouble with this hypothesis is that at equal interfacial tension, the small pores should have higher stresses than the large ones and should collapse first in both cases.

The situation is very different for materials made by supercritical drying, as shown by the pore size distributions in Figure 3. These experiments used a catalyst concentration of 0.40% HF, in the middle of the range in Figure 1. The supercritically-dried, microemulsion-based silica gel has a high

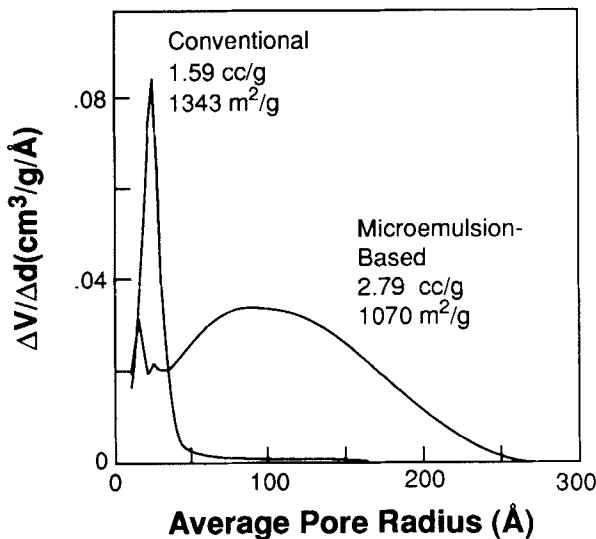


Figure 3. Pore size distributions in supercritically dried silica gels.

These gels were made with 0.4 wt. % HF, in the middle of the range in Figure 1. The microemulsion-based gel has the same specific surface area as the vacuum-dried gel, but the conventional supercritically dried gel has a much larger specific area.

specific surface area ($1,070 \text{ m}^2/\text{g}$) which is essentially the same as that for vacuum drying in Figure 1. This implies that supercritical drying in microemulsion does not alter the collapse of local structures. The microemulsion-based silica gel contains small pores with a radius on the order of 25 \AA , which are responsible for much of the surface area. These pores have sizes similar to the 20-\AA ones found in the vacuum-dried silica gel mentioned above. They are also similar to the 17-\AA pores observed in undried, unextracted microemulsion-based organic polymers described by Burban et al. (1995). We assume that these are due to the detergent in the microemulsion.

In addition, the microemulsion-based silica gel in Figure 3 contains a spectrum of larger pores, responsible for much of the pore volume and some of the surface area. We believe that these larger pores are a result of polymerization of the bicontinuous microemulsion. The radius of these pores, averaging around 90 \AA , is consistent with the size of the silica particles formed in the aqueous domain of the microemulsion. They also seem reminiscent of those 250-\AA pores which appear during the polymerization of microemulsions of organic monomers (Burban et al., 1995).

The specific pore volume of the microemulsion-based silica gel ($2.8 \text{ cm}^3/\text{g}$) is smaller than what might be expected from the composition of the microemulsion. Given the specific volume of the silica gel ($1.59 \text{ cm}^3/\text{g}$), and knowing that the microemulsion was 32% sol and the sol is two-thirds silane, we might expect the pore volume to be about $7.5 \text{ cm}^3/\text{g}$. Our measured pore volume is less because of the shrinkage of the microemulsion-based gel during the supercritical drying, which we measured as 60%. Thus, we expect the pore volume to be roughly 40% of our expected pore volume or $3.0 \text{ cm}^3/\text{g}$, close to that observed.

The supercritically-dried silica gel made in homogeneous solution without microemulsion contains a narrow distribution of pores with an average radius of about 25 \AA . This silica gel

has a very high specific surface area ($1,342 \text{ m}^2/\text{g}$) associated with these small pores. This area is about twice that in the vacuum-dried structure, reinforcing the common view that supercritical drying avoids the usual capillary stresses. Because this gel shrank less than 10 vol. % during drying, it has a specific volume consistent with the volume fraction of silica in the sol ($1.59 \text{ cm}^3/\text{g}$).

So far, we have shown that silica gels produced in bicontinuous microemulsions have large surface areas, around $1,000 \text{ m}^2/\text{g}$. We have shown that this surface area can be produced both by simple vacuum drying and by supercritical drying. Compared with these microemulsion-based gels, the conventional silica gels produced by vacuum drying have about half the surface area, though those made by supercritical drying have about 30% more area.

We now report measurements of the structures formed during silane polymerizations within these microemulsions. These measurements, made by small angle X-ray scattering are parallel to those of methacrylate polymerizations in similar microemulsions (Burban et al., 1995). Because these experiments are so similar, we want to review briefly the four chief results of these earlier methacrylate polymerizations. First, we saw a single peak corresponding to a 17-\AA radius in the original microemulsion. Second, we saw both this peak and a larger 250-\AA peak in a polymerizing structure; the size of this larger peak did not change with time. Third, extraction destroyed the smaller peak, but not the larger peak. Fourth, drying this polymer gave materials whose surface areas were consistent with pores the size of the larger peak. We will use these four results for methacrylate polymerizations as a benchmark for our silica results.

First, we again seek a peak in the initial microemulsion, as shown in Figure 4 just after the microemulsion was made. The composition of this particular microemulsion was 48.5 wt. %

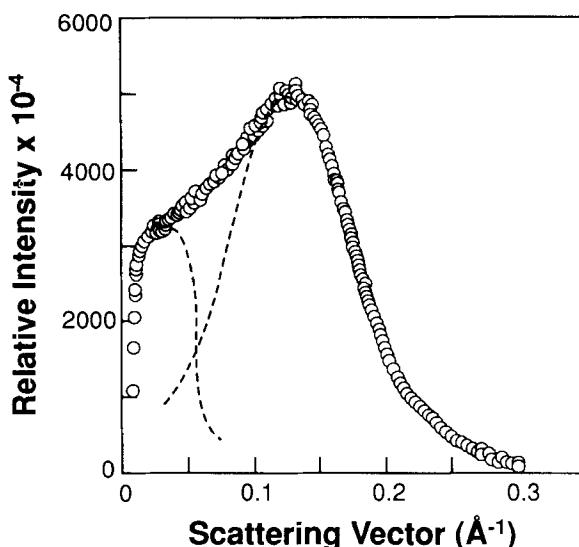


Figure 4. Small-angle X-ray scattering of the microemulsion.

The scattering may show two partly superimposed peaks. That at a higher vector, corresponding to 25 \AA , is probably due to the microemulsion itself. The other peak, at a lower vector, probably corresponds to the initial sol formation.

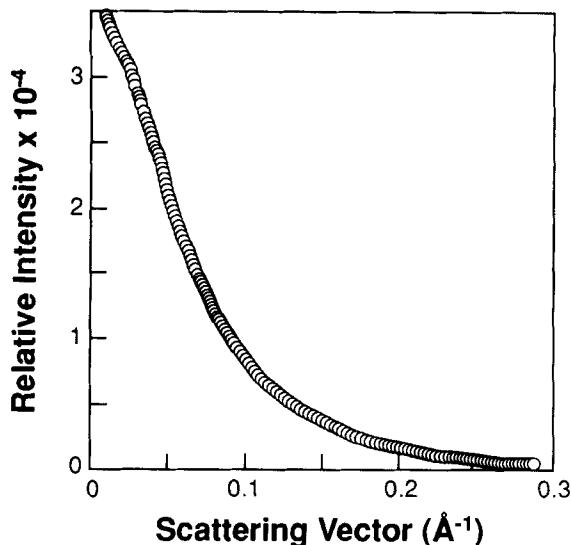


Figure 5. Small-angle X-ray scattering of a conventional silica gel.

This material was made under the same conditions as Figures 4 and 6, but without any microemulsion.

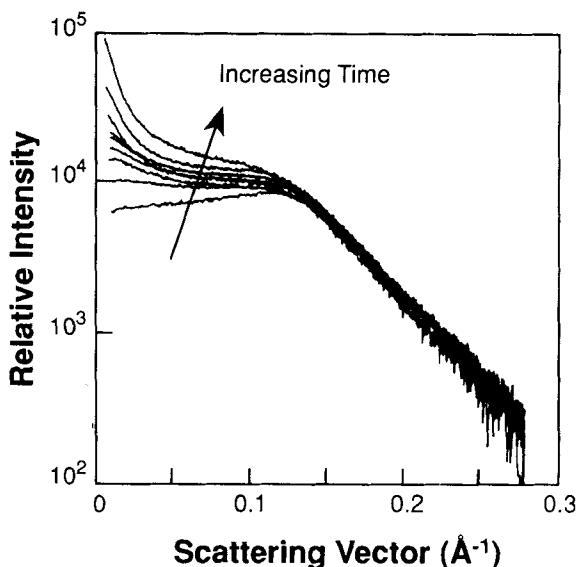


Figure 6. Small-angle X-ray scattering during polymerization of a microemulsion.

The microemulsion composition is like that in Figure 4, but with the catalyst concentration reduced to increase the gelation time.

didodecyldimethylammonium bromide, 19.4 wt. % decane, and 32.1 wt. % silica sol. The silica sol consisted of 33.3 wt. % 0.25M H₂SO₄ and 66.7 wt. % tetramethoxysilane, again resulting in a hydrolysis ratio of four moles water per mole alkoxide. Unlike the nearly Gaussian peak in the vinyl polymerizations, the peak in Figure 4 is asymmetric. It is the two peaks suggested by the dashed line in the figure. One of these two peaks, located at a scattering vector of about 0.13 Å⁻¹, is due to the microemulsion structure; it corresponds to a size of 24 Å, close to the 17 Å observed for the microemulsion containing the acrylate mixtures. We suspect that the difference reflects the altered microemulsion composition, including having the acrylate monomer in the organic phase in one case and the silica sol in the aqueous phase in the other.

The second peak in Figure 4, at a scattering vector around 0.04 Å⁻¹, corresponds to a radius of around 100 Å. We believe that this peak is associated with the start of the silica polymerization, which has begun before the microemulsion is made. We should repeat that, as explained above, these microemulsions were not made with tetramethoxysilane, which is insoluble in water. Instead, these microemulsions were made by first hydrolyzing the silane to produce a hydrophilic silica sol. We believe the 100 Å peak corresponds to this sol's size.

We also measured the X-ray scattering of a silica gel made conventionally from an aqueous phase at the same concentrations as that in the microemulsion, but without any detergent or any organic phase. The results, exemplified by the data in Figure 5, are for a silica gel well past the point of gelation and made with hydrolysis ratio of four, identical to the one used in the microemulsion formation. The scattering profile of the pure silica gel in Figure 5 differs considerably from the microemulsion scattering profile in Figure 4. A peak in scattering intensity is not observed, nor was it expected (Bohlen, 1990). The maximum intensity occurs at low scattering vector, and the intensity decreases rapidly with increasing scattering vector. The intense scattering at low scattering vector is usually at

tributed to the presence of silica particles produced during the gelation.

Scattering profiles for a bicontinuous silica microemulsion of the composition above undergoing polymerization are shown in Figure 6. This polymerization is retarded by reducing the hydrofluoric acid concentration to 2,200 ppm in the same silica sol formulation used in the microemulsion in Figure 4. At this catalyst level, the gelation time, on the order of 4,700 min at room temperature, is large compared to the time required to obtain each scattering profile (approximately 30 min). These scattering profiles have two important features. First, the intensity at low scattering vector increases more than an order of magnitude during the polymerization. Second, the microemulsion peak in the scattering profiles shifts slightly to a lower scattering vector during the polymerization. We discuss each feature in turn.

The original microemulsion does not exhibit significant scattering intensity at low scattering vector, as shown in Figure 4. The silica gel scatters strongly at low scattering vector, as shown in Figure 5. In the polymerizing microemulsion in Figure 6, the increase in scattering intensity at low scattering vector is attributed to the growth of structures within the aqueous domain of the bicontinuous microemulsion. We can apply the Guinier analysis to the scattering profiles to obtain the Guinier radius as a function of time, but we defer discussion of these results until later.

The slight decrease in the microemulsion peak position is more difficult to explain. During the polymerization, the growing silica particles in the aqueous domain of the microemulsion are larger than the characteristic size in the microemulsion of 24 Å. If the microemulsion structure is incorporated into the growing silica sol, slightly increasing its size, we would see a shift in the microemulsion peak position to lower scattering vectors. While the final peak position is obscured by overlap between the microemulsion and the silica structures, we estimate its final position to occur at a scattering vector of about

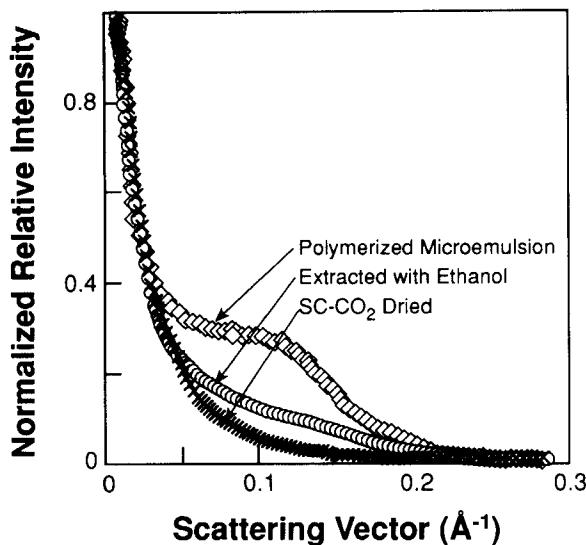


Figure 7. Small-angle X-ray scattering after extraction and drying.

The extraction destroys the peak at 0.12 \AA^{-1} , which is characteristic of microemulsion structure.

0.07 \AA^{-1} , corresponding to a radius of 50 \AA caused by the microemulsion.

We also used small-angle X-ray scattering to measure the effects of extraction and drying on the silica gel structure. As explained above, these are the third and fourth steps in making these materials. Scattering profiles are shown in Figure 7 for microemulsions after polymerization, after extraction, and after drying, which in this case is supercritical. In this figure, we divided the relative scattering intensity of each scattering profile by its maximum intensity to obtain the normalized curves for comparison.

Figure 7 shows that the polymerized microemulsion's scattering profile contains the characteristic peak of the bicontinuous microemulsion, but the other two scattering profiles do not. This implies that surfactant extraction collapses any pores due to the microemulsion. This implication may not be correct; instead, the change might be an artifact of the X-ray scattering. Scattering of X-rays is due to electron density differences within a sample (Glatter and Kratky, 1982). In the polymerized microemulsion, we have a hydrophilic silica polymer swollen with water which contains the surfactant's bromide counterions and the HF catalyst, and which is separated by a monolayer of surfactant molecules from an oil phase. When we replace the surfactant, oil, and water with ethanol, we might remove the components responsible for the electron density difference. On the other hand, the apparent destruction of microemulsion structure by detergent extraction conveniently explains why the microemulsion-based silica gels do not have surface areas around $1,000 \text{ m}^2/\text{g}$, which would be expected from the 24 \AA peak in Figure 4. All in all, we are more convinced by the simpler explanation that the extraction destroys the microemulsion structure.

We have shown that microemulsion-based silica gels have the same specific surface area if dried in vacuum or with supercritical solvents. These new gels have larger areas than conventional vacuum-dried gels, though less than some

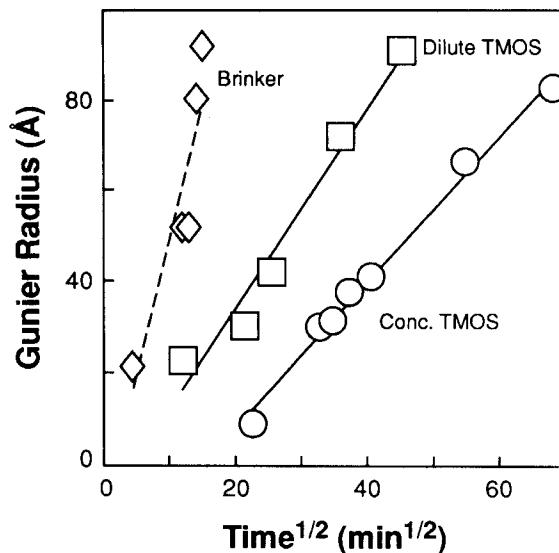


Figure 8. Guinier radii at short times.

The data for microemulsion systems are somewhat slower than those for conventional gels (Brinker et al., 1984). The variation of size with the square root of time is typical of a diffusion process.

supercritically dried gels. We have also shown that the microemulsion-based gels retain still finer microemulsion structure during the silica sol condensation, but they lose that finer structure during extraction and drying.

We now want to return to the kinetics of the polymerization in Figure 6, especially to the development of structure vs. time. We are concerned with two time scales, those less than a few days and those over several weeks. The data at the shorter time scale lead to the large specific surface areas; the results at the larger time scale are often described as gel "aging."

The results at short times in Figure 8 show that the Guinier radius in these systems depends on the square root of time. Our results, for an acid-catalyzed sol constrained in a bicontinuous microemulsion, agree with results for a conventional silica gel synthesis effected by a two-step, acid-plus-base catalysis (Brinker et al., 1984). The slopes are within a factor of four, surprising agreement for data on such different systems. This agreement may imply that the silica chemistry involved is the same, but that the chemical kinetics in the microemulsions is slightly constrained by the 24 \AA structure. The variation of size with the square root of time in Figure 8 often is indicative of a diffusion-controlled process (Cussler, 1984). We are not at all sure what is diffusing; moreover, we recognize that the lines in Figure 8 have nonzero intercepts, suggesting that any diffusion-based mechanism must not be controlling at short times.

Finally, we turn to the gel properties which evolve over weeks, that is, to gel aging. Aging is sometimes urged as a means to increase the gel's mechanical strength and to decrease its shrinkage and fracture during drying. These effects may occur because condensation reactions continue. They may occur because silica dissolves in regions of high curvature and reprecipitates in regions of lower curvature, a process like Ostwald ripening. Ostwald ripening usually results in a decrease in surface area and a decrease in shrinkage during drying (Brinker and Scherer, 1990).

This is exactly what we observe for the conventional super-

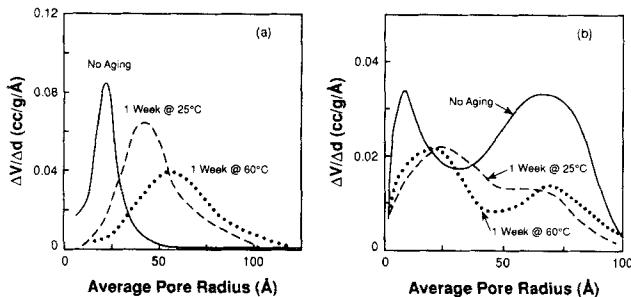


Figure 9. Pore size distributions at long times.

While the conventional gels in (a) behave as expected, the larger pores in the microemulsion-based beds shown in (b) disappear with time.

critically dried silica gels but not for the microemulsion-based supercritically dried silica gels. For the conventional gels, the pore size distribution in Figure 9a is initially monodisperse and shifts to higher sizes and greater polydispersity on aging. For the microemulsion-based gels, the pore size distribution in Figure 9b is initially binodal, just as in Figure 3. With aging, the smaller pores seem to grow and become more polydisperse, just as in the conventional case. However, the larger pores, which are due to the detergent but larger than the original microemulsion structure, seem to disappear. These large pores seem less stable, but we do not know why. Perhaps, their disappearance stabilizes the smaller pores and allows the vacuum-dried gels to retain the larger surface areas (cf. Figure 1).

Conclusions

Our conclusions from this research are a combination of successes and frustrations. We have successfully used microemulsions to make silica gels with higher specific surface areas than conventional vacuum-dried gels, but we cannot make macroscopic sheets of these new gels. We have kept the detailed microemulsion structure during the silane condensation, but we lose this structure when we extract the surfactant. In this condensation polymerization, the structure size in the microemulsion increases with the square root of time. In sharp contrast, in addition to polymerization, structure size in the microemulsion does not change with time (Burban et al., 1995). We are frustrated by the broader meaning of these results. We only hope that future experiments—by us and others—will remove these frustrations.

Acknowledgments

This work was supported by the Defense Advanced Research Projects Administration (grant 92-05112) and by the National Science Foundation (grant CTS 91-23837).

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Manuscript received Oct. 25, 1993, and revision received Feb. 1, 1994.