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CONTROLLED SYNTHESIS AND FUNCTIONALIZATION OF NANOPOROUS SOLGEL SILICA PARTICLES AND GELS

Bing Tan
University of Kentucky

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ABSTRACT OF DISSERTATION

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ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By Bing Tan

Lexington, Kentucky

Director: Dr. Stephen E. Rankin, Professor of

Lexington, Kentucky

2005
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Abstract

Controlled Synthesis and Functionalization of Nanoporous Sol-Gel Silica Particles and Gels

This dissertation addresses three research areas in the sol-gel synthesis of functional materials. The first is the kinetics of hydrolysis and condensation of various organoalkoxysilanes. Two mathematical models are developed for the sol-gel reaction in basic conditions with and without nearest-neighbor effects. Effects on reactivity are measured with systematic changes in the organic group structure. Replacing one methoxy group on the precursor with a methyl group decelerates hydrolysis under basic conditions, but accelerates condensation under acidic conditions. Replacing two methyl-functional precursors with one ethylene-bridged precursor accelerates hydrolysis in base, but decelerates condensation in acid. Replacing an ethylene bridge with a hexylene bridge always decelerates the sol-gel reactions. Adding an amine into the hexylene bridge always accelerates the sol-gel reactions. These trends show inductive effects playing a role only under basic conditions, while steric effects play a role at all pH values. The second topic of this thesis is the synthesis of organic-inorganic materials with bridging or non-bridging organics. The structure of the organic-inorganic hybrids is partially correlated with the kinetics of the precursors, but the trends indicate an additional structural role of siloxane cyclization. The third topic of this thesis is the synthesis of surfactant-templated nanoporous particles. The key to preparing ordered hybrid materials is found to be encouraging aggregation with a surfactant while discouraging random condensation of silanes independent of the surfactants. A homologous series of cationic pyridinium chloride fluorinated surfactants with varying chain length are used as pore templates. Typical pore structures such as hexagonal close-packed cylinders are synthesized, as well as new pore structures including random mesh phase pores and vesicular silica particles with bilayer or multilayer shells. Fluorosurfactants enable the formation of unusually small pores (1.6 nm) and pores formed from discs or bilayers. In the presence of ethanol, spherical particles with radially oriented pores are shown by TEM to form by precipitation of disordered silica-surfactant particles followed by assembly into organized structures. High-capacity hollow particles with ordered mesoporous shells are prepared by dual latex / surfactant templating.
Finally, we load amine-functionalized mesoporous silica with highly dispersed superparamagnetic iron oxide nanoparticles.

CONTROLLED SYNTHESIS AND FUNCTIONALIZATION OF NANOPOROUS SOL-GEL SILICA PARTICLES AND GELS

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Dissertation

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Chapter 1. An Overview of Mesoporous Silica, Organic-Inorganic Hybrid Materials, and the Sol-Gel Reaction

1.1. Surfactant templated sol-gel materials

The discovery of surfactant-templated mesoporous materials in 1992 induced a rapidly developing research area in material science.\textsuperscript{1,2} Mesoporous materials have pore sizes in the range from 2 nm to 50 nm. Those materials with pore size less than 2 nm are called microporous materials and those with pore size larger than 50 nm are defined as macroporous materials.\textsuperscript{3} There has recently been much progress in the synthesis of well-defined mesoporous materials through a so-called templated sol-gel process, which is also called a self-assembly process sometimes. This process and the materials made by this technique, have been the subject of numerous reviews.\textsuperscript{4-8} In this process, an amphiphilic compound that can form micelles in solution is used as the pore template.

A good example of the kind of pore template that can be used is cetyltrimethylammonium chloride (CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{15}-N(CH\textsubscript{3})\textsubscript{3}·Cl). As we know, a surfactant contains a hydrophobic tail and a hydrophilic head group. When dissolved in water, the hydrophobic tail of a surfactant molecule will be repelled by water and attracted to the hydrophobic regions of other molecules or other phases. At the same time, the hydrophilic head of this molecule will remain in contact with the water. Micelles (aggregates of surfactants) will be formed when the concentration of surfactant exceeds the critical micelle concentration (cmc) of that surfactant in water at the temperature under investigation.\textsuperscript{9} In these micelles, the hydrophobic chains will aggregate inside while the hydrophilic heads stay in contact with water. As the concentration of surfactant increases beyond the cmc, the micelles grow and may change shape to form elongated or threadlike micelles. At very high concentrations, the micelles pack together into liquid crystalline mesophases. Depending on the exact nature of the micelle, the types of aggregates that can be found in aqueous solutions as the concentration of surfactant increases include spherical micelles, elongated micelles, discontinuous cubic mesophases, hexagonal close-packed cylinder mesophases, bicontinuous cubic mesophases, mesh phases, and lamellar phases.\textsuperscript{10} The transition of phases can be illustrated in Figure 1.1.\textsuperscript{11} With an increase of the surfactant (cetyltrimethylammonium
bromide, CTAB) concentration, the phase transits from micellar to hexagonal to cubic to lamellar. In some cases the bilayers can fold upon themselves to form round or elongated vesicles.

When a silica precursor is added into the above solution, it will be hydrolyzed to form negatively charged molecules if the solution is basic. These molecules will surround the surfactant micelles as the results of electrostatic interactions and hydrogen bonding. Hydrolyzed precursors then react together by condensation. The result is a condensed product with surfactant micelles organized within a framework of silica. After removing the surfactant, mesopores will be left behind that have the structure of the micelles. The process is illustrated in Figure 1.2 with cetyltrimethylammonium chloride (CTAC) as the surfactant and a mixture of bis(triethoxysilyl)ethane (BTESE) and n-(2-aminoethyl)-3-aminopropyltrimethoxysilane as the precursors.

By adjusting the compositions and the reaction conditions, the pore size and the pore structure of mesoporous materials obtained by surfactant templating can be controlled. One way to control the pore size and the pore structure is to employ different compounds as templates. For instance, using a surfactant with a larger hydrocarbon tail will generally lead to larger pores. By using the hydrocarbon templates, pore sizes as small as 1.96 nm have been reported in the literature. Further reduction of the pore size is limited by the poor ability of shorter hydrocarbon surfactants to self-assemble. For a single chain hydrogenated surfactant, no micelles are observed if the chain length is less than six carbons. In addition to pores with different sizes, pores with different types of long-range order and connectivity can be obtained by using different surfactants. The packing parameter of the surfactant can be used as a guide to the types of pore structures that it is likely to form. Pore structures such as wormhole-like, hexagonal close-packed cylinders, cubic, lamellar, and vesicle have been synthesized with various surfactants. There are, however, more varieties of liquid crystal phases existing in nature that have not been replicated in mesoporous materials. It remains a challenge to continue to reduce the pore size and to increase the variety of pore structures available in surfactant-templated ceramics.

To address these challenges, one of the approaches taken in this thesis is to use fluorinated surfactants. Fluorinated surfactants are very special members of the family of
surfactants. They are characterized by very strong intramolecular bonds (C-F) and very weak intermolecular interactions.\textsuperscript{19} They are not only hydrophobic, but also lipophobic. When dissolved in solution, fluorinated surfactants tend to form highly stable and well organized films, bilayers, vesicles, cylinders and tubules.\textsuperscript{20} Compared with their hydrogenated counterparts, perfluoroalkyl chains are stiffer and larger, and fluorinated surfactants tend to form micelles with less interface curvature at much lower concentration.\textsuperscript{20} Moreover, because of their hydrophobicity, fluorinated surfactants can form micelles with shorter chain compared to the corresponding hydrogenated surfactants. The rule of thumb in the literature is that the cmc of a fluorinated surfactant is roughly equal to that of a hydrocarbon surfactant with the same headgroup and a 50\% longer tail.\textsuperscript{19,21} Thus, an 8-carbon perfluorinated surfactant has the same self-assembly driving force as a 12-carbon hydrocarbon analogue. Because of these special properties of fluorinated surfactants, we can anticipate exciting discoveries by using these surfactants in the sol-gel process. Because surfactants act as templates in the surfactant templated sol-gel process, the shape and pore sizes of the mesoporous materials are determined by the properties of the micelles formed in solution. The properties of fluorinated surfactants provide opportunities to tailor the pore structure and reduce the pore size. This is one of the primary foci of this thesis, and the effect of fluorinated surfactant structure and processing conditions on the structure of mesoporous silica will be studied in depth in Chapters 7 and 8. Other strategies for preparing well-defined porous particles based on hydrocarbon templates will also be discussed. In Chapter 5, the mechanism of forming spherical particles with radially oriented pores will be examined. In Chapter 6, hollow particles with mesoporous shells will be synthesized by combining surfactants and latex particles as templates. The hollow cores of these particles are attractive for high-capacity adsorption.

1.2 Characterization

Before discussing the rest of the aspects of sol-gel materials that will be a part of this thesis, the characterization techniques for porous materials are introduced. Several techniques are needed to characterize pore properties and structures. Nitrogen sorption, powder X-ray diffraction (XRD), and transmission electron microscopy (TEM) focus on
different aspects of a pore structure. Pore properties such as surface area, pore volume, and pore size can be obtained from the nitrogen sorption. XRD provides information about the long range ordering of the pore arrangement. For both nitrogen sorption and XRD, researchers obtain the information about the pore structure by analyzing the obtained data based on assumptions about the pore shape or symmetry. With TEM, researchers can observe the pore structure directly. The disadvantage for this technique is that it only provides information in a local area. For some pore structures, it is difficult to distinguish among them by using TEM. Therefore, information from XRD is needed to confirm or distinguish the pore structures from each other. Also, with TEM, researchers only obtain two dimensional projections of the particles. Three dimensional structures need to be reconstructed from the two dimensional images. Three dimensional images can be obtained by scanning electron microscopy (SEM). However, because of limited resolution, SEM only provides information about the particle morphology.

1.2.1 Nitrogen sorption

Nitrogen sorption is an important method to characterize mesoporous materials. The adsorption isotherms are determined by measuring the volume of a gas adsorbed as a function of partial pressure in the phase above the sample. In our case, we use the adsorption of nitrogen in vacuum at the boiling point of nitrogen (~ 77 K).

Two mechanisms contribute to adsorption of a gas on a material with fine pores. One is the adsorption of a layer of adsorbate on the surface of the material. This layer is generally thicker than a monolayer and becomes thicker as the relative pressure in the gas phase increases. The second mechanism of adsorption is capillary condensation. In extremely fine pore (< 100 nm in diameter), condensation of a vapor occurs at a pressure lower than the condensation pressure of the bulk fluid. This phenomenon of capillary condensation allows us to observe increases in the amount of fluid adsorbed at relative pressure corresponding to the sizes of different pores.

The desorption branch of the isotherm (measured as the pressure decreases from close to a relative pressure \( P/P_0 = 1 \)) has been used frequently for mesopore size analysis.\(^{22,23}\) However, this method has some limitations because the desorption isotherm can be influenced by network connectivity effects, variation of pore size along single channels,
and cavitation of the adsorbate below a certain relative pressure.\textsuperscript{22} The pore size
distribution (PSD) obtained from a desorption isotherm may therefore give an incorrect pore size.\textsuperscript{22} Therefore, the adsorption branch of the isotherm will be used to estimate the PSD of all samples in this dissertation. One of the most frequently used methods to calculate the PSD is the Barrett-Joyner-Halenda (BJH) method. However, this method underestimates the pore size when the pore size is less than 6.5 nm.\textsuperscript{22} Most materials discussed in this dissertation have pore sizes in the range of 2.0 nm to 5.0 nm. To evaluate PSDs in this range, the Kruk-Jaroniec-Sayari (KJS) modified BJH will be used.\textsuperscript{24} This method uses the following equations to relate the pore radius and the partial pressure:

\begin{align*}
r(P/P_0) &= \frac{2\gamma}{RT\ln(P/P_0)} + t(P/P_0) + 0.3 \text{ nm} \quad (1.1) \\
t(P/P_0) &= 0.1 \left[ \frac{60.65}{0.03071 - \log(P/P_0)} \right]^{0.3968} \quad (1.2)
\end{align*}

Where \( r(P/P_0) \) is the pore radius expressed in nanometers, \( t(P/P_0) \) is the statistical film thickness curve based on Harkins-Jura equation, \( p \) and \( p_0 \) are the equilibrium vapor pressure and saturation pressure of the nitrogen adsorbate, \( \gamma = 8.88 \times 10^{-3} \text{ N/m} \) is the surface tension of liquid nitrogen at temperature 77 K, \( V_1 = 34.68 \text{ cm}^3/\text{mol} \) is the liquid molar volume of nitrogen, \( T \) is the absolute temperature (K), and \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \) is the universal gas constant. Using the modified equations (1.1) and (1.2) with the BJH method, it is possible to calculate the PSD from the adsorption branch of the nitrogen sorption isotherm.

Another way to estimate the diameter of the pores in a material with hexagonal close-packed cylindrical pores is derived based on the pore geometry. This equation is:

\[ w_d = cd \left( \frac{\rho V_p}{1 + \rho V_p} \right)^{1/2} \quad (1.3) \]

where \( c = 1.213 \) is a constant, \( d \) is the (100) interplanar spacing obtained from XRD (see below), \( \rho = 2.2 \text{ g/cm}^3 \) is the density of amorphous silica, and \( V_p \) is the specific primary pore volume which can be evaluated from the nitrogen sorption data.

The average pore size can also be calculated by \( d_p = 4V/A_s \), where \( V \) is the volume and \( A_s \) is the surface area of pores, which is the difference between the total surface area
and the external surface area. This equation is derived on the assumption that the pores are cylindrical, but they do not need to be ordered for this equation to apply. The pore wall thickness is calculated by \( b_d = 2d/\sqrt{3} - w \), where \( d \) is the (100) spacing and \( w \) is the pore diameter.

The Brunauer-Emmett-Teller (BET) method is normally used to estimate the total surface area. This method is based on an over-simplified model of physisorption, which limits the range of applicability of this method to the relative low pressures \( (P/P_0) \) (normally \( P/P_0 = 0.04 \) to 0.2). The total surface area can also be obtained with empirical methods of isotherm analysis such as t-plots and \( \alpha_s \)-plots. These empirical methods are recommended for obtaining external surface area, mesopore volume, and micropore volume because they take into account the interactions between the adsorbate and the adsorbent. \( \alpha_s \)-plots are going to be used in this dissertation to evaluate the pore properties. The basic idea of \( \alpha_s \)-plot is to estimate the average pore texture properties (surface areas and pore volumes) relative to a reference macroporous silica material (LiChrospher Si-1000 silica, \( S_{BET} = 22.1 \ m^2 \ g^{-1} \) for \( \omega = 0.135 \ nm^2 \) per molecule). The quantity \( \alpha_s \) is the volume of nitrogen adsorbed on the reference material at a given \( P/P_0 \) value, divided by the volume adsorbed on the reference material at \( P/P_0 = 0.4 \). An example is illustrated in Figure 1.3. This shape of the plot is typical for a mesoporous material. It has a sharp inflection starting near \( \alpha_s = 0.7 \), indicating the capillary condensation in mesopores. The total surface area is calculated by \( S_t = (\eta_1 S_{BET,ref})/ V_{0.4,ref} \), where \( S_{BET,ref} \) and \( V_{0.4,ref} \) are the BET surface area (22.1 m\(^2\) g\(^{-1}\)) and the amount of vapor nitrogen adsorbed at \( P/P_0 = 0.4 \) for the reference adsorbent (9.12 cm\(^3\) STP g\(^{-1}\)) and \( \eta_1 \) is the slope of a line fit to the \( \alpha_s \)-plot data at low pressure before the beginning of the capillary condensation in mesopores. The external surface area is calculated by \( S_{ext} = (\eta_2 S_{BET,ref})/ V_{0.4,ref} \), where \( \eta_2 \) is the slope of the \( \alpha_s \)-plot at high pressure after the capillary condensation in mesopores. The primary pore volume is estimated by the intersection with y-axis of the line fit to the \( \alpha_s \)-plot data at high pressure.

In the nitrogen sorption technique, nitrogen needs to be able to adsorb to the surface of the pores. As-synthesized materials therefore can not be used for the measurement since the template blocks the pores. Nitrogen adsorption-desorption isotherms in this dissertation are obtained at 77 K using a Micromeritics Tristar 3000 automated
adsorption apparatus. All samples are degassed at 120 °C or 150 °C for 4 hours under flowing nitrogen prior to the measurement.

1.2.2 X-Ray powder diffraction (XRD)

X-ray diffraction is based on the coherent scattering of x-rays from the atoms from an ordered material. This scattering gives rise to peaks in the XRD pattern of the sample. By considering an incoming beam of x-rays reflecting from two planes of atoms with spacing \( d \) (the d-spacing) between them, it is possible to show that constructive interference from the two planes will occur when Bragg’s law is satisfied:

\[
n\lambda = 2d \sin(\theta)
\]  

where \( \lambda \) is the wavelength of the x-rays, \( n \) is an integer, and \( \theta \) is the angle of incidence of the x-ray beam.

For any type of ordered structure, there will be a series of reflections in the XRD pattern corresponding to reflections from different planes of atoms with distinguishable d-spacings. The relationship between the d-spacings can be used to infer the type of structure giving rise the pattern by indexing the d-spacings. For example, if a lamellar material is present, then there is only one spacing between planes of differing density. However, because of the integer appearing in Bragg’s law, it is possible to see reflections at different angles corresponding to \( n = 1, n = 2, \) etc. These are referred to as (001), (002), etc. reflections in the lamellar pattern. For a 2D hexagonal close packed structure, one can usually resolve (100), (110), and (200) reflections where \( d_{110} = (\sqrt{3}/2) d_{100} \) and \( d_{200} = (1/2) d_{100} \). Other types of pore structure will have other relationships among the reflections.

In a real sample, the long-range order is not perfect. Distortions from a perfectly organized array of pores will induce two changes in an XRD pattern. First, the reflections will appear to be broader for smaller ordered domains or for domains that are curved or otherwise defective. Second, the number of peaks will be reduced when the material is less ordered. In mesostructures, the lowest-angle peaks (with the largest d-spacings) have the greatest intensity. The higher-order reflections (such as 110 and 200 in a hexagonal structure) have lower intensity. The intensity of the higher-order reflections becomes even less when the structure is defective. Therefore, a qualitative
measure of the quality of ordering in a sample will be obtained from the width of the reflections and the number of higher-order reflections that can be resolved.

XRD patterns of all samples to be discussed were recorded on a Siemens D5000 diffractometer using Cu Kα radiation with wavelength 0.15406 nm. Powder samples were mounted in a metal holder for the characterization. Powders were filled either from the back or the side of a holder with the corresponding cavity. For hexagonally packed pore structures, the repeat distance ($a_0$) between the nearest pore centers was calculated from the XRD data with the equation $a_0 = 2d_{100}/\sqrt{3}$.

1.2.3. Transmission electron microscopy (TEM)

The primary concern while preparing samples for TEM is that they be thin enough to transmit electrons. This usually means that the sample must be a few hundred nm thick or less. Fortunately, most of the powders discussed in this thesis are already thin enough to be electron transparent, so no sectioning or thinning is required. Samples were either ultrasonic dispersed in acetone and then a drop of the solution was put onto a lacy carbon grid or dried samples were put on a grid directly. TEM images were recorded by using JEOL 2010F Filed-Emission TEM with an acceleration voltage of 200 kV.

1.3. Organic-inorganic hybrid sol-gel materials

The second primary focus of this thesis is the use of organically modified silanes to create functional organic-inorganic hybrids. The study of organic-inorganic hybrid materials, sometimes called nanocomposites, is also a rapidly expanding research area in materials science.\textsuperscript{29,30} With the development of technology for specialized applications, the disadvantages of pure inorganic or organic materials become more obvious. For example, organic materials such as plastics are tough but not very strong, and therefore can be easily scratched. Inorganic materials are very strong, but also very brittle, so ceramic materials such as a catalyst may be susceptible to cracking and degradation upon thermal cycling. Composite materials combine the strengths of both types of materials. The desire to obtain new materials with combined properties of organic and inorganic materials becomes stronger and stronger. For a wide variety of applications, including adsorption, catalysis, and chromatography, there is also strong interest in preparing
hybrid materials with controlled porosity which have the structural and thermal stability of a ceramic combined with the chemical functionality of an organic.

Hybrid materials usually are classified into two categories. In class I, one of the organic or inorganic components is entrapped within the network of the other component. The interactions between the two components are only weak bonds as Van der Waals, hydrogen or ionic bonds. The as-made materials prepared during surfactant templating are an example of this class of organic-inorganic hybrids. In class II, the organic and inorganic parts are linked by covalent or ionic-covalent bonds. For conventional composite materials, organic and inorganic compounds are just mixed together. The interactions between the organic compound and inorganic compound are only weak bonds. For instance, glass particles and fibers can be added to plastics to improve some properties of the compounds. These compounds are mixed with macroscopic size domains like blends of two polymers. Many useful composites, such as fiber-glass reinforced polymers, have been prepared, but their applications are still limited. People are constantly looking for a method to mix the inorganic and organic parts in a more intimate way. This was not widely available until the sol-gel process began to be used in this area about 25 years ago. In this process, an organic group can be introduced as part of the precursor which is used to synthesize the hybrid material. This organic group in this case is linked by covalent bond to the inorganic part. Because the organic component is actually a functional group attached to the precursor, the mixture of organic and inorganic parts is on the molecular or nanometer scale.

The sol-gel process is the key technology enabling the synthesis of both surfactant-templated materials and organic-inorganic hybrids. The “sol-gel” method uses a molecular precursor to generate a ceramic material chemically through polymerization rather than through melting and reforming an existing ceramic. One of the greatest advantages of this process is the mild reaction condition under which it occurs, which is critical in making hybrid materials. Obviously, the high temperature required to melt or sinter ceramics cannot be used for the synthesis of hybrid materials because of the low decomposition temperature of organics. The hybrids prepared by the sol-gel route are mixed at the nanometer scale, so it is easy to design and tailor the products with homogeneous and unusual properties. Some of their applications include optical filters,
electrical materials, biomaterials, coatings, membranes, tunable solid-state lasers, shape-selective catalysts, chemical sensors, molecular sieves, catalyst supports, and selective adsorbents. 30,32

Products with special properties have been reported by using precursors with different organic groups. One of the challenges in this research area is to synthesize materials with high surface areas and narrow pore size distributions containing a large organic content, or using bridged alkoxy silanes with long bridging chains. Bridged alkoxy silanes are a family of silanes that contain a variable organic group attached to two or more trifunctional alkoxy silyl groups (Figure 1.4). 35 The unique properties of bridged alkoxy silanes stem from the bridging organic groups that are incorporated as an integral part of the whole network structure of the hybrids. In this way, the organic and inorganic parts are constrained to coexist intimately. Because the bridging organic moiety is part of the monomer, homogenous hybrids can be easily prepared without the problem of phase separation. However, materials made from alkoxy silanes with long bridging chains normally lack high surface areas due to the collapse of pores after extracting the template or removing the solvent. 35 Special drying process such as supercritical drying may help to preserve pore structures. 36 However, this process is generally applied to remove the solvent from sol-gel materials, and has not been applied as a way to preserve pore structures in surfactant-templated materials. One of our goals is to be able to produce well-defined porous inorganic-organic hybrids by surfactant templating, so supercritical drying may not be an option.

Within the sol-gel process, synthesis methods can be classified as a non-templated sol-gel process and a templated sol-gel process (discussed earlier). The difference between a non-templated process and a templated sol-gel process lies in the supramolecular templates used in the latter method. In the latter method, a material is formed by silanol polycondensation in the presence of a template that is later removed to leave well-defined pores behind.

The non-templated sol-gel process has advantages including lower costs, simpler formulations and fewer processing steps. The solvent is generally volatile, and can be removed easily by evaporation or supercritical extraction / drying. Materials obtained from this process normally are gels. These gels can be classified as xerogels or aerogels
depending on the drying conditions. Xerogels are prepared by evaporation of a liquid solvent, and the pores may shrink and collapse during drying. Aerogels are formed by conducting the solvent removal at supercritical temperature and pressure or by replacing the solvent with supercritical CO$_2$. The absence of liquid menisci in the pores during drying allows the pore structure to be well preserved in aerogels. Even with supercritical drying, however, the non-templated sol-gel process has several obvious disadvantages. The materials prepared by the non-templated method usually lack long-range order. Small pore sizes and narrow pore size distributions can only be obtained at the expense of pore volume. The surface areas of the materials usually are low unless the solvent is removed by supercritical drying. They are very fragile due to non-uniform pore wall thickness. Templated materials overcome some of these disadvantages because they have pores of uniform size and uniform walls thicknesses.

1.4. Sol-gel reaction mechanisms

Irrespective of whether a pore template is present, the chemistry of the sol-gel process consists of hydrolysis and condensation reactions of alcoholic or other low molecular weight organic solutions of alkoxides M(OR)$_z$ (M = Al, B, Ce, Cr, Mo, Si, Sn, Ti, Zr, Zn, Vo, W, etc.). The M(OR)$_z$ are hydrolyzed to produce intermediate products with hydroxyl groups. Then these intermediate products react together by polycondensation of the hydroxyl groups to form three-dimensional networks. Transition metals can also polymerize through sol-gel reaction to form M-O-M links, but only silane sol-gel polymerization will be studied here. In the presence of a template, the hydrolyzed species will be attracted to surround the template described earlier (Figure 1.2). Depending on the nature of the synthesis conditions, a mixture of micelles and sol-gel precursors may precipitate prior to co-assembly, or the precursor-coated micelles may form first and then assemble. Either way, the condensation reaction should be accelerated by localization of silica species near the surfactant. The rates of hydrolysis and condensation reactions will affect the pore structures by changing the charge density of the charged silica. The rate to form network structure will be also important to the development of long-range ordering. The kinetics of these reactions is incompletely understood for organically modified silanes, especially for bridged alkoxysilane...
precursors. Further investigation on the kinetics and mechanism of this reaction is thus necessary. The kinetics of various organically modified silanes will be measured and modeled in Chapters 2 and 3, and the impact of the kinetics on the structure of non-templated and surfactant-templated materials will be investigated in Chapter 4. Here, the mechanism of the sol-gel reaction will be introduced.

A typical sol-gel reaction is illustrated in equations (1.5) to (1.7). In general, the sequence of steps begins with hydrolysis of an alkoxide to generate a silanol group (SiOH) and alcohol (equation 1.5). Once silanols are present, they can react by condensation with other hydrolyzed silicon sites to generate siloxanes and water (equation 1.6). Alternatively, a reaction between a silanol and an unhydrolyzed silicon can produce a siloxane and alcohol (equation 1.7). In general, all three reactions are reversible, depending on the conditions under which the reaction is performed. They are also usually carried out in the presence of a catalyst which can be an acid, a base, or fluoride ions. Many factors influence these reactions beyond just the reaction temperature and reactant concentrations. The pH and the type of solvent are especially important in determining the reaction pathway and the kinetics of the reaction.\textsuperscript{34}

The reaction in acid and basic solutions will be explained with different mechanisms.\textsuperscript{34} In basic solution, the mechanism of the hydrolysis reaction follows a sequence of steps summarized by Brinker and Scherer.\textsuperscript{34} The hydrolysis reaction is illustrated in Figure 1.6. The reaction begins with the attack of a hydroxide anion on a silicon site. The system passes through two transition states (T.S. 1 and T.S. 2) and a stable pentacoordinated intermediate is formed during the reaction. The decay of this intermediate by loss of an alkoxide group leads to the products, which are a silanol group and an alkoxide. Both the hydroxide and alkoxide anions in solution are assumed to be at equilibrium with their protonated forms. The reaction proceeds through an anionic transition state.

Condensation under basic conditions proceeds by the attack of a deprotonated silanol on another silicon site (Figure 1.7). First, a hydroxyl anion attacks an existing silanol to produce a deprotonated anion (SiO\textsuperscript{-}) and water. This reaction (equation 1.8) is presumed to be fast and to stay at quasi-equilibrium. The deprotonated silanol then attacks another silicon site through an S\textsubscript{N}2 reaction, where hydroxide is the leaving group. The reaction
mechanism of a base-catalyzed condensation is generally believed to be similar to the mechanism of hydrolysis. It also involves penta- or hexacoordinated intermediate or transition state.\(^{34}\)

In addition to the mechanism of the reaction, researchers have studied the relative rates of the sol-gel steps shown in Figure 1.5. Under basic condition, the condensation step is usually much faster than hydrolysis. Therefore, the hydrolysis reaction is the rate determining step for the overall sol-gel reaction (at least at the early stages of the process). Because of the participation of charged pentacoordinated intermediates in both hydrolysis and condensation, both steric and inductive factors affect the reaction rates.\(^{34}\)

The reaction in acidic condition is explained with a different mechanism. The hydrolysis could be described with a S\(_{N}\)2-type mechanism involving a protonated alkoxide (Figure 1.8). The protonated alkoxide can be assumed to form reversibly and quickly from an alkoxide and acid. Water attacks the silicon of the pronated species, and partially acquires a positive charge. A pentacoordinated transition state forms. Alcohol then leaves the transition state and the hydrolysis completes. Again, because charged intermediates and a pentacoordinate transition state are involved, the reaction is influenced by both steric and inductive effects. A less crowded structure in the transition state surely improves the stability of this state, which increases the hydrolysis rate. The effect of inductive factor is not as great as the steric effect for this reaction.\(^ {34}\)

The mechanism of acid-catalyzed condensation (pH below 4.5) has been explained according to a similar mechanism (Figure 1.9).\(^ {34}\) First, there is a pre-equilibrium in which silanols are protonated. The protonated silanol becomes a better leaving group, and therefore the condensation reaction proceeds through the attack of a silanol on the silicon of a protonated silanol. The reaction proceeds through a pentacoordinated transition state. The condensation reaction rate will be affected by both inductive and steric factors.\(^ {34}\)

As shown above, hydrolysis is catalyzed by hydroxide anions or by protons. If the log of the rate coefficient for hydrolysis is plotted on a log scale as a function of pH, a v-shaped curve will result with a minimum at pH 7. The position of the minimum is determined by the uncatalyzed rate of hydrolysis (which is usually small but non-zero). Moving away from this minimum in either direction are lines with slopes of magnitude 1 due to the direct involvement of hydroxides or protons in hydrolysis.\(^ {42}\) For condensation,
on the other hand, the reaction is between two silanols. Base-catalyzed condensation involves a deprotonated silanol and acid-catalyzed condensation involves a protonated silanol. Therefore, the pH dependence of the condensation rate coefficient is determined by the balance of protonation or deprotonation of silanols. The isoelectric point of silica is close to pH 2. At pH > 2, silica has a net negative charge due to deprotonation, and at pH < 2, silica is protonated and develops a positive charge. Again, if the log of the condensation rate coefficient is plotted vs. pH, a v-shape curve is found where the minimum is at the isoelectric point of the silanol. Because the v-shaped curves have different minima, the hydrolysis and condensation curves cross each other. At high pH, as mentioned above, hydrolysis is the slower reaction. However, at low pH, condensation is rate determining because of the crossover of the curves. The crossover occurs at a pH higher than the isoelectric point of the silanol and defines the transition from hydrolysis being rate-limiting (high pH) to condensation being rate-limiting (low pH).

Kinetic studies of sol-gel precursors have been carried out extensively. However, the kinetics of bridged silanes have been rarely studied in quantitative detail. Only once has a high molecular weight epoxy bridged silane been compared to its nonbridged counterpart. Comparisons of the kinetics of non-bridged silane with its corresponding bridged silane for common bridges (ethylene, hexylene, etc.), and of bridged silanes with different bridging chains have not been conducted. Therefore, this will be the subject of Chapters 2 and 3 of this thesis. In Chapter 8, surfactant templating and organic-inorganic hybrid materials will be brought together through the formation by surfactant templating of multilamellar vesicular bridged silsesquioxane particles with various bridging chains.

1.5. Applications of sol-gel silica supports and scope of the thesis

The final aspect of sol-gel materials that will be discussed in this thesis is related to the applications of these types of materials. Mesoporous silica has been reported to have benefits for a wide range of applications including catalysis, absorption, drug delivery, and so on. Chapter 9 of this thesis will briefly describe the use of functionalized mesoporous silica as a support for the deposition of iron oxide nanoparticles. The unique approach being taken is to place amine groups on the surface of the material as a means
of encouraging deposition of nanoparticles on the surface of the pores. This is just one example of the many ways that porous ceramics materials can be functionalized and loaded with other metals and metal oxides. Chapter 9 only hints at the great potential that these kinds of materials have for the preparation of supported nanoparticles.

The synthesis of controlled-porosity ceramics and hybrid materials is a vast and complex problem. This thesis addresses several of the many aspects associated with this problem. The scope of this thesis includes kinetic studies of the sol-gel reactions of a series of bridged and non-bridged silane precursors (Chapters 2-3), synthesis of organic-inorganic hybrid materials with and without pore templates (Chapters 4 and 8), synthesis of mesoporous materials with controlled architecture by using hydrocarbon surfactants, fluorinated surfactants, and latex particles (Chapter 5-8), and the application of mesoporous materials as supports for the controlled deposition of nanoparticles (Chapter 9).

1.6. References

Figure 1.1. Schematic diagram of CTAB in water. Reprinted with permission from (Raman et al. Chem. Mater. 1996, 8, 1682). Copyright (1996) American Chemical Society.\textsuperscript{11}
Figure 1.2. Schematic diagram of the surfactant templated sol-gel process. Reprinted with permission from (Burleigh et al. Chem. Mater. 2001, 13, 4760). Copyright (2001) American Chemical Society.
Figure 1.3. Typical $\alpha_s$-plot for mesoporous silica.

\[(\text{RO})_3\text{Si-}[\_\_\_]-\text{Si(OR)}_3\]

where $R$ is an alky chain, $[\_\_\_]$ is an organic group.

Figure 1.4. Bridged alkoxy silanes.
RO-Si + H₂O \xrightarrow{\text{Hydrolysis}} \text{Si-OH} + \text{ROH} \quad (1.5)

\text{Reesterification}

\text{HO-Si + HO-Si} \xrightarrow{\text{Water-producing condensation}} \text{Si-O-Si} + \text{H}_2\text{O} \quad (1.6)

\text{Hydrolysis}

\text{RO-Si + HO-Si} \xrightarrow{\text{Alcohol-producing condensation}} \text{Si-O-Si} + \text{ROH} \quad (1.7)

\text{Alcoholysis}

R: An alkyl group such as CH₃-, CH₂CH₂-, etc.

**Figure 1.5.** Hydrolysis and condensations in a sol-gel reaction.³⁴

\[
\begin{align*}
\text{Si-OR} + \text{OH}^- & \quad \leftrightarrow \quad \text{RO-Si} \quad \leftrightarrow \quad \text{Si-OH} + \text{RO}^- \\
\text{T.S. 1} & \\
\text{RO-Si} \quad \leftrightarrow \quad \text{Si-OH} + \text{RO}^-
\end{align*}
\]

**Figure 1.6.** Base-catalyzed hydrolysis.³⁴

\[
\begin{align*}
\text{Si-OH} + \text{OH}^- & \quad \xrightarrow{\text{Fast}} \quad \text{Si-O}^- + \text{H}_2\text{O} \\
\text{Si-OH} + \text{Si-O}^- & \quad \xrightarrow{\text{Slow}} \quad \text{Si-O-Si} + \text{OH}^-
\end{align*}
\]

**Figure 1.7.** Base-catalyst condensation.³⁴
Figure 1.8. Acid-catalyzed hydrolysis.\textsuperscript{34}

\[
\text{HOH} + \text{RO} \text{SiOR} + \text{H}^+ \rightleftharpoons \delta^+ \text{RO} \text{Si} \text{OR} \delta^+ \text{OH} \rightarrow \text{HO} \cdots \text{Si} \cdots \text{OH} \rightarrow \text{RO} \text{SiOR} + \text{ROH} + \text{H}^+
\]

T.S.

Figure 1.9. Acid-catalyzed condensation.\textsuperscript{34}

\[
\begin{align*}
\text{R-Si-OH} + \text{H}^+ & \rightleftharpoons \frac{k_1}{k_{-1}} \text{R-Si-} \quad \text{fast} \quad \text{H} + \text{H} \\
\text{R-Si-} + \text{R-Si-OH} & \rightleftharpoons \frac{k_2}{k_{-2}} \text{R-Si-O-Si-R} + \text{H}_3\text{O}^+ \quad \text{slow} \\
\end{align*}
\]

\[-d[\text{silanetriol}]/dt = k_1k_2/k_{-1} [\text{RSi(OH)}_3]^2[H^+].\]

Figure 1.9. Acid-catalyzed condensation.\textsuperscript{34}
Chapter 2. Kinetics of the Sol-Gel Reaction of 3-Aminopropyltrimethoxysilane (APTMS) and Comparison to a Silane with an Amine-functional Bridging Organic

2.1. Introduction

Organically functionalized alkoxysilane precursors have been used for decades as coupling reagents to promote adhesion between polymers and inorganic fillers. They are also used to make functionalized ceramic and organic-inorganic hybrid materials for applications such as catalysts, adsorbents, and chemical sensors. The chemistry involved is so-called sol-gel chemistry, which consists of hydrolysis and condensation reactions starting with alkoxysilane groups. The general hydrolysis and condensation reactions are expressed in Figure 2.1.

The mechanism of the sol-gel reaction has been investigated for many years. Under acidic conditions, the mechanism of the reaction has been well characterized and is fairly well understood, although it is complex. However, the mechanism for the reaction in basic condition still has not been fully resolved. The reason that this is difficult to do is that there are many intermediate products involved in the sol-gel reaction. Under acidic conditions, the solutions remain homogeneous and react slowly, so that $^{29}$Si NMR can be used to gain insights into the distribution of intermediates. Under basic condition, phase separation typically occurs which causes a loss of NMR signal intensity from intermediate species. This seems to make the modeling of this system impossible. Efforts to obtain the hydrolysis and condensation rate coefficients under basic conditions have been reported before. Harris et al assumed that TEOS reacts with $\text{[OH}^-]$ and water and the condensation occurs only between completely hydrolyzed silica species. The same assumptions were used by Piana et al. The hydrolysis is assumed to be a third order reaction in their work. In Dubitsky et al’s report, hydrolysis was assumed to be a second order reaction without considering the concentration of $\text{[OH}^-]$.

Aminosilanes are an important class of silanes with many uses for materials synthesis. They are used to provide coupling to polymers (for instance, in hybrid nylon-6, 6 / kaolin composites) and can themselves act as electron donors, catalysts, adsorption sites for metals, or proteins. Amines can also be chemically modified to
produce new materials. The polymerization of aminosilanes in basic conditions is of most interest since most materials made with these precursors are formed in basic solutions. The reactions of these silanes are somewhat complicated because the amine can act as a catalyst for the sol-gel reaction, either by being protonated and raising the pH of the environment, or through specific interactions with silica sites. It is also very interesting to compare the kinetics of a non-bridged amine-functional precursor with its corresponding bridged precursor. For instance, 3-aminopropyltrimethoxysilane (APTMS) and bis(trimethoxysilylpropyl)amine (BTMSPA) are both commercially available as coupling agents, and they can be compared to study the effects of the connectivity of the organic groups on the product properties. The comparison may indicate how to explain the obvious difference in gel times found by using the two precursors under similar reaction conditions. The gel time of BTMSPA is much shorter than it of APTMS. Under similar conditions, a solution with BTMSPA gelled in 12 minutes, while the solution with APTMS did not gel for days. The information will be helpful to control the sol-gel reaction, thus to improve the qualities of the product made from organically modified silanes. It is not clear at this stage, for instance, whether it is preferable to use a bridged or a non-bridged silane to make a bulk amine-functional porous solid.

Several studies of the reactions of amine-functional silanes have been conducted. Rousseau et al investigated the polycondensation of APTMS and (trimethoxysilylpropyl)diethylenetriamine (TRIAMO) using $^{29}$Si NMR to monitor the reactions. Rousseau et al also studied the hydrolysis and condensation of (N,N-Diethylaminopropyl)trimethoxysilane (NNDE). Bourgeois et al investigated systems composed of glycidoxypropyltrimethoxysilane (GPTS), 3-aminopropyltriethoxysilane (APTES) and mixtures of the two silanes. The work of Rousseau et al on the polycondensation of aminosilanes is particularly informative. We will establish our mathematical model based on this work. Even though there is detailed discussion about the kinetics of APTMS, no mathematics model has been proposed to describe the reaction. The kinetics of a bridged precursor was discussed once, but no discussion about amine-functionalized bridged precursor was reported before.

In this chapter, we established a mathematical model for the polymerization of APTMS based on the NMR investigation of Rousseau et al. Another model based on a
simplified assumption is also proposed for the comparison. These models are applied to FTIR data collected in situ during the reactions of amine-functional silanes. Comparisons of the model with data collected with added HCl or NaOH are made, and discussed in terms of the adequacy of the model. The kinetics of APTMS is finally compared to that of BTMPA under identical conditions.

2.2. Experimental section

2.2.1 Materials. 3-aminopropyltrimethoxysilane (APTMS) was purchased from Gelest in the purest form available. The silane was handled under flowing nitrogen to prevent absorption of water and gradual contamination. Other solvents and reagents used were deionized untrafiltered water (Fisher Scientific), methanol (HPLC grade, Fisher EMD), NaOH (1N, Alfa), HCl (1 N, Alfa). All chemicals were used without further purification.

2.2.2 Instrumentation. FTIR spectroscopy was used to monitor the evolution of the concentrations of APTMS and water. Spectra were collected using a ThermoNicolet Nexus 470 FTIR spectrometer with a DTGS detector. The spectra were collected by averaging 16 scans at a resolution of 4.0 cm\(^{-1}\). All experiments were performed in a stainless steel demountable flow-through liquid cell (Harrick Scientific) with germanium windows. The cell features a vertical flow path between the windows which allows us to use mismatched PTFE spacers to create a wedge-shaped sample. This avoids the appearance of interference fringes in the FTIR spectra due to partial reflection of the IR beam. One of the spacers used was 0.12 mm thick and the other was 0.025 mm thick.

2.2.3 Procedure. Two solutions were prepared before the start of the kinetic experiment. One consisted only of the required amount of APTMS in methanol, and the other of water and any added catalyst in methanol. After setting up the acquisition parameters, these solutions were mixed together very quickly in a vial and the mixed solution was injected by syringe into the liquid cell. Series data were collected automatically after the introduction of the reacting sample. The time was recorded at the point of mixing and while collecting each spectrum. All reactions were conducted at room temperature (21 ± 2 °C).
2.2.4 Modeling of the reaction kinetics.

The kinetics of a sol-gel reaction in basic condition is very complicated because of the participation of a large number of intermediate products.\textsuperscript{2} The real process is still not completely understood. However, a simplified general reaction process can be represented by Scheme 2.1.\textsuperscript{2,5} In this scheme, T represents a single trifunctional silicon site (with 3 hydrolyzable alkoxide groups), the subscript represents the number of siloxane bonds that have been attached to the site, and the superscript represents the number of hydroxyl groups attached to the site. The original monomer is represented in the upper left corner. As hydrolysis reactions replace methoxy groups with hydroxyl groups, we move from left to right across the scheme (the participation of water in these reactions is implied but not shown). As condensation reactions occur, we move downward in the scheme. Each arrow represents several condensation reactions that can occur with any of the other silicon sites in the system. As Kay and Assink have shown, if each site has a different rate coefficient for hydrolysis and condensation with every other site, then there are dozens of rate coefficients to be determined.\textsuperscript{5}

This process can be further simplified based on the analysis of the polycondensation behavior of APTMS in the APTMS/water/methanol system. Rousseau et al. have characterized in detail the intermediates present during polymerization of APTMS, and the simplifications that will be used are based on their observations. For the sol-gel reaction with APTMS in methanol solution, no $T_{0}^{2}$ and $T_{0}^{3}$ species were identified by $^{29}$Si.\textsuperscript{17} This indicates either that the further hydrolysis of $T_{0}^{1}$ is not likely to happen or that $T_{0}^{2}$ and $T_{0}^{3}$ species are extremely reactive toward condensation. Because the dominant $T_{1}$ species is $T_{1}^{0}$, it is more likely that the condensation rate from $T_{0}^{1}$ to $T_{1}^{0}$ is much faster than the hydrolysis rate of $T_{0}^{1}$ to produce $T_{0}^{2}$. In the paper of Rousseau et al., low-intensity peaks are found for both $T_{1}^{1}$ and $T_{1}^{2}$. There is only one intense $T_{2}$ peak, which was assigned to $T_{2}^{0}$.\textsuperscript{17} Given that both $T_{1}^{1}$ and $T_{1}^{2}$ are present, it may make more sense to attribute this sharp peak to $T_{2}^{1}$, since $T_{1}^{2}$ is expected to be more reactive toward condensation due to both the number of silanols and a favorable inductive effect. If the $T_{2}^{1}$ species is assumed to be the dominant $T_{2}$ species, then a simplified scheme based on Scheme 2.1 can be proposed, as shown in Scheme 2.2. Note, however, that the final
mathematical model generated will be the same even if the dominant $T_2$ species is in fact $T_2^0$.

In basic solution, it is generally found that the hydrolysis reaction is the rate-limiting step, and water producing condensation is dominant over alcohol producing condensation. The reverse hydrolysis reaction can be neglected even with a relatively large amount of alcohol because of the high condensation rate.

Without considering the reverse reactions and alcohol producing condensation steps, the reactions involved can be expressed as the following elementary scheme, where rate coefficients are given following each equation.

$$T_0^0 + H_2O \rightarrow T_0^1 + CH_3OH \quad k_{h1} \quad (2.1)$$

$$T_0^1 + T_0^1 \rightarrow 2 T_1^0 + H_2O \quad k_{c1} \quad (2.2)$$

$$T_1^0 + H_2O \rightarrow T_1^1 + CH_3OH \quad k_{h2} \quad (2.3)$$

$$T_1^1 + H_2O \rightarrow T_1^2 + CH_3OH \quad k_{h3} \quad (2.4)$$

$$T_1^2 + T_1^2 \rightarrow 2T_2^1 + H_2O \quad k_{c2} \quad (2.5)$$

$$T_2^1 + T_2^1 \rightarrow 2T_3^0 + H_2O \quad k_{c3} \quad (2.6)$$

Based on the $^{29}$Si NMR data of Rousseau et al., $T_0^1$, $T_1^1$, and $T_1^2$ species can be treated as being at pseudo-steady state. Also from their data, $k_{h2}$ is estimated to be half of $k_{h1}$ (see below for derivation) and $k_{h3}$ is almost 10 times the value of $k_{h2}$. The larger value of $k_{h3}$ compared to $k_{h2}$ is consistent with the assumption that reaction (2.4) is much faster than (2.3). $T_2$ (and then $T_3$) species were reported to be observable only after a sufficient proportion of $T_1$ ($T_2$) species are present. Two factors may be responsible for this behavior. Either the hydrolysis rate of $T_1^0$ ($T_2^0$) is much slower than the hydrolysis rate of $T_0^0$ ($T_1^0$), or the condensation rate from $T_1$ ($T_2$) to $T_2$ ($T_3$) is much slower than the rate of the preceding condensation step. Since $k_{h2}$ is just half of $k_{h1}$, we expect that the condensation reaction is responsible for the late appearance of $T_2$ ($T_3$). This is reasonable, since the steric effect of adding siloxane bonds should make condensation reaction (2.5) [(2.6)] much slower than reaction (2.2) [(2.5)].
Among the condensation reactions, (2.6) is the slowest and may be less favorable thermodynamically because of the steric crowding of the reacting sites. This may explain why condensation still continues for months after gelation. The condensation (2.6) complicates the process of modeling the sol-gel reaction, because no data have been obtained to allow an accurate estimate of $k_{c3}$. However, since this reaction is very slow and it starts very late, we don’t need to consider it at the early stage of a sol-gel reaction. If the time scale for the final reaction is much longer than that of the other steps, then the inverse of the gel time should be related to $k_{c3}$.

Neglecting reaction (2.6), the differential equations for the scheme above can be written as:

\[
\begin{align*}
\frac{dT_0^0}{dt} &= -k_{h1}T_0^0[H_2O] \quad (2.7) \\
\frac{dT_0^1}{dt} &= k_{h1}T_0^0[H_2O] - 2k_{c1}(T_0^1)^2 \quad (2.8) \\
\frac{dT_1^0}{dt} &= 2k_{c1}(T_0^1)^2 - k_{h2}T_1^0[H_2O] \quad (2.9) \\
\frac{dT_1^1}{dt} &= k_{h2}T_1^0[H_2O] - k_{h3}T_1^1[H_2O] \quad (2.10) \\
\frac{dT_1^2}{dt} &= k_{h3}T_1^1[H_2O] - 2k_{c2}(T_1^2)^2 \quad (2.11) \\
\frac{dT_2^1}{dt} &= 2k_{c2}(T_1^2)^2 \quad (2.12) \\
\frac{d[H_2O]}{dt} &= -(1/2) k_{h1}T_0^0[H_2O] - (3/2) k_{h2}T_1^0[H_2O] \quad (2.13)
\end{align*}
\]

With the assumption that species $T_0^1$, $T_1^1$, and $T_1^2$ are all at pseudo-steady state, the above equations are rewritten as:

\[
\begin{align*}
\frac{dT_0^0}{dt} &= -k_{h1}T_0^0[H_2O] \quad (2.7) \\
\frac{dT_1^0}{dt} &= k_{h1}T_0^0[H_2O] - k_{h2}T_1^0[H_2O] \quad (2.14) \\
\frac{dT_2^1}{dt} &= k_{h2}T_1^0[H_2O] \quad (2.15) \\
\frac{d[H_2O]}{dt} &= -(1/2) k_{h1}T_0^0[H_2O] - (3/2) k_{h2}T_1^0[H_2O] \quad (2.16)
\end{align*}
\]

When the concentration of $T_1^0$ reaches its maximum, $k_{h2}/k_{h1} = ([T_0^0]/[T_1^0])_{max}$. By using the $^{29}$Si data of Rousseau et al., $k_{h2}/k_{h1}$ is estimated to be about 0.5. 17

Because we use FTIR to monitor the reaction, we have to obtain a relationship between the total concentration of Si-OCH$_3$ and the species concentrations being modeled since only total [Si-OCH$_3$] is monitored. The relationship can be written as [Si-OCH$_3$] = 3$[T_0^0]$ + 2$[T_1^0]$ (neglecting the small contribution from $T_1^1$). Using equations (10) and (17) and the relationship $k_{h2}/k_{h1} = 0.5$, we can obtain

\[
[T_0^0] = (2[T_0^0]_0^{1/2} - (4[T_0^0]_0 - [Si-OCH_3])^{1/2})^2
\]  
(2.17)
and \([T_1^0] = 2[T_0^0]_0^{1/2}[T_0^0]^{1/2} - 2[T_0^0]\) \tag{2.18}

From equations (2.7), (2.16), (2.17), and (2.18), we can derive the following equations:

\[
[H_2O] = [H_2O]_0 - 2[T_0^0]_0 + 3[T_0^0]_0^{1/2}[T_0^0]^{1/2} - [T_0^0] \tag{2.19}
\]

\[
k_{h1}t = A \ln\left(\frac{h}{h_0}\right) + B \ln\left(\frac{h - c1 - c2}{h_0 - c1 - c2}\right) + C \ln\left(\frac{h - c1 + c2}{h_0 - c1 + c2}\right) \tag{2.20}
\]

with \(h = [T_0^0]^{1/2}\), \(h_0 = [T_0^0]_0^{1/2}\), \(c1 = \frac{3h_0}{2}\), \(c2 = \frac{h_0^2}{4} + [H_2O]_0^{1/2}\), \(A = \frac{2}{(c1 - c2)(c1 + c2)}\), \(B = \frac{1}{c2(c1 + c2)}\), and \(C = -\frac{1}{c2(c1 - c2)}\).

Equation (2.20) is written so that \([T_0^0]_0\) is the only independent variable appearing on the right hand side. If we know the relationship between \([T_0^0]_0\) and \(t\), we can fit the data with this equation by linear regression to obtain \(k_{h1}\). Since we have just shown that \([T_0^0]\) can be obtained from \([SiOCH_3]\), we should be able to calculate \(k_{h1}\) by fitting the experimental FTIR data with equation (2.20).

For the sol-gel reaction in basic condition, researchers have sometimes assumed that all of the SiOCH3 species have the same reactivity. This is the “functional group kinetics” approach described by Assink and Kay.\(^4\) Hydrolysis is expected to proceed according to one rate, which depends on the total concentration of SiOCH3 and the water concentration. Because the hydrolysis reaction is rate-limiting in a base-catalyzed sol-gel reaction, it can be assumed that once SiOH is produced, it will condense immediately. The water-producing condensation is dominant over the alcohol-condensation.\(^21\) Reactions (1.5) and (1.6) are the only two reactions involved with all reverse reactions are neglected (see Chapter 3 for details).

The simplified scheme for this model is shown in Scheme 2.3. With these assumptions, a single differential equation for the concentration of SiOCH3 can be written and solved to give:

\[
1 - \frac{[SiOCH_3]_0 - 2[H_2O]_0}{[SiOCH_3]} = 2[H_2O]_0^{1/2} - 2[H_2O]_0^{1/2} [SiOCH_3]_0^{-1/2} \cdot e^{-\frac{1}{2}([SiOCH_3]_0 - 2[H_2O]_0) k_{h1} t} \tag{2.21}
\]

or
\[
1 - (1 - b \exp(-\frac{a}{2} k'_{h} t_{r})) \frac{A(SiOCH_{3})}{A(SiOCH_{3})_{r}} = b \exp(-\frac{a}{2} k'_{h} t)
\]  

(2.22)

where \( k'_{h} \) is the general hydrolysis coefficient in equation (1.5), \( a = [SiOCH_{3}]_{0} - 2[H_{2}O]_{0}, \) \( b = 2[H_{2}O]_{0}/[SiOCH_{3}]_{0}, \) \( A(SiOCH_{3}) \) and \( A(H_{2}O) \) are the absolute band intensities for SiOCH\(_{3}\) and H\(_{2}\)O and \( A(SiOCH_{3})_{r}, A(H_{2}O)_{r} \) are the absolute intensities at the reference time \( t_{r}. \)

Further discussion about this model will be given in Chapter 3. By plotting the left side of equation (2.22) versus time, we can obtain \( k'_{h}. \) If \( k'_{h_{1}}, k'_{h_{2}}, k'_{h_{3}} \) are the general hydrolysis rate coefficients for \( T_{0}, T_{1}, \) and \( T_{2} \) in this model, \( k'_{h_{1}} \) is expected to be 3 times of \( k'_{h} \) since each \( T_{0} \) species has three SiOCH\(_{3}\) groups. \( k'_{h_{2}} \) is twice of \( k'_{h} \) and \( k'_{h_{3}} \) is equal to \( k'_{h}. \) In this model, \( k'_{h_{2}} \) is 2/3 of \( k'_{h_{1}}, \) which is close to the ratio of 1/2 assumed in the first model. The main difference between these two models is the different reaction route followed after \( T_{1} \) is produced.

2.3. Results and discussion

2.3.1. The interpretation of the FTIR data

FTIR has been successfully used to monitor the kinetics of the sol-gel reaction of APTMS under various conditions. Before measuring the kinetics, we prepared a series of samples to check the linear relationship between the concentration of APTMS in methanol and the absorbance. According to the Beer’s law, the relationship between concentration and absorbance is \( A = \Sigma l \varepsilon_{i} C_{i} \) with \( A \) is for absorbance, \( l \) is the pathlength, \( \varepsilon_{i} \) is the absorptivity of a particular band associated with species \( i, \) and \( C_{i} \) is the concentration of species \( i. \)

A typical spectrum for the APTMS/water/methanol system is compared to the FTIR spectrum of methanol in Figure 2.2. The band from 1164 cm\(^{-1}\) to 1228 cm\(^{-1}\) is associated with the asymmetric stretching vibrations of the Si-O-C bond from the SiOCH\(_{3}\) group.\(^{19}\) The band from 1629 cm\(^{-1}\) to 1583 cm\(^{-1}\) is associated with the amine group of APTMS and the band from 1629 cm\(^{-1}\) to 1714 cm\(^{-1}\) is assigned to H\(_{2}\)O.\(^{10}\)

For a methanol/water spectrum (not shown), there is no peak at the band assigned to SiOCH\(_{3}\) and the baseline at this position is almost flat. This confirms that the band is only due to the presence of SiOCH\(_{3}\). According to Beer’s law, the integrated intensity \( A \)
should only be proportional to the concentration of SiOCH₃. For the same chemical system the absorptivity of a species can be reasonable treated as a constant. If the same liquid cell and spacers are used, then the pathlength is also constant and we can assume that A=eC where e is a constant for the APTMS/water/methanol system. A plot of integrated absorbance vs. concentration of APTMS in methanol is shown in Figure 2.3. The line in Figure 2.3 was fitted to the data, and shows an excellent linear relationship between concentration and absorbance in the concentration range from 0 to 1.8 mol/l.

2.3.2. Kinetics of APTMS

2.3.2.1. Kinetics of APTMS without addition of catalyst

Three samples (N1 through N3) with different H₂O:Si ratio were monitored by FTIR to follow the kinetics of hydrolysis of APTMS. Sample N4 is one of the samples reported by Rousseau et al. with the published ²⁹Si data used.¹⁷ The compositions of all samples are reported in Table 2.1.

Kinetic data were collected for samples N1, N2, and N3 over the course of 1350 seconds, and we find that both of the models described above can be fitted to the kinetic data very well (Figures 2.4, 2.5, and 2.6). The rate coefficients obtained are reported in Table 2.1. kₜ is the hydrolysis rate coefficient for T₀ calculated from the first model, while k'ₜ is the general methoxysilane hydrolysis rate coefficient calculated from the second model by ignoring nearest-neighbor effects. Sample N2 was reproduced as N2-r. The average hydrolysis coefficient obtained from samples N2 and N2-r is 2.1 ± 0.1 mM⁻¹s⁻¹ for kₜ and 2.3 ± 0.1 mM⁻¹s⁻¹ for k'ₜ. The small deviation shows that the hydrolysis coefficient is reproducible. The deviation, however, is much larger than the standard error, which is obtained by fitting one set of experimental data with equation (2.20) or (2.22). In this paper, the standard error is shown for each sample. The smaller is this value, the better is the fitting. For each sample, kₜ is similar to k'ₜ. This indicates that the reactions following the formation of T₁ do not affect the hydrolysis rate significantly for these samples under the current conditions. The concentration of T₁ in sample N3 calculated with equation (2.18) is plotted with time in Figure 2.7. The concentration of T₁ increases quickly over the time until it reaches close to its maximum concentration (at 0.277 mol/l). Since both concentrations of T₁ and T₁² are in pseudo-steady states, the
concentration of $T_1$ species is similar to that of $T_1^0$. This means that the concentration of $T_1$ is at most half of the initial concentration of $T_0$.

The main difference among N1, N2, and N3 is the initial concentration of water. The hydrolysis coefficient $k_{hl}$ is almost the same among these samples. This means that the model correctly accounts for the order of the reaction with respect to water.

Sample N4 was adopted from the work by Rousseau et al.\textsuperscript{17} The $^{29}$Si data published in their paper were used to estimate the hydrolysis coefficients, $k_{hl}$ and $k'_{hl}$ using our models. Data collected at first 480 seconds are used for fitting. The hydrolysis coefficients calculated from the two models are close. The slight difference indicates that the reactions following $T_1^1$ affect the hydrolysis rate for this sample. The water: Si ratio of sample N4 is almost as the same as that of sample N3. The difference in the hydrolysis rates between the two samples may be because of the high concentrations of APTMS and water in sample N4.

2.3.2.2. Effect of NaOH on the reaction kinetics

To examine the catalytic effect of the amine on APMTS, five samples were prepared with different concentrations of NaOH. The compositions and calculated hydrolysis coefficients are shown in Table 2.2. FTIR data in the first 240 seconds are used to fit equations (2.20) and (2.22). All samples are very well fitted by the models. The fit of the model to the data for sample B1 is illustrated in Figure 2.8 as an example.

Without the addition of any NaOH, the solution is expected to be basic due to the presence of the amine group. The addition of NaOH to the solution increases the hydrolysis rate coefficient. The increase of the hydrolysis coefficient normally has a linear relationship with the added concentration of NaOH. However, the effect of NaOH on the reaction kinetics over the range investigated is not obvious. The addition of NaOH has only increased the hydrolysis rate slightly. The reason might be that all solutions investigated have pH values larger than 10. For reactions in this pH region, the linear relationship between the hydrolysis coefficient and the NaOH added no longer exists.\textsuperscript{2}
2.3.2.3. Effect of HCl on the reaction kinetics

In this section, HCl instead of NaOH was added to the APTMS system. Four samples were prepared with different concentrations of HCl. The compositions of the solutions and hydrolysis coefficients are compared in Table 2.3. The hydrolysis coefficients of these samples are almost the same. This indicates that the addition of HCl doesn’t affect the reaction kinetics under the current conditions over the range of concentrations tested.

For the reaction system with APTMS as the precursor and methanol as the solvent, the addition of both NaOH and HCl has little effect on the reaction kinetics. The reaction kinetics is independent of the catalyst. This is similar to results reported for the sol-gel reaction carried out at pH > 10.\(^2\) A high pH value might cause the independent relationship between the addition of NaOH or HCl and the reaction kinetics in our experiments. The amine group acts as a base. The pKa of a primary alkyl amine is 10.75, which suggests that the pH in sample B1 is higher than 10. Since the added amount of HCl concentration is much smaller than the concentration of the amine in samples A1-A4, the added HCl is not expected to change the pH dramatically. For example, the pH value in sample A4 is around 12.3 without considering the acidity of the methanol. This confirms the independent relationship between the added HCl or NaOH and the reaction kinetics.

2.3.3. Comparison to the kinetics of a bridged amine precursor, BTMSPA

In addition to showing that we have a model which describes the sol-gel reaction kinetics of APTMS, we wish to compare this precursor to a bridged silane. We compare APTMS with the analogous bridged silane, bis(trimethoxysilylpropyl)amine. We are interested in comparing the two precursors because, while BTMSPA readily forms gels (see Chapter 4 for an in-depth investigation), APTMS forms gels much more slowly if at all. This is counterintuitive from a kinetic point of view, since the bridged silane forces two silicon sites to coexist in a smaller space than the APTMS precursor does, which may lead to slower kinetics because of the steric effect. Therefore, we compare the reaction kinetics here. Two samples were made with BTMSPA under conditions comparable to
the conditions used for APTMS samples. The compositions and hydrolysis rate coefficients are listed in Table 2.3.

The composition for Br1 is similar to N2 and Br2 is similar to N3. Under similar conditions, we find that (1) the specific hydrolysis coefficient $k_{h1}$ and the general hydrolysis coefficient $k'_{h1}$ agree very well, and (2) the hydrolysis coefficients of BTMSPA are nearly identical to those of APTMS. Thus, although two silicon sites are present on BTMPA, the propylene ligands separate them enough that their hydrolysis kinetics are actually identical. In this case, the presence of the bridging chain does not affect the kinetics.

In spite of identical functional group kinetics, it is much easier for BTMPA to gel than APTMS. Specific examples studied here are sample Br2, which gelled within 12 hours, and sample N3 which took well over 2 months to gel. The difference in gel times should be caused by other factors than hydrolysis kinetics. Gel time is related to the monomer’s functionality according to the random gel theory. A solution will reach its gel point when the conversion of the monomer is $\alpha_g = 1/(f-1)$ with $f$ is the functionality of the monomer. For the sol-gel reaction, we can take this theory as the basis to estimate the difference of gel times for APTMS and BTMPA. The functionality of APTMS is 3 and the required conversion is 0.5 for the gelation. The functionality of BTMSPA is 6 and its required conversion is 0.2. For the samples N3 and Br2, random branching theory would therefore predict (based on the kinetic models above) that the gel time difference should be that the gel time for N3 is 4 times longer than Br2. This is far away from the real difference in gel times.

The explanation for the slow gelation of APTMS is that during sol-gel reactions, the siloxanes are prone to form small cubic cages in the early stages. In a tetrafunctional system, a gel is actually formed by the condensations among the unhydrolyzed silanol groups of the siloxane cages. If the precursor is a non-bridged trifunctional precursor, these cages are unable to connect together, and therefore gelation is prevented or slowed substantially. Under appropriate conditions, it has actually been possible to isolate perfect octa(3-aminopropyl) octasilsequioxane cages and octa(3-chloroammoniumpropyl) octasilsequioxane cages from APTMS. In contrast, for a bridged precursor, any cages that form are already connected to each other through the bridging organic. So, the
structure of the precursor allows easy gelation, and the gel time is expected to be much faster than it for the non-bridged precursor.

2.4. Conclusions

Mathematical models based on the previous work were proposed to describe the sol-gel reaction under basic condition. One model is established especially for APTMS based on prior NMR studies and the other model is more generally applicable to all precursors in basic conditions. Simplified equations were deduced for the reaction under specific conditions. These equations were then successfully applied to obtain the hydrolysis coefficients for several reaction systems monitored by FTIR. The hydrolysis coefficients are almost the same with an increase in the $\text{H}_2\text{O}:\text{Si}$ ratio. An increase of NaOH has enhanced the hydrolysis rate slightly while an increase of HCl did not change the hydrolysis rate. The lack of linear relationship of the added HCl or NaOH and the hydrolysis coefficient is probably because of the high pH value in the solutions. The success of these models proves the possibility to model the sol-gel reaction in basic condition. The same models were applied to BTMSPA. Results show that BTMSPA has a similar reactivity as its corresponding non-bridged precursor APTMS. The difference in the gel times between APTMS and BTMSPA is attributed to their different structures. The bridging chain in BTMSPA helps to form a three-dimensional network structure.

2.5. References

### Table 2.1. Compositions and hydrolysis rate coefficients for APTMS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si : H₂O : CH₃OH</th>
<th>kₙ₁ (10⁻³ M⁻¹s⁻¹)</th>
<th>k'ₙ₁ (10⁻³ M⁻¹s⁻¹)</th>
<th>kₙ₁/k'ₙ₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>1 : 0.49 : 40.8</td>
<td>2.22 ± 0.02</td>
<td>2.31 ± 0.03</td>
<td>1</td>
</tr>
<tr>
<td>N2</td>
<td>1 : 0.99 : 40.7</td>
<td>2.07 ± 0.01</td>
<td>2.22 ± 0.02</td>
<td>1</td>
</tr>
<tr>
<td>N3</td>
<td>1 : 1.49 : 39.7</td>
<td>2.07 ± 0.02</td>
<td>2.26 ± 0.02</td>
<td>1</td>
</tr>
<tr>
<td>N4*</td>
<td>1 : 1.50 : 9.6</td>
<td>4.3 ± 0.2</td>
<td>5.0 ± 0.1</td>
<td>0.9</td>
</tr>
</tbody>
</table>

* ⁵⁹Si data from the literature was used for the calculation.¹⁷

### Table 2.2. Compositions and hydrolysis rate coefficients for APTMS hydrolysis with NaOH added as a co-catalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si : NaOH : CH₃OH : H₂O</th>
<th>kₙ₁ (10⁻³ M⁻¹s⁻¹)</th>
<th>k'ₙ₁ (10⁻³ M⁻¹s⁻¹)</th>
<th>kₙ₁/k'ₙ₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>1 : 3.77 : 0 : 40.77</td>
<td>2.59 ± 0.03</td>
<td>2.88 ± 0.02</td>
<td>0.90</td>
</tr>
<tr>
<td>B2</td>
<td>1 : 3.76 : 0.017 : 40.76</td>
<td>2.70 ± 0.03</td>
<td>3.01 ± 0.02</td>
<td>0.90</td>
</tr>
<tr>
<td>B3</td>
<td>1 : 3.77 : 0.034 : 40.75</td>
<td>2.81 ± 0.01</td>
<td>3.14 ± 0.01</td>
<td>0.90</td>
</tr>
<tr>
<td>B4</td>
<td>1 : 3.80 : 0.048 : 40.79</td>
<td>3.15 ± 0.01</td>
<td>3.57 ± 0.02</td>
<td>0.86</td>
</tr>
<tr>
<td>B5</td>
<td>1 : 3.76 : 0.068 : 40.77</td>
<td>3.61 ± 0.03</td>
<td>4.10 ± 0.02</td>
<td>0.88</td>
</tr>
</tbody>
</table>
Table 2.3. Compositions and hydrolysis rate coefficients for APTMS hydrolysis with HCl added as a co-catalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si: H₂O: HCl: CH₃OH</th>
<th>kₘ₁ (10⁻³ M⁻¹s⁻¹)</th>
<th>k'ₘ₁ (10⁻³ M⁻¹s⁻¹)</th>
<th>kₘ₁/k'ₘ₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1: 3.75: 0.012: 40.78</td>
<td>2.33 ± 0.02</td>
<td>2.57 ± 0.01</td>
<td>0.85</td>
</tr>
<tr>
<td>A2</td>
<td>1: 3.75: 0.025: 40.65</td>
<td>2.47 ± 0.02</td>
<td>2.74 ± 0.01</td>
<td>0.85</td>
</tr>
<tr>
<td>A3</td>
<td>1: 3.76: 0.050: 40.72</td>
<td>2.59 ± 0.01</td>
<td>2.89 ± 0.01</td>
<td>0.80</td>
</tr>
<tr>
<td>A4</td>
<td>1: 3.76: 0.069: 40.78</td>
<td>2.59 ± 0.02</td>
<td>2.84 ± 0.01</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 2.4. Compositions and hydrolysis rate coefficients for BTMSPA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si: H₂O: CH₃OH</th>
<th>kₘ₁(10⁻³ M⁻¹s⁻¹)</th>
<th>k'ₘ₁ (10⁻³ M⁻¹s⁻¹)</th>
<th>kₘ₁/k'ₘ₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br1</td>
<td>1: 0.95: 38.4</td>
<td>2.3</td>
<td>2.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Br2</td>
<td>1: 1.50: 40.4</td>
<td>2.3</td>
<td>2.4</td>
<td>1.0</td>
</tr>
</tbody>
</table>
\begin{align*}
\text{RO-Si} + \text{H}_2\text{O} & \xrightarrow{\text{Hydrolysis}} \text{Si-OH} + \text{ROH} \quad (1.5) \\
\text{HO-Si} + \text{HO-Si} & \xrightarrow{\text{Hydrolysis}} \text{Si-O-Si} + \text{H}_2\text{O} \quad (1.6) \\
\text{RO-Si} + \text{HO-Si} & \xrightarrow{\text{Alcoholysis}} \text{Si-O-Si} + \text{ROH} \quad (1.7)
\end{align*}

R: An alkyl group such as CH$_3$-, CH$_3$CH$_2$-, etc.

**Figure 2.1.** General sol-gel reaction.

**Figure 2.2.** Comparison of spectra of APTMS/water/methanol system and methanol.
Figure 2.3. Relationship between the concentration and the absorbance of SiOCH$_3$.

Figure 2.4. Fittings of experimental data with equations (2.20) and (2.22) for sample N1: dots are experimental data and lines are fitted data.
Figure 2.5. Fittings of experimental data with equations (2.20) and (2.22) for sample N2: dots are experimental data and lines are fitted data.

Figure 2.6. Fittings of experimental data with equations (2.20) and (2.22) for sample N3: dots are experimental data and lines are fitted data.
Figure 2.7. Evolution of $[T_1^0]$ in sample N3 estimated using equation (2.18).

$y = 0.0027t$
$R^2 = 0.979$

Figure 2.8. Fittings of experimental data with equations (2.20) and (2.22) for sample B2: dots are experimental data and lines are fitted data.

$y = e^{0.0012t}$
$R^2 = 0.9924$
where $T_{ij}$ stands for trifunctional alkoxysilanes with $i$ is the number of condensed groups and $j$ is the number of hydrolyzed groups.

**Scheme 2.1.** Sol-gel reaction process.

\[ T_0^0 \rightarrow T_0^1 \rightarrow T_0^2 \rightarrow T_0^3 \]
\[ T_1^0 \rightarrow T_1^1 \rightarrow T_1^2 \]
\[ T_2^0 \rightarrow T_2^1 \]
\[ T_3^0 \]

**Scheme 2.2.** Simplified sol-gel reaction process.

\[ T_0^0 \rightarrow T_0^1 \rightarrow T_1^0 \rightarrow T_1^1 \rightarrow T_1^2 \rightarrow T_2^1 \rightarrow T_3^0 \]

**Scheme 2.3.** Simplified route for the sol-gel reaction.

\[ k'_{h1} \rightarrow k'_{h2} \rightarrow k'_{h3} \]

\[ T_0^0 \rightarrow T_0^1 \rightarrow T_1^0 \rightarrow T_1^1 \rightarrow T_2^0 \rightarrow T_2^1 \rightarrow T_3^0 \]
Chapter 3. Comprehensive Comparison of A Series of Organoalkoxysilane Precursors for Advanced Materials I. Reaction Kinetics

3.1. Introduction

The sol-gel process of ceramic synthesis has been known for hundreds of years, but it has recently received significant attention as a method of forming nanostructured materials.\textsuperscript{1} This process is defined as the polymerization of inorganic precursors to produce a sol, which eventually crosslinks sufficiently to form a metal oxide gel network. Figure 3.1 illustrates the sol-gel reactions of alkoxyisilane precursors, which consist first of hydrolysis of the precursor to produce silanols, and condensation polymerization of the silanols to produce siloxane bonds.

Because these reactions proceed near ambient conditions, it is possible to incorporate organic components into sol-gel ceramics by three routes. First, supramolecular templates such as surfactants can be introduced. These templates self-assemble into molecular aggregates which physically assemble with silicates through the \textit{Si-OH} groups.\textsuperscript{2} The surfactants can be retained to create organic-inorganic hybrids, or removed to generate mesoporous products. The second method of introducing organic components is by replacing one, two, or three alkoxyisilane groups of some of the precursors with non-hydrolyzable organics (for instance, by using methyltrimethoxysilane). This will lead to materials with dangling organics which we can call non-bridging organics. The third method of introducing organic components is to use bridged silanes, which are precursors in which two trialkoxysilyl moieties are joined by an organic molecule (for instance, 1,2-bis(trimethoxysilyl) ethane).

All three methods of organic modification are useful for controlling some aspect of the structure and properties of a sol-gel material. Surfactant incorporation is an excellent method of introducing an organic component with long-range order in the organic domains. Because the interactions with the material are only physical, the surfactant can also be easily extracted to generate a mesoporous material. Non-bridging organics are covalently incorporated into the material structure, and can be used to introduce specialized functionality or modifying the surface properties of the material. A wide
variety of organotrialkoxysilanes is available for this purpose. However, siloxane cyclization may limit the ability of these silanes to form networks. Bridged silanes overcome this limitation because they gel much more easily than trifunctional alkoxy silanes do. They also introduce organic components directly into the gel network without blocking the accessibility of any pores that are obtained after drying.

Recently, there have been several demonstrations of combining these methods of organic modification to create advanced materials with combinations of useful properties. For instance, combining the use of a bridged silane with a surfactant leads to mesoporous organic-inorganic hybrid materials with highly accessible pores. In another example, several bridged and non-bridged silanes are combined to create multifunctional “smart” hybrid materials. Finally, there are many situations in which tetraalkoxysilanes and organo-trialkoxysilanes are combined to tune the properties and network-forming ability of a system. In order to better understand and control these types of mixed systems, we need to understand in detail the effects of silane modification on the kinetics and interactions among components. In this chapter, we systematically investigate a series of alkoxy silanes to pick apart the effects of organic modification on the reaction kinetics. In the following chapter, we will compare materials made using the same set of silanes, with and without surfactant templating.

Regardless of the type of precursor used, the relevant functional-group reactions that occur are the hydrolysis and condensations reactions illustrated in Figure 3.1. Depending on the reaction conditions, different reactions are rate-controlling. In a non-templated sol-gel process, hydrolysis has been shown to be the rate-limiting step in alkaline solution. On the other hand, in acidic condition, condensation reactions are the rate-limiting reactions. In a templated process under basic condition, hydrolyzed silica species will be attracted to aggregate with surfactant micelles through electrostatic interactions or hydrogen bonding. The local density of Si-OH is therefore much higher than in the non-templated process, and condensations should be accelerated. Therefore, hydrolysis should still be the rate limiting step in this process. Under highly acidic conditions with a surfactant template, condensation reactions should still be accelerated. Therefore, it is less obvious that condensation will be the rate limiting step. In addition, the process involves partitioning of partially hydrolyzed and condensed silanes between
the bulk solution and a condensed phase, and therefore the process is much more complicated to analyze compared to that without any template.

To gain insight into the essential factors, kinetic studies of the sol-gel reactions are normally carried out for homogeneous, non-templated sol-gel reactions. The effects of the type and number of alkoxy groups, and the length and type of functional groups on sol-gel reactions have been investigated.\cite{1,7,8} Effects of steric and inductive factors were discussed before.\cite{1} However, comparisons of the kinetics of non-bridged silane with its corresponding bridged silane, and among bridged silanes with different bridging organics have not been made. In fact, only few bridged silane has been the subject of a kinetic investigation before.\cite{9}

In this chapter, we investigate a series of silanes in which structural and chemical differences are gradually introduced. We will investigate the early reaction kinetics of tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMS), 1,2-bis(trimethoxysilyl)ethane (BTMSE), 1,6-bis(trimethoxysilyl)hexane (BTMSH), and bis(trimethoxysilyl)propyl)amine (BTMSPA). The difference between TEOS and TMOS is the size of the alkoxy groups. When one of the methoxy groups in TMOS is substituted with a methyl group, the resulting molecule is MTMS. While TMOS has four functional groups capable of being hydrolyzed and condensed, MTMS has only three functionalities. BTMSE is bridged silane corresponding to joining together two MTMS molecules. The effect of the length of the bridging chain can be observed by comparing BTMSH (six carbons in the bridging chain) to BTMSE (two carbons in the bridging chain). The final member in this series, BTMSPA, has a bridging chain with six carbons and one amine. Thus, the main difference between BTMSPA and BTMSH is the amine functional group located at the center of the BTMSPA chain. All three of the bridged silanes used here, they have a total of hydrolysable functional groups. With this series of silanes, we have included structural differences including the size of alkoxy groups, functionality of the organic, length of the organic, and whether the organic group is attached to one or two trialkoxysilyl groups.

3.2. Experimental Section

3.2.1. Materials. Tetraethoxysilane (TEOS, 99+%), tetramethoxysilane (TMOS, 99+%),
methyltrimethoxysilane (MTMS), bis(trimethoxysilyl)ethane (BTMSE, 95+%), Bis(trimethoxysilyl)hexane (BTMSH), and Bis(trimethoxysilylpropyl)amine (BTMSPA, 95%) were bought from Gelest. Methanol (HPLC) was from Fisher EMD, normalized 1.0 N HCl and 1.0 N NaOH were from Alfa. Dipropylamine (99+) was from Aldrich. All chemicals were used as received.

3.2.2. Sample Preparation. Before each kinetic experiment, two solutions were prepared. The first consisted of methanol and precursor, the second contained methanol, water and HCl or NaOH. After setting up the spectrometer for the experiment, solutions were mixed in a polypropylene centrifuge tube very quickly, and the mixed solution was injected into the liquid transmission cell using a syringe. Series data were collected automatically at regular intervals after injection into the instrument. Time was recorded from the time of mixing the two stock solutions together.

Samples B1 to B5 and B7 were made with the initial concentrations of 1.1 M SiOCH$_3$ (SiOCH$_2$CH$_3$ in the case of TEOS), 1.1 M H$_2$O, 23 M CH$_3$OH and 0.021 M NaOH. The precursors used for these samples are listed in Table 3.1. A quantity of dipropylamine equivalent to one amine per hexyl chain was added to the sample B6 (prepared with BTMSH) to compare its effects to the effects of the integral amine in the chain of BTMSPA of sample B7. Sample B6 has the composition of 1.1 M SiOCH$_3$, 1.1 M H$_2$O: 22 M methanol, 0.021M NaOH, and 0.18 M dipropylamine.

Five samples were made in highly acidic conditions with the same compositions. The precursors are TEOS, TMOS, MTMS, BTMSE, and BTMSH for samples A1 through A5, respectively (see Table 3.2). The concentration is 1.72 M, 0.28 M, 22 M, and 5 mM for SiOCH$_3$ (SiOCH$_2$CH$_3$), water, methanol, and HCl, respectively. Two samples, A6 and A7, were prepared specifically to compare the effects of an amine during the sol-gel reactions of BTMSH and BTMSPA. In the sample prepared with BTMSH (A6), a quantity of dipropylamine equivalent to the amount of amine in BTMSPA was added (comparable to the amine content of sample A7). The initial composition is 1.69 M SiOCH$_3$, 1.69 M H$_2$O, 21 M methanol, 0.309 M HCl, and x M propylamine (x = 0.282 for A6, x = 0 for A7). An excess of HCl was added (above the moles of amine present) to
ensure that the reaction proceeded under acidic conditions, even after complete titration of the amine.

3.2.3. Characterization. FTIR Spectra were collected with a ThermoNicolet Nexus 470 Fourier transform infrared spectrometer (FTIR) with a DTGS detector. Kinetics were measured in situ in a demountable flow-through stainless steel transmission cell (Harrick Scientific) in which the liquid sample was introduced between two round germanium windows. Germanium was chosen for its non-reactive nature, and its low solubility in water and alcohols. To avoid interference fringes in the FTIR spectra, it was necessary to separate the germanium windows with two mismatched PTFE half-spacers which were 0.025 mm and 0.100 mm in thickness. The liquid sample between the windows thus formed a wedge. Spectra were collected at time intervals of 16.0 seconds for a total of 30 minutes. For each spectrum, 16 scans were averaged at a resolution of 4 cm\(^{-1}\) over the range of 650-4000 cm\(^{-1}\).

3.3 Modeling of the reaction kinetics

Using the FTIR data (see below), we will only be able to quantitatively monitor functional group kinetics, specifically, the concentrations of water, ethanol, and alkoxide groups. Modeling of the sol-gel reactions thus is based on the evolution of these components. The assumptions used in the model will be different depending on the reaction conditions (acidic or basic). For both of basic and acidic conditions, the relative importance of hydrolysis and condensations will be discussed in terms of three variables, defined as \(\chi\), \(r\) and \(\alpha\). \(\chi\) is the average degree of hydrolysis, defined as \([\text{SiOH}]/([\text{SiOH}]+[\text{SiOR}])\). \(r\) is the fractional conversion of alkoxides, defined as \(([\text{SiOR}]_0-[\text{SiOR}])/[\text{SiOR}]_0\). \(\alpha\) is the siloxane bond conversion, defined as \(2[\text{SiOSi}]/[\text{SiOR}]_0\). The functional group kinetics of hydrolysis, re-esterification, and water-producing condensation can be defined by equations 3.1-3.3.

\[
\begin{align*}
Si - OR + H_2O & \xrightarrow{k_h} Si - OH + ROH \\
Si - OH + ROH & \xrightarrow{k_h'} Si - OR + H_2O \\
Si - OH + SiOH & \xrightarrow{k_c} Si = O - Si + H_2O
\end{align*}
\]
Based on the stoichiometry of equations (3.1) to (3.3), we can derive expressions for $\chi$ and $\alpha$ from the two quantities that we will be able to independently measure at all times by FTIR (see below), the concentration of water and the concentration of alkoxide groups. The resulting expressions are:

$$\chi = \frac{2w-r}{2w+1-2r} \quad (3.4)$$

$$\alpha = 2(r-w) \quad (3.5)$$

where $w = ([H_2O]_0-[H_2O])/[SiOR]_0$.

These overall parameters can be used to judge the relative rates of hydrolysis and condensation. If hydrolysis is the rate-limiting step, $\chi$ would be expected to be very small since [SiOH] is negligible. If $\chi = 0$, then from equation (3.4), $2w = r$, and from equation (3.5), $r$ is expected to have a linear relationship with $\alpha$ with slope close to 1. On the other hand, if condensation is rate-limiting, then $\chi$ would be expected to be approximately constant. $r$ would be expected to jump to a relatively large value (equal to $\chi$) and then it would have a linear relationship with $\alpha$. At this stage, the hydrolysis would remain almost at equilibrium since it is much faster than the condensation.

In basic condition, hydrolysis has been proven to be the rate-limiting step by using TMOS \(^4\) and TEOS \(^5\) as the precursors. Yoon et al. have proposed that water-producing condensation should be dominant over alcohol-producing condensation, so reaction (3.3) adequately describes the condensation.\(^5\) Since the condensation is much faster than the hydrolysis, re-esterification (reaction 3.2) can be reasonably neglected. The reverse water-producing condensation is also negligible at the early stage of the reaction. The functional group sol-gel reactions can therefore be simplified as equations (3.1) and (3.3) in basic conditions.

Based on these assumptions, the rate expressions in basic conditions are:

$$d[SiOR]/dt = -k_h[SiOR][H_2O] \quad (3.6)$$

$$d[H_2O]/dt = -k_h[SiOR][H_2O] + k_c[SiOH]^2 \quad (3.7)$$

$$d[SiOH]/dt = k_h[SiOR][H_2O] - 2k_c[SiOH]^2 \quad (3.8)$$

Since the condensation rate is much higher than the hydrolysis, the concentration of SiOH can be treated as being at pseudo-steady state.\(^10\) With this assumption, equation
(3.5) is set equal to zero, and the differential equations can be integrated to yield the following expressions:

\[
[\text{SiOCH}_3] = \frac{a}{1 - b \exp\left(-\frac{a}{2} k_h t\right)}
\]  

(3.9)

and

\[
[H_2O] = \frac{a/2}{1 - \frac{b}{1} \exp\left(-\frac{a}{2} k_h t\right) - 1}
\]

(3.10)

where \(a = [\text{SiOCH}_3]_0 - 2[H_2O]_0\), \(b = 2[H_2O]_0/[\text{SiOCH}_3]_0\).

Absolute intensities of the bands for \(\text{SiOCH}_3\) and \(H_2O\) can be measured from the FTIR spectra. The concentrations of \(\text{SiOCH}_3\) and \(H_2O\) would be expected to follow Beer’s law, but since the solution is a ternary \(H_2O/methanol/silane\) system, the extinction coefficients of \(\text{SiOCH}_3\) and \(H_2O\) could be different than those in binary \(H_2O/methanol\) or \(silane/methanol\) mixtures. Moreover, the extinction coefficient of \(\text{SiOH}_3\) may be different for different silanes. To avoid the effect of differences in extinction coefficient, equations (3.9) and (3.10) can be re-expressed in terms of the absorbance measured at a particular reference time, \(t_r\).

\[
1 - (1 - b \exp\left(-\frac{a}{2} k_h t_r\right)) \frac{A(\text{SiOCH}_3)_r}{A(\text{SiOCH}_3)} = b \exp\left(-\frac{a}{2} k_h t\right)
\]

(3.11)

\[
1 + \left(\frac{b}{1} \exp\left(-\frac{a}{2} k_h t_r\right) - 1\right) \frac{A(H_2O)_r}{A(H_2O)} = \frac{1}{b} \exp\left(-\frac{a}{2} k_h t\right)
\]

(3.12)

where \(A(\text{SiOCH}_3)\) and \(A(H_2O)\) are the absolute band intensities for \(\text{SiOCH}_3\) and \(H_2O\) and \(A(\text{SiOCH}_3)_r, A(H_2O)_r\) are the absolute intensities at the reference time. The hydrolysis rate coefficient can be determined by nonlinear regression using equation (3.11) or equation (3.12).

In the above model, the precursor has the same alkyl group as the alcoholic solvent. For the sol-gel reaction of TEOS in methanol, the transesterification reaction also has to be considered. Reactions analogous to the above scheme, but with transesterification and different rate coefficients for hydrolysis of ethoxy or methoxy groups can be written as follows.

\[
\text{Si} - OCH_2CH_3 + CH_3OH \xrightarrow{k_t} \text{Si} - OCH_3 + CH_3CH_2OH
\]

(3.13)
Here, $k_{hn}$ can be estimated by independently studying the sol-gel reaction of TMOS in methanol solution.

If the transesterification reaction is competitive with the hydrolysis of TEOS, SiOCH$_3$ groups are expected to appear during the reaction. This brings the difficulty to interpret concentrations of SiOCH$_3$ and SiOCH$_2$CH$_3$ since the band at 1196 cm$^{-1}$ will overlap with the band at 1169 cm$^{-1}$. In this case, ethanol can be used instead of SiOCH$_2$CH$_3$ to monitor the reaction.

With the assumption that $\frac{d[SiOH]}{dt} \approx 0$, we obtain

$$\frac{d[SiOCH_2CH_3]}{dt} = -k_f[SiOCH_2CH_3][CH_3OH] - k_{he}[SiOCH_2CH_3][H_2O]$$

$$\frac{d[CH_3CH_2OH]}{dt} = k_f[SiOCH_2CH_3][CH_3OH] + k_{he}[SiOCH_2CH_3][H_2O]$$

$$-2 \frac{d[H_2O]/dt}{[H_2O]} = k_{hn}[SiOCH_3] + k_{he}[SiOCH_2CH_3]$$

If the initial solution does not have ethanol, then $[SiOCH_2CH_3] = [SiOCH_2CH_3]_0 - [CH_3CH_2OH]$. Large amount of methanol will be used for the sample with TEOS as the precursor. Thus the concentration of methanol can be treated as a constant. We observed that the reaction rate of water was much slower than the rate of ethanol in our system. At the early stage of the reaction, the concentration of water almost kept constant even $d[H_2O]/dt$ was not zero.

Based on the observation, we can obtain $[SiOCH_3] = [CH_3CH_2OH]$, $[CH_3OH] = [CH_3OH]_0$, and $[H_2O] = [H_2O]_0$ at the early stage of the reaction. Equations (3.18) and (3.19) will be rewritten as,

$$1 - \frac{[CH_3CH_2OH]}{[SiOCH_2CH_3]_0} = \exp(-kt)$$

where $k = k_f[CH_3OH]_0 + k_{he}[H_2O]_0$.

And
\[-2 \frac{d[H_2O]}{dt} = (k_{hm} - k_{he})[CH_3CH_2OH] + k_{he}[SiOCH_2CH_3]_0 \quad (3.21)\]

The left side of equation (3.21) can be rewritten as 
\[-2 \frac{dA[H_2O]}{dt} \frac{dt}{A[H_2O]} , \text{where } A[H_2O] \]
is the absolute intensity of the peak for water. The extinction coefficient of water thus is
not needed for equation (3.21). The extinction coefficient of CH₃CH₂OH is estimated
from the reference ethanol/methanol system. By fitting the data into equation (3.21), we
can calculate k_{he}. For this purpose, the water vs. time data are differentiated numerically.
After obtaining k_{he}, we can calculate the value of k_i by fitting the concentration of ethanol
into equation (3.20).

In contrast to the situation analyzed above, when the sol-gel reaction is carried out
under acidic conditions, the condensation is much slower than hydrolysis. At the very
early stage of the reactions, the condensation can be neglected. The silanol concentration
will build up rapidly at first, and then decrease. Condensation reversibility can be
neglected in acidic conditions as well, but both water-producing and alcohol-producing
condensation should be considered. This situation can be analyzed in terms of reactions
(3.1) and (3.2) combined with (3.22) and (3.23) below:

\[Si - OH + Si - OH \xrightarrow{k_{wc}} Si - O - Si + H_2O \quad (3.22)\]
\[Si - OR + Si - OH \xrightarrow{k_{ac}} Si - O - Si + CH_3OH \quad (3.23)\]

The functional group kinetics under acidic conditions can be expressed as:

\[d[SiOR]/dt = -k_h[SiOR][H_2O] + k_h^1[SiOH][ROH] - k_{ac}[SiOR][SiOH] \quad (3.24)\]
\[d[H_2O]/dt = -k_h[SiOR][H_2O] + k_h^1[SiOH][ROH] + k_{wc}[SiOH]^2 \quad (3.25)\]
\[d[SiOH]/dt = k_h[SiOR][H_2O] - k_h^1[SiOH][ROH] - 2k_{wc}[SiOH]^2 - k_{ac}[SiOR][SiOH] \quad (3.26)\]

In a sol-gel reaction under acidic condition, Rankin et al. found that the hydrolysis
reaches quasi-equilibrium when the water: SiOR molar ratio is large (≥1). \(\chi\) is constant,
so \([SiOH] = \{\chi/(1-\chi)\}[SiOR] \). Equation (3.27) can be obtained as,

\[d[SiOR]/dt = -2\chi(\frac{k_{wc}}{1-\chi} + k_{ac})[SiOR]^2 \quad (3.27)\]
or

\[
\frac{1}{[\text{SiOR}]} - \frac{1}{[\text{SiOR}]_q} = 2k_{ac}\chi\left(\frac{k_{wc}/k_{ac}}{1-\chi} + 1\right)(t-t_q)
\]  

(3.28)

where \([\text{SiOR}]_q\) is the concentration of SiOR at a specific time \(t_q\) during the quasi-equilibrium hydrolysis.

The sol-gel reaction of TMOS in acidic condition was studied by Assink et al.\textsuperscript{6} \(k_{wc}\) was estimated to be 0.006 ± 0.001 l/(mol*min) and \(k_{ac}\) was estimated to be 0.0010 ± 0.0002 l/(mol*min). The value of \(k_{wc}/k_{ac}\) is thus estimated to be around 6. Since most of precursors used in this chapter have the same SiOCH\(_3\) groups, we assumed that this value is the same among these precursors. With this assumption, \(k_{ac}\) could be obtained by fitting equation (3.28) to the \([\text{SiOCH}_3]\) vs. time data.

The concentration of water is needed to calculate the constant \(\chi\) in equation (3.28). The extinction coefficient of water obtained from the binary water-methanol system will be used.

When the water: SiOR ratio is very small (< 1), \(\chi\) will decrease with the sol-gel reaction in acidic conditions.\textsuperscript{3} However, it is reasonable to assume that all water is consumed after the fast hydrolysis.\textsuperscript{6} The sol-gel reaction can be divided into two steps. In the first step, only fast hydrolysis happens. The second step consists of the condensation and the hydrolysis. Since the hydrolysis is much faster than the condensation, water produced from the condensation will be consumed by hydrolysis immediately. No water is supposed to be built up in the second step since hydrolysis is much faster than the condensation. The change of water concentration is negligible compared to the change of SiOR concentration. In this case,

\[
[H_2O] = 0
\]

and

\[
-d([\text{SiOR}])/dt = k_{wc}[\text{SiOH}]^2 + k_{ac}[\text{SiOR}][\text{SiOH}]
\]

(3.30)

with \([\text{SiOH}] = [\text{SiOR}]-[\text{SiOR}]_0 + 2[H_2O]_0\).

The above equation can be integrated to give:

\[
\frac{([\text{SiOR}]_0-a)([\text{SiOR}]_0-ha)}{([\text{SiOR}]-ha)([\text{SiOR}]_0-a)} = \exp(-k_{wc}a(t-t_c))
\]

(3.31)
\[ a = [\text{SiOR}]_0 - 2[H_2O], \quad h = k_{\text{wc}}/(k_{\text{wc}} + k_{\text{ac}}), \quad t_c \text{ is the time of the start of condensation,} \]

\[ [\text{SiOR}]_c = [\text{SiOCH}_3]_0 - [H_2O]. \]

\[ h = 0.86 \] was estimated by using the values of \( k_{\text{aw}} \) and \( k_{\text{cw}} \) reported by Assink et al \(^6\) for TMOS. The concentration of SiOR at the start of the second step can be estimated as

\[ [\text{SiOR}]_c = [\text{SiOR}]_0 - [H_2O]. \]

The absolute intensity of SiOR at this time will be obtained from the FTIR spectra. Therefore, we can obtain the extinction coefficient from the relationship between the concentration and the band intensity at the start of the condensation. This will avoid using the extinction coefficient obtained from a different system. Therefore, low \( H_2O : \text{SiOR} \) ratio will be used for most samples in this investigation.

3.4. Results and Discussion

3.4.1. FTIR band assignments

Spectra of the precursors and solvents were collected using FTIR spectroscopy for solutions in contact with a ZnSe ATR crystal. The angle of incidence of the IR beam was 45 degrees, and multiple reflections occurred along the 80 mm crystal.

Spectra of all solvents and precursors are compared in Figure 3.2. To quantitatively monitor the reaction, we must identify non-overlapping bands associated with reacting species. From the comparison of the spectra in Figure 3.2, we notice that a well-separated band for water is available at 1657 cm\(^{-1}\). No band at this position is observed in the other spectra. The band at approximately 1196 cm\(^{-1}\) is ideal to monitor the concentration of SiOCH\(_3\) because it is sharp and clearly resolved from the other peaks associated with the methoxysilane precursors. Similarly, the band at 1169 cm\(^{-1}\), present in the spectrum of TEOS, can be used to monitor the evolution of SiOCH\(_2\)CH\(_3\). This band, however, will overlap with the band of SiOCH\(_3\) at 1196 cm\(^{-1}\) if both of them exist in the same system. Another strong band at 961 cm\(^{-1}\) is associated with ethoxysilane groups, but this band will not be used to monitor SiOCH\(_2\)CH\(_3\) because it will overlap with the growing Si-OH peak, as we will discuss later. The evolution of SiOCH\(_2\)CH\(_3\) can be indirectly monitored by the band at 881 cm\(^{-1}\) of ethanol.

Because it is a non-invasive technique, ATR-FTIR with a ZnSe crystal is a common technique to monitor reaction kinetics. The short pathlength provided by the ATR
method is ideal for solutions containing a significant concentration of water. However, the ZnSe crystal is not sufficiently robust under strongly basic or acidic conditions for our investigations. In the rest of this chapter, we will report data collected in a liquid cell with Ge windows and mismatched Teflon spacers.

To identify bands associated with intermediates, four spectra collected using the liquid cell are shown in Figure 3.3. Trace \( a \) is the spectrum of pure methanol. Trace \( b \) is a solution of water in methanol. Trace \( c \) is a mixed water-methanol-NaOH-TMOS solution 210 seconds after mixing. Trace \( d \) is a mixed water-methanol-HCl-TMOS solution 210 seconds after mixing. The band at around 1657 cm\(^{-1} \) in trace \( b \) appears at the same position as the band in the spectrum of pure water, and will be used to quantify the amount of water present. The bands at 1196 cm\(^{-1} \) and 833 cm\(^{-1} \) in trace \( c \) are from Si-OCH\(_3\). Because it is more clearly resolved, the band at 1196 cm\(^{-1} \) is used to monitor the evolution of Si-OCH\(_3\). Both methanol and TMOS have strong bands in the regions at around 1112 cm\(^{-1} \) to 1025 cm\(^{-1} \). The stretching bands of Si-O-Si are also found in this region. The relative intensities of the bands in this region have been used to trace the appearance of linear and cyclic Si-O-Si species before.\(^{11} \) However, these bands cannot be used to quantitatively monitor the kinetics of the sol-gel reactions because they overlap strongly and because they are mostly saturated because of the large pathlength of the transmission cell.

Below, we will also discuss some of the qualitative features that evolve during the polycondensation of the silanes under investigation. However, following the assignments made here, we will use the integrated intensities of bands at 1657 cm\(^{-1} \), 1196 cm\(^{-1} \), and 881 cm\(^{-1} \) to quantitatively monitor the evolutions of H\(_2\)O, SiOCH\(_3\), and CH\(_3\)CH\(_2\)OH, respectively.

### 3.4.2. The quantitative interpretation of FTIR data

FTIR has been successfully used to monitor the evolution of Si-OCH\(_3\) in a sol-gel reaction before.\(^{9,12} \) According to Beer’s law, the relationship between the concentration and the absorbance can be expressed as \( A = a_0C + b_0 \) where \( A \) is the absolute absorbance, \( C \) is the concentration, \( a_0 \) is the product of extinction coefficient and pathlength, and \( b_0 \) is the intensity contributed from the solvent.
a_0 and b_0 are constants as long as the same pathlength and solvent are used for a particular species.

The linear relationships between the absorbance and the concentration for SiOCH_3, H_2O, and CH_3CH_2OH are shown in Figure 3.4. TMOS, water, and ethanol in methanol solution were used to calibrate the bands for SiOCH_3, water, and CH_3CH_2OH respectively. The background solvents (water, methanol) are flat at around 1169 cm\(^{-1}\). Any peak in these regions, therefore, is attributed only to presence of SiOCH_3. It can be assumed that b_0 is zero for the bands in these positions. Absolute absorbencies for SiOCH_3 could be obtained by simply integrating the peak areas. Absolute absorbencies for H_2O and CH_3CH_2OH were obtained after subtracting the methanol background spectrum. In all cases, a reasonably good linear relationship is found by regression for SiOCH_3, H_2O, and CH_3CH_2OH in methanol.

While we have shown here that Beer’s law is obeyed by the precursors and water used, the extinction coefficient of each species may differ from that in the reference silane/methanol and water/methanol systems. However, it is reasonable to assume that a_0 doesn’t change during the reaction within a relative short time for a given system. We designed our modeling equations (see above) so that they depend as little as possible on specific values of extinction coefficients.

3.4.3. Comparison of the hydrolysis kinetics in basic conditions

The hydrolysis kinetics of silanes with different alkoxy groupus has been compared before.\(^1,8\) The bulkier the alkoxy chain is, the slower the hydrolysis reaction. The effects of the length of the functional group was also compared among silanes with different alkyl chains.\(^8\) The longer the alkyl chain, the slower the hydrolysis. These effects are observed because hydrolysis reactions in basic condition are nucleophilic substitution reactions.\(^1\) Larger groups attached to a silicon site lead to steric hindrance which inhibits the nucleophilic reactions. However, no study has been carried out on the differences in sol-gel reaction kinetics between non-bridged organotrialkoxysilanes and their corresponding bridged silanes. Moreover, effects of the length and type of the bridging chains of bridged silanes on the hydrolysis have not been investigated. In this section, we
investigated effects of alkoxy groups, bridging chains on the hydrolysis in basic condition.

For all samples in basic condition, no silanol band could be observed. This confirms the validity of the pseudo-steady state assumption used to model these systems. For samples B2-B7, intensities of both SiOCH$_3$ and H$_2$O decreased during the reaction. The evolution of selected spectra of sample B2 is shown in Figure 3.5. Peaks at 1196 cm$^{-1}$ and 831 cm$^{-1}$ are belonged to SiOCH$_3$ groups. Both of them decrease in intensity with time. A weak shoulder of the peak at 1196 cm$^{-1}$ appears after several minutes of reaction and increases in intensity. In a sol-gel reaction with TEOS as the precursor, the Si-O-(Si) stretching band can be deconvoluted in four or five peaks at around 1040 cm$^{-1}$, 1080 cm$^{-1}$, 1100 cm$^{-1}$, 1160 cm$^{-1}$, and 1200 cm$^{-1}$. Among them, the peaks at 1080 cm$^{-1}$ and 1200 cm$^{-1}$ are attributed to cyclic structures while the others belong to linear structures. The presence of the peak at 1216 cm$^{-1}$ might indicate the production of cyclic Si-O-Si species. The qualitative features of the evolving spectra for samples B5, B6 and B7 are similar to those of sample B2. (Figure 3.6-Figure 3.8) The bands associated with SiOCH$_3$ and H$_2$O decrease with time, and a weak shoulder appears during reaction near the SiOCH$_3$ peak at 1196 cm$^{-1}$.

The spectral evolutions of samples B3 and B4 are different than sample B2. For pure MTMS (Figure 3.2), two peaks related to the attached methyl group are identified at 1265 cm$^{-1}$ and 738 cm$^{-1}$. Peaks at 1265 cm$^{-1}$ and 738 cm$^{-1}$ can be assigned to a CH$_3$ symmetric deformation vibration and a Si-C stretching vibration of Si-CH$_3$, respectively. Three peaks are related to the SiOCH$_3$ groups at 1191 cm$^{-1}$, 833 cm$^{-1}$, and 784 cm$^{-1}$. The peak at 738 cm$^{-1}$ was not observed in the reacting system possibly because of the relatively low intensity of this band in the mixed system. As the reaction proceeds, intensities of all SiOCH$_3$ peaks decrease. A peak appears at position 772 cm$^{-1}$ and becomes stronger. At the same time, the intensity of the peak at 1272 cm$^{-1}$ also increases. This indicates that a new species has been formed during the reaction. This species happens to have a band at the positions of 1272 cm$^{-1}$ and 772 cm$^{-1}$. Some structural change must be responsible for these changes because otherwise, the intensities of the peaks at 1272 cm$^{-1}$ and 772 cm$^{-1}$ would be expected to remain constant or zero since no reaction is associated with the Si-CH$_3$ bond. Also, unlike samples B2 and B5-B7, no weak peak was identified at the
shoulder of the peak at 1191 cm\(^{-1}\) for B3. The peaks at 1272 cm\(^{-1}\) and 772 cm\(^{-1}\) are the only peaks that became stronger during the reaction. This indicates that the increase of these peaks is due to the formation of condensed species containing Si-O-Si bonds. The peak at 772 cm\(^{-1}\) may belong to the symmetric stretching vibration of Si-O-Si bonds from ring structures. This is reasonable since MTMS may tend to form rings or cages due to the presence of one non-reactive methyl group.

A similar trend is observed during the reaction of sample B4 (Figure 3.10). A weak peak appeared at 1272 cm\(^{-1}\) and increased in intensity during the reaction. Also, no weak shoulder was identified near the SiOCH\(_3\) band at 1196 cm\(^{-1}\). However, unlike sample B3, a peak did not appear near 772 cm\(^{-1}\). Because sample B4 contains no methyl groups (it is made with BTMSE), the increasing band at 1272 cm\(^{-1}\) must be caused by a particular Si-O-Si structure which is found only for products of MTMS and BTMSE. It is also possible that the condensed species in B3 and B4 are similar to those found in B2, B5, B6 and B7, but that the frequencies associated with the structures are much different.

r-α plot was plotted for all samples from B2-B7 (Figure 3.11). The slope of any r-α plot is close to 1, which is consistent with the assumption that the hydrolysis is the rate-limiting step. Hydrolysis coefficients were calculated by nonlinear regression using the data collected during the first 360 seconds of reaction for all samples. Fits of equations (3.11) and (3.12) with the experimental data are shown in Figure 3.12. Evolution curves were also calculated from equations (3.9) and (3.10) with the estimated hydrolysis coefficients. Comparisons of the experimental data with these calculated curves for the first 1800 seconds are shown in Figure 3.13 and Figure 3.14. The calculated data are more consistent with the experimental data for samples B3, B5, and B6. This indicates that the model describes the sol-gel reaction better for these three samples than B2, B4, and B7. Experimental data in B2, B4, and B7 level off after 1000 seconds. This indicates the sol-gel may have reached equilibrium. Since no reverse reactions are considered, it is not a surprise that our model can not fit the experimental data well after the sol-gel reaction has reached a certain level. There is another challenge to use the data in the late stage of a sol-gel reaction. A peak from Si-O-Si species was identified at the shoulder of the SiOCH\(_3\) band (1196 cm\(^{-1}\)) for samples B2, B5, B6, and B7. At the begging of the sol-gel reaction, the production of condensed silica species is negligible since the shape of
the peak at 1196 cm\(^{-1}\) does not change. In the late stage of the sol-gel reaction, the peak for Si-O-Si is very obvious. It is overlapping with the SiOCH\(_3\) peak, which brings the difficulty to integrate the intensity for the latter peak. In Figure 3.13, the SiOCH\(_3\) peak intensity in B2, B5, B6, and B7 has included the contribution from the Si-O-Si species. This will help to increase the concentration of SiOCH\(_3\) at the late stage of the reaction.

This is consistent with the difference between the experimental data and the predicted data after 1000 seconds in B2 and B7. The experimental SiOCH\(_3\) concentration is higher than the predicted concentration. The consistency of experimental data with calculated data in B5 and B6 is because the hydrolysis reaction is much slower with BTMSH as the precursor. The reverse reactions and the contribution from Si-O-Si species have not played important roles in the first 1800 seconds of the sol-gel reaction. To avoid the difficulties to include the reverse reactions and to integrate SiOCH\(_3\) peak at the late stage of the reaction, we choose the experimental data in first 360 seconds to estimate the hydrolysis coefficient. Comparisons of the hydrolysis coefficients are shown in Table 3.1.

The evolution of the water band in sample B1 (Figure 3.15) is similar to the evolution of the band in the other samples. No peak other than the water band can be identified in the region of the spectrum near 1650 cm\(^{-1}\). Also, consistent with the fact that TEOS was the precursor, no SiOCH\(_3\) band was observed for B1 initially. Peaks at 1298 cm\(^{-1}\), 1169 cm\(^{-1}\), 970 cm\(^{-1}\), and 789 cm\(^{-1}\) belong to TEOS. As the reaction proceeds, a weak peak appears at the position expected for the SiOCH\(_3\) band at 1195 cm\(^{-1}\). The intensity of this peak increases at first and then decreases. A band associated with CH\(_3\)CH\(_2\)OH appears at around 882 cm\(^{-1}\) and grows as the reaction proceeds. The evolution of the spectra is consistent with the reactions associated with TEOS in methanol. The appearance of SiOCH\(_3\) is due to the transesterification of SiOCH\(_2\)CH\(_3\) with methanol. At the same time, SiOCH\(_2\)CH\(_3\) and SiOCH\(_3\) are consumed because of hydrolysis and subsequent condensation reactions. There is a competition between the production and the consumption of SiOCH\(_3\) which is the reason that the intensity of SiOCH\(_3\) increases first and then decreases. Ethanol is produced from both the transesterification and the sol-gel reactions of SiOCH\(_2\)CH\(_3\). Since the production of SiOCH\(_3\) was obvious in the basic condition, it indicates that the rate of transesterification reaction is competitive with the rate of hydrolysis of SiOCH\(_2\)CH\(_3\).
SiOCH\(_2\)CH\(_3\) at 1169 cm\(^{-1}\) is overlapping with the peak of SiOCH\(_3\) at 1195 cm\(^{-1}\). It is difficult to integrate the absolute absorbance for each of them. The kinetics, however, can be monitored by the peak at 881 cm\(^{-1}\) of ethanol and the peak at 1660 cm\(^{-1}\) of water. The concentration of water almost keeps at constant at the early stage of the reaction (Figure 3.16). This verifies the assumption we used in our model that the concentration of water is constant at this stage. By fitting the data obtained from FTIR into equations (3.20) and (3.21), we will obtain \(k_r\) and \(k_{he}\). The fits are shown in Figure 3.17 and Figure 3.18. The transesterification coefficient calculated is \((0.38 \pm 0.05) \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}\). The hydrolysis coefficient of TEOS is \((2.93 \pm 0.04) \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}\). Deviations in all coefficients calculated in this chapter are the calculated 95% confidence intervals. Because of the presence of a large amount of methanol (22 M), the transesterification rate of TEOS is comparable to its hydrolysis rate.

The hydrolysis coefficients found for all base-catalyzed samples are summarized in Table 3.1, and allow us to observe the kinetic trends induced by gradually changing features of the structure of the silane. The hydrolysis coefficients calculated from the SiOCH\(_3\) band and the H\(_2\)O band are consistent for all samples. This indicates that our model and method of fitting is reasonable. The first thing that we notice about the data is that the hydrolysis coefficient of TEOS is much smaller than that of TMOS. This is consistent with the steric bulk associated with the ethoxy ligand. Moving down the table, we find that the hydrolysis of MTMS is only slightly slower than that of TMOS. The substitution of a methoxy group with a methyl group would not be expected to induce a change in the steric bulk near the reaction center. However, a methyl group would be expected to be more electron donating than a methoxy group, which should increase the electron density at the silicon, which in turn slows down the hydrolysis under basic conditions.\(^1\) This is as expected. Next, we observe the effects of bridging. BTMSE is the bridged silane corresponding to MTMS. It has two –Si(OCH\(_3\))\(_3\) groups connected with a short ethylene chain. The modifying group in BTMSE is larger than it is in MTMS, but the bridging chain is so short that we anticipate that the electron density of the silicon in BTMSE decreases because of the OSi at the other end of the silane. The hydrolysis rate of BTMSE thus increases somewhat. In contrast, for BTMSH, the bridging chain is too long for the two –Si(OCH\(_3\))\(_3\) groups to interact with each other. The electron density of
the silicon increases, as we would expect for a long alkyl group attached to silicon. At the same time, BTMSH is much bulkier than BTMSE. Both factors favor a decrease in the hydrolysis rate, and a large decrease is, in fact, observed. The next change in the silanes is in going from BTMSH (B5) to BTMSPA (B7). The introduction of the amine into the hexylene bridge causes a large increase in the hydrolysis rate of the precursor. Because an amine can affect the pH of the solution, or could act as a specific catalyst for sol-gel reactions, we measured the hydrolysis kinetics in sample B6, with BTMSH and a concentration of dipropylamine equivalent to that in sample B7. As Table 3.1 shows, the hydrolysis rate increases only slightly due to the addition of the amine. Therefore, we can rule out any catalytic effect associated simply with having amines in the solution. Alky amines are well known as electron donors. The electron density of the silicon in BTMSPA is expected to be higher than that in BTMSH. This will lead a lower reactivity of BTMSPA. This is contradictory to the observation in our experiments. BTMSPA and BTMSH should be equally bulky near the hydrolysis reaction site, so we can not attribute the increase in the hydrolysis rate to either steric effect or electronic induction effects. The increase in the hydrolysis rate, however, can be explained considering the electrostatic attractions and the hydrogen bonding between partially hydrolyzed silica species and the amines in the bridging chains. The partially hydrolyzed silica species will be attracted to the amines, which leads to an increase in the local concentration of the SiOCH$_3$ groups since these groups are contained in the silica species. This leads to an increase of the hydrolysis rate. The amines may also attract water and hydroxyl anions to increase their concentrations near the SiOCH$_3$ groups resulting in an increase of the hydrolysis rate.

From the investigation of silane hydrolysis in basic conditions, we see that the reactivity of a silane is determined by its inductive and steric factors. Both of them are very important for the sol-gel reaction under basic condition. Both the high electron density of the silicon and the bulky size of the silane slow down the reaction. The presence of an ethoxy group instead of a methoxy group reduces the reactivity of the silane. The substitute of a methoxy group with methyl group decreases the hydrolysis rate slightly. When the bridging chain is short as an ethylene, the two Si(OCH$_3$)$_3$ groups interact with each other and the inductive factor is dominant over the steric factor. Thus,
the hydrolysis rate increases. When the bridging chain is as long as hexylene, the steric factor is predominant, and the bridging organic retards the reaction rate. The presence of an amine group in the bridging chain increases the reaction rate by increasing the local concentrations SiOCH$_3$, water, and hydroxyl anions.

3.4.4. Comparison of the kinetics of condensation in acidic conditions

In acidic condition, hydrolysis is much faster than condensation$^{4,6}$ and the sol-gel reaction rate is dominated by the condensation. The condensation reaction in acidic condition is nucleophilic substitution, so it is expected influenced by steric and inductive factors, as the hydrolysis in basic condition is.$^1$ Bulky groups attached to silicon retard the condensation because of the steric effect.$^1$ The condensation reaction should be more sensitive to steric effects near silicon than hydrolysis because two silicon sites participate in the reaction (rather than one silicon site and water). The inductive effect depends on the pH value of the solution. An increase of the electron density at silicon reduces the acidity of the corresponding silanol. Since the minimum condensation rate happens at pH 2, an decrease in the acidity will slow down the condensation if it is acid-catalyzed, but increase the condensation rate if the reaction is base-catalyzed condensation.$^1$ Normally, the condensation happening at pH < 2 follows the acid-catalyzed mechanism, while the condensation at pH > 2 will follow a base-catalyzed mechanism.$^1$

For samples A2- A5, representative spectra collected at various times are shown in Figures 3.19 through 3.22. The bands at 1196 cm$^{-1}$ and 826 cm$^{-1}$ in Figure 3.19 are assigned to SiOCH$_3$. The band at 948 cm$^{-1}$ is assigned to SiOH groups. The bands at 1194 cm$^{-1}$, 848 cm$^{-1}$, and 796 cm$^{-1}$ in Figure 3.20 are assigned to SiOCH$_3$. The peak at 1270 cm$^{-1}$ is assigned to SiCH$_3$ as the pure MTMS. This peak as well as the peak at 771 cm$^{-1}$ has also been assigned to condensed species as being discussed in the base-catalyzed samples. Intensities of these peaks increase over time in sample A3, indicating condensed species have been produced. Peaks at 1194 cm$^{-1}$, 1148 cm$^{-1}$, 812 cm$^{-1}$, and 783 cm$^{-1}$ in Figure 3.21 belong to BTMSE. All of them decrease over time. There is a peak at 1270 cm$^{-1}$ in Figure 3.21. This peak is assigned to condensed species (see section 3.4.3). The intensity of this peak increases over time. Like spectra in B5, peaks at 1193 cm$^{-1}$ and 793 cm$^{-1}$ are assigned to SiOCH$_3$ groups in BTMSH.
There is a band at around 920 cm\(^{-1}\) (948 cm\(^{-1}\) for A2) for all samples which can be assigned to the stretching vibration of Si-OH\(^{13,14}\). The intensity of this peak decreases over time in all samples. The existence of this peak suggests that hydrolysis is much faster than the condensation as we proposed in our model. A smaller peak may appear at the shoulder of the major peak at 920 cm\(^{-1}\), which has a lower wavenumber.\(^{13}\) This peak is associated with non-bridging free broken Si-O` bonds.\(^{13}\) A peak appears at 900 cm\(^{-1}\) for sample A5. This peak belongs to pure BTMSH.

As in the base-catalyzed case, all spectra show a methoxy band near 1196 cm\(^{-1}\) which decays over time. Unlike the base-catalyzed samples, no shoulder is observed for any of these samples during the entire 1800 seconds that the reactions were monitored. This indicates that the contribution of the condensed SiOSi species to the intensity of this peak is negligible. The intensity of the peak at 1196 cm\(^{-1}\) would therefore be expected to have a linear relationship with the concentration of SiOCH\(_3\). For all systems, no measurable peak for water is observed. This confirms that almost all water was consumed after the initial hydrolysis, as we proposed in the model.

Parameter \(r\) was plotted versus \(\alpha\) (Figure 3.23). A straight line with slope 2 is obtained for each of the sample. This confirms that condensation is dominant after the initial hydrolysis. If the hydrolysis dominates, the slope should be 1. Relationships between [SiOCH\(_3\)] and the intensity of the SiOH peak are shown in Figure 3.24. A linear relationship is observed for each of the samples. This is consistent with the linear relationship between [SiOCH\(_3\)] and [SiOH], which is \([\text{SiOH}] = [\text{SiOR}]-[\text{SiOR}]_0+2[\text{H}_2\text{O}]_0\) in our model for small water: SiOCH\(_3\) ratio. The condensation coefficient \(k_{ac}\) was estimated by fitting the experimental data in the first 1800 seconds with equation (3.31). The fitted plots are shown in Figure 3.25. All the experimental data could be very well fitted. This indicates that the assumptions made to the model are reliable.

The evolution of spectra for the sample A1 is shown in Figure 3.26. A weak peak for SiOCH\(_2\)CH\(_3\) at around 1169 cm\(^{-1}\) was identified at around 55 seconds. This peak was not observed after 100 seconds of the reaction. The other band associated with SiOCH\(_2\)CH\(_3\), at 789 cm\(^{-1}\), also disappeared within 100 seconds. Consistent with the loss of ethoxy groups, a peak for CH\(_3\)CH\(_2\)OH was observed at 882 cm\(^{-1}\) whose intensity remained nearly constant during the entire time interval monitored. The peak for SiOCH\(_3\) was very strong.
after 55 seconds of reaction, and its intensity decreased slowly with time after that. No peak for water was observed after 55 seconds. And at the same time, the SiOH peak at 948 cm\(^{-1}\), appeared after 55 seconds and slowly decays. All of these trends indicate that transesterification and hydrolysis occurred very quickly - much faster than condensation. Within 100 seconds, almost all SiOCH\(_2\)CH\(_3\) groups had been consumed by hydrolysis and transesterification, which is consistent with the high concentration of methanol in this system. The state of this system after 100 seconds actually was similar to the reaction system with TMOS as the precursor except that a small amount of ethanol was present in the solvent. By fitting the experimental data into equation (3.31), we obtained \(k_{ca}\) of SiOCH\(_3\) with the presence a small amount of ethanol. \(k_{ac}\) is \(0.00014 \pm 0.00001\) M\(^{-1}\)S\(^{-1}\), which is close to that of SiOCH\(_3\) from TMOS (Table 3.2). This is consistent with the expectation that the condensation of TEOS in methanol solution is similar to the condensation of TMOS in the same system. The fit of the experimental data into equation (3.31) is shown in Figure 3.25.

A relatively large ratio of H\(_2\)O: SiOCH\(_3\) (molar ratio 1:1) was used for samples A6 and A7. Evolutions of spectra of samples A6 and A7 are shown in Figure 3.27 and Figure 3.28. In both spectra, peaks for SiOCH\(_3\) decreased with time. Intensities of the peaks for water kept almost constant. Along the reaction, a peak appeared at 1209 cm\(^{-1}\) in sample A7. This peak was attributed to the cyclic Si-O-Si band.\(^{13}\) A pear appeared at 884 cm\(^{-1}\) in sample A7, which was attributed to the non-bridging free broken Si-O bonds.\(^{13}\) Since a large ratio of H\(_2\)O: SiOCH\(_3\) was used, the sol-gel reaction was expected to be fast. Data collected within the first 360 seconds thus were used. \(\chi\) is almost constant for samples A6 and A7 (Figure 3.29). This supports the assumption that the hydrolysis was in a quasi-equilibrium state. Equation (3.28) thus can be used as the model for these two samples. The extinction coefficients calculated from the corresponding basic systems were used to estimate the concentration of SiOCH\(_3\). The extinction coefficient of water was estimated from the concentration of H\(_2\)O at the start of the quasi-equilibrium of the hydrolysis. At the start of the quasi-equilibrium state, \([H_2O]_q \approx [H_2O]_0 - [SiOCH_3]_0 + [SiOCH_3]\) by assuming the condensation in the fast hydrolysis step is negligible. The fits of the experimental data into equation (3.28) are shown in Figure 3.30.
The concentration of water kept almost constant in both samples (Figure 3.31). This suggests that the change of water concentration was negligible compared to the change of SiOCH$_3$ concentration. The model for small H$_2$O: SiOCH$_3$ ratio should be also applicable except $a = [\text{SiOCH}_3]_0 - 2[H_2O]_0 + 2[H_2O]_c$, where $[H_2O]_c$ is the concentration of water in the quasi-equilibrium state. By fitting the data with equation (3.31), we can obtain the condensation coefficients (Table 3.2). The fits are shown in Figure 3.32. The condensation coefficients for samples A6 and A7 are almost the same by using the two different models (equation (3.28) and equation (3.31)). There confirms that these two models are consistent with each other.

$k_{ac}$ for all samples are compared in Table 3.2. The pH value calculated from the acid concentration (assuming ideal mixing) for samples A2- A5 was around 2.3. For samples A6 and A7, the calculated pH value was 1.6 by assuming all amine groups are titrated by the acid. Condensation coefficients of TEOS can not be measured because the fast transesterification reaction. Comparing A2 and A3, we find that the condensation rate of TMOS is slower than that of MTMS. The difference between TMOS and MTMS is due the inductive effect of the methyl group. Methyl group is electron-providing and methoxy group is electron-withdrawing. When a methoxy group is replaced with a methyl group, the electron density of the silicon will increase which reduces the silanol acidity. Since the pH value (2.3) in samples A2 and A3 is higher than 2.0, the decrease of acidity will increase the condensation rate. When BTMSE is used instead of MTMS, the electron density of Si will decrease as discussed in the basic situation. This will increase the silanol acidity. The condensation rate thus will decrease. The distance between the two silicon ends in BTMSH is much longer than BTMSE. The inductive effect might be negligible. BTMSH is much bulkier than BTMSE. This retards the condensation obviously. Different reaction conditions have been used for samples A5 and A6. The pH value in A6 is below 2, which suggests that the condensation in A6 is acid-catalyzed. The condensation in A6 is faster than that in A5. Effects of the amine groups in A6 and the different pH values in samples A5 and A6 might contribute to this difference. For BTMSPA, the silanol acidity is expected to decrease because of the electron-donating properties of the amine group. The condensation rate is expected to decrease since it moves to the minimum condensation at pH 2. Moreover, the bridging chain in BTSMPA
is slightly longer than that in BTMSH, which also reduces the condensation. This is consistent with our observation (Table 3.2). In highly acidic conditions, both the silica species and the amines are positively charged. The attractions between the silica and the amines are negligible. This is different to the situation in basic conditions, where we demonstrated the attractions have enhanced the hydrolysis rate.

Both of the inductive and steric factors are important to the kinetics of the condensation in acidic conditions. The bulkier of the molecule, the slower is the condensation. The inductive effect will be different in different pH solutions. In a solution with pH > 2, the higher electron density of the silicon, the faster is the condensation. Differences in the reactivities of silanes in samples A2- A5 are consistent with the expectations from the base-catalyzed condensation, which suggests that at the pH investigated (above the isoelectric point of silica), the reaction proceeds with transition states involving deprotonated silanols.

### 3.5. Conclusions

To summarize, six silanes have been selected to investigate effects of organic substitution and bridging on the sol-gel reaction kinetics in basic and acidic conditions. The differences in kinetics can be understood in terms of the differences in steric and inductive effects expected for different organic substitutes. SiOCH₂CH₃ is bulkier than SiOCH₃. The substitution of a methoxy group in TMOS with a methyl group increases the electron density of the silicon. The two Si(OCH₃)₃ ends in BTMSE interact with each other since the bridging chain is short. Electron densities of both of the silicon decrease. The size of BTMSH is much bulkier than BTMSE. This retards the sol-gel reaction very obviously. The main difference between BTMSH and BTMSPA is the amine group contained in BTMSPA. This group helps to increase the local concentration of the precursor in basic conditions. In basic conditions, the sol-gel reaction is dominated by the hydrolysis. The reaction will be slower if the electron density of the silicon is higher. In acidic conditions, the condensation is the rate-limiting step. When the pH is higher than 2, an increase of the electron density of the silicon will reduce the acidity of the silanol. The condensation thus will be faster. The inductive effect in highly acidic condition (pH < 2) might be negligible compared to the steric effect.
3.6. References

**Table 3.1.** Sol-gel reaction in basic conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>( k_{b1} (10^{-3}, \text{M}^{-1}\text{s}^{-1}) )</th>
<th>( k_{b2} (10^{-3}, \text{M}^{-1}\text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>TEOS</td>
<td>0.293 ± 0.004</td>
<td>/</td>
</tr>
<tr>
<td>B2</td>
<td>TMOS</td>
<td>2.35 ± 0.03</td>
<td>2.70 ± 0.03</td>
</tr>
<tr>
<td>B3</td>
<td>MTMS</td>
<td>1.97 ± 0.01</td>
<td>1.71 ± 0.02</td>
</tr>
<tr>
<td>B4</td>
<td>BTMSE</td>
<td>2.69 ± 0.03</td>
<td>2.28 ± 0.02</td>
</tr>
<tr>
<td>B5</td>
<td>BTMSH</td>
<td>0.305 ± 0.004</td>
<td>0.323 ± 0.007</td>
</tr>
<tr>
<td>B6</td>
<td>BTMSH</td>
<td>0.369 ± 0.007</td>
<td>0.28 ± 0.01</td>
</tr>
<tr>
<td>B7</td>
<td>BTMSPA</td>
<td>1.54 ± 0.02</td>
<td>1.61 ± 0.01</td>
</tr>
</tbody>
</table>

\( k_{b1} \): Calculated from the band of SiOCH\(_3\);

\( k_{b2} \): Calculated from the band of H\(_2\)O.

**Table 3.2.** Sol-gel reaction in acidic conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>( k_{ac}^1 (10^{-4}, \text{M}^{-1}\text{s}^{-1}) )</th>
<th>( k_{ac}^2 (10^{-4}, \text{M}^{-1}\text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>TEOS</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>A2</td>
<td>TMOS</td>
<td>1.08 ± 0.09</td>
<td>/</td>
</tr>
<tr>
<td>A3</td>
<td>MTMS</td>
<td>3.6 ± 0.2</td>
<td>/</td>
</tr>
<tr>
<td>A4</td>
<td>BTMSE</td>
<td>1.05 ± 0.07</td>
<td>/</td>
</tr>
<tr>
<td>A5</td>
<td>BTMSH</td>
<td>0.18 ± 0.05</td>
<td>/</td>
</tr>
<tr>
<td>A6</td>
<td>BTMSH</td>
<td>0.41 ± 0.01</td>
<td>0.43 ± 0.01</td>
</tr>
<tr>
<td>A7</td>
<td>BTMSPA</td>
<td>0.22 ± 0.01</td>
<td>0.24 ± 0.01</td>
</tr>
</tbody>
</table>

\( k_{ac}^1 \): Calculated from equation (3.31).

\( k_{ac}^2 \): Calculated from equation (3.28).
Si – OR + H₂O → Si – OH + ROH  \hspace{1cm} \text{Hydrolysis}
Si – OH + RO → SiOR + H₂O  \hspace{1cm} \text{Esterification}
Si – OH + SiOH → Si – O – Si + H₂O  \hspace{1cm} \text{Water - producing condensation}
Si – O – Si + H₂O → SiOH + SiOH  \hspace{1cm} \text{Siloxane hydrolysis}
Si – OH + SiOR → Si – O – Si + ROH  \hspace{1cm} \text{Alcohol - producing Condensation}
Si – O – Si + ROH → Si – OH + SiOR  \hspace{1cm} \text{Siloxane alcoholyis}

\textbf{Figure 3.1.} General sol-gel reaction.
Figure 3.2. FTIR spectra of solvents and precursors: a. methanol; b. ethanol; c. TEOS; d. TMOS; e. MTMS; f. BTMSE; g. BTMSH; h. BTMSPA; i. water; Offset vertically by 0.5, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 for b, c, d, e, f, g, h, and i respectively.
Figure 3.3. FTIR spectra of solvents and reacting solutions: a. methanol; b. water/methanol binary system ([H$_2$O] = 1.24 M); c. TMOS/NaOH/H$_2$O/methanol (initial compositions: [SiOCH$_3$] = 1.1 M, [NaOH] = 0.021 M, [H$_2$O] = 1.1 M, and [CH$_3$OH] = 23 M) at 210 seconds; and d. TMOS/HCl/H$_2$O/methanol (initial compositions: [SiOCH$_3$] = 1.72 M, [HCl] = 0.005 M, [H$_2$O] = 0.28 M, and [CH$_3$OH] = 22 M) at 210 seconds.
Figure 3.4. Relationships of concentration vs. absorbance at: a. 1196 cm$^{-1}$ (SiOCH$_3$); b. 1650 cm$^{-1}$ (H$_2$O); c. 881 cm$^{-1}$ (CH$_3$CH$_2$OH).
Figure 3.5. FTIR spectra of B2 (TMOS) at different times after mixing.
Figure 3.6. FTIR spectra of B5 (BTMSH) at different times after mixing.
Figure 3.7. FTIR spectra of B6 (BTMSH-amine) at different times after mixing.
Figure 3.8. FTIR spectra of B7 (BTMSPA) at different times after mixing.
Figure 3.9. FTIR spectra of B3 (MTMS) at different times after mixing.
Figure 3.10. FTIR spectra of B4 (BTMSE) at different times after mixing.
Figure 3.11. r-α plots for samples B2-B7
Figure 3.12. Fits of experimental data with the equation (3.11) and (3.12): a. SiOCH\(_3\); b. H\(_2\)O.
Figure 3.13. Comparisons of the experimental data (scattered points) and the calculated curves (continuous curves) for SiOCH₃.
Figure 3.14. Comparisons of the experimental data (scattered points) and the calculated curves (continuous curves) for H$_2$O.
Figure 3.15. FTIR spectra of B1 (TEOS) at different times after mixing.

Figure 3.16. Concentrations of H$_2$O and CH$_3$CH$_2$OH at the early stage of the reaction.
Figure 3.17. Fitting of the experimental data with equation (3.20).

Figure 3.18. Fitting of the experimental data with equation (3.21).
Figure 3.19. FTIR spectra of A2 (TMOS) at different times after mixing.
Figure 3.20. FTIR spectra of A3 (MTMS) at different times after mixing.
**Figure 3.21.** FTIR spectra of A4 (BTMSE) at different times after mixing.
Figure 3.22. FTIR spectra of A5 (BTMSH) at different times after mixing.
Figure 3.23. $r$-$\alpha$ plots for A2, A3, A4, and A5.
$y = 5.5842x - 5.6504$
$R^2 = 0.987$

$y = 11.441x - 12.554$
$R^2 = 0.9946$

$y = 18.726x - 22.929$
$R^2 = 0.9796$

$y = 18.341x - 23.02$
$R^2 = 0.4223$

**Figure 3.24.** [SiOCH$_3$] vs. A[SiOH] (peak intensity of SiOH) for A2, A3, A4, and A5.
Figure 3.25. Fits of experimental data with equation (3.31).

Figure 3.26. FTIR spectra of A1 (TEOS) at different times after mixing.
Figure 3.27. FTIR spectra of A6 (BTMSH-amine) at different times after mixing.
Figure 3.28. FTIR spectra of A7 (BTMSPA) at different times after mixing.
Figure 3.29. $\chi$ vs. time for samples A6 and A7.

Figure 3.30. Fits of the experimental data with equation (3.28).
Figure 3.31. Evolutions of water with time

Figure 3.32. Fits of experimental data with equation (3.31).
4.1. Introduction

The sol-gel process has been widely used to make microporous and mesoporous ceramic materials with high surface areas and pore volumes.\(^1\) An advantage of this process is that it can be carried out at room temperature, allowing the incorporation of organic components into highly porous organic-inorganic hybrid materials.\(^2,3\) In principle, by adjusting the reaction conditions, one should be able to prepare a porous material with controlled functionality, porosity, and responsiveness to the environment by polycondensation of alkoxy silanes. However, a limiting disadvantage of this process is that it normally requires controlled drying process (very slow drying or drying under supercritical conditions) to obtain porous materials with high surface areas, and even then the pore size distributions are relatively broad.

Beginning with its discovery in 1992, the templated sol-gel process has begun to be widely utilized as a way of making porous materials with better-defined porosity.\(^4,5\) A variety of templating agents can be incorporated into a sol prior to gelation which will be incorporated into a sol-gel material as noncovalently bound organics. Removal of the templates after gelation generates pores with better size and structure control than the pores normally formed by the ordinary sol-gel process. Cationic surfactant templated and non-ionic surfactant templated processes are among the two most common processes used to make mesoporous materials in this way. A cationic surfactant-templated sol-gel process normally is carried out in basic conditions, while non-ionic surfactant templating is carried out in acidic conditions, sometimes with a two-step synthesis procedure. In the cationic surfactant templated sol-gel process, basic conditions are used to promote the formation of deprotonated silanols which co-assemble with the surfactant through Coulombic interactions.\(^6,7\) Under these conditions, the hydrolysis reaction is expected to be the rate-limiting step.\(^1\) Precipitation of co-assembled particles occurs when a sufficient concentration of the nucleating species develops, which is again dictated by the dynamics of hydrolysis. Differences in the properties of products made from different precursors
would therefore be expected to be related either to differences in the kinetics of hydrolysis, or to differences in the structures of the precursors. On the other hand, in the non-ionic surfactant-templated process, the silica precursor is normally hydrolyzed for some time in acidic solution (pH ≈ 2) in the first step. During this step, hydrolysis proceeds until it reaches equilibrium but condensation is the rate limiting step. In the first step, the extent of condensation is expected be low since condensation in acidic condition is the slowest at pH 2.0. In the second step, a base or NaF is added as a catalyst to accelerate condensation. At the start of this step, most silanes are already hydrolyzed, and therefore condensation can proceed rapidly. By using the two-step procedure, hydrolysis is separated from the condensation stage in the sol-gel reaction scheme. Since co-assembly occurs through hydrogen bonding, there are not great differences in this interaction among different precursors (assuming that hydrolysis goes to completion before condensation is initiated). The difference in the kinetics is expected to have little effect on the pore structures. Properties of the products are expected to be more related to the structure of the precursor (especially the arrangement of functional groups).

In addition to noncovalently bound pore templates, the sol-gel method allows the incorporation of covalently bound organics through the use of organically modified alkoxy silane precursors. These precursors can be classified as non-bridged (containing dangling organic groups) or bridged (with an organic group bridging two trialkoxysilyl sites). Bridged silanes with various types of bridging chains have been used to make porous materials in both non-templated and templated sol-gel processes. In the non-templated process, the dried products normally have large surface areas when they are prepared in basic conditions. Under acidic conditions, the materials are more elastic and they tend to collapse during drying. In the templated sol-gel process, bridged silanes with long alkylene bridging chains (>C5) are seldom used. Because of their stiffness, phenylene and polyphenylene bridging group can be used for ordered materials. However, no material with narrow pore size distribution has been reported by using a silane with long flexible chain (>C5) as the sole precursor. The reason has been attributed to the flexibility of the bridging chain, which makes the material too soft to withstand drying stresses after the removal of the pore template.
In this chapter, we systematically investigate a series of materials prepared using the series of silanes whose early-stage reaction kinetics we have measured (see Chapter 3). The precursors include tetralkoxysilanes and alkoxydesilanes with a dangling methyl group, a bridging ethylene, a bridging hexylene chain, and a bridging dipropylamine chain. Materials are prepared in the absence of a surfactant under acidic or basic conditions, and using either a cationic surfactant (CTAB) or a nonionic polymeric surfactant (polyoxyethylene 10 lauryl ether, a PEO-based surfactant) as the pore template. The results are discussed in terms of what we would have expected based on the kinetic trends for the hydrolysis and condensation reactions of the precursors, and on the structures of the precursors. Using this series of precursors, we test the influence of gradual changes in precursor structure on the pore properties of the products. We find that the part of the reason that templated materials cannot be made with long-chain bridged silanes may be a reduced driving force for co-assembly into an ordered structure due to favorable interactions of the template with the bridging chain.

4.2. Experiment Section

4.2.1. Materials. Tetraethoxysilane (TEOS, 99+%), tetramethoxysilane (TMOS, 99+%), methyltrimethoxysilane (MTMS), bis(trimethoxysilyl)ethane (BTMSE, 95+%), Bis(trimethoxysilyl)hexane (BTMSH), and Bis(trimethoxysilylpropyl)amine (BTMSPA, 95%) were purchased from Gelest. Cetyltrimethylammonium bromide (99%, CTAB) and polyoxyethylene 10 lauryl ether (C_{12}E_{10}) were purchased from Sigma. The solvents and reagents used were deionized untrafiltered water (DIUF, Fisher Scientific), anhydrous ethanol (Aaper Alcohol and Chemical), concentrated aqueous HCl (36.5%, Fisher Scientific), and NaF (technical grade, MCB). All chemicals were used as received.

4.2.2. Sample Preparation.

Sol-gel process. To prepare the sol-gel materials, two solutions were initially prepared where one consisted only of methanol and the precursor, and the other contained water and acid or base in methanol. The solutions were mixed together and the time was recorded.
Seven samples (B1 to B7) were prepared with the same compositions but with the precursors being TEOS, TMOS, MTMS, BTMSE, BTMSH, BTMSH, and BTMSPA, respectively. The initial molar ratios were \(1 \text{SiOCH}_3\) (\(\text{SiOCH}_2\text{CH}_3\) with TEOS): \(1 \text{H}_2\text{O}: 20\) methanol: \(0.018\) NaOH: \(x\) dipropylamine (\(x = 0.17\) for sample B6, \(x = 0\) for the others). The samples, B6 and B7, were prepared to compare the effect of an amine external to the bridging chain of BTMSH (B6), or integral in the bridging chain of BTMSPA (B7).

Five samples (A1 to A5) were prepared under acidic conditions with the same series of precursors: TEOS, TMOS, MTMS, BTMSE, and BTMSH, respectively. The molar ratio of \(\text{SiOCH}_3\) (\(\text{SiOCH}_2\text{CH}_3\) with TEOS): \(\text{H}_2\text{O}: \text{HCl}: \text{methanol}\) for any sample in this series (A1-A5) is \(1: 1: 0.018: 6.8\). Samples A6 and A7 were again prepared to compare the effect of the amine between BTMSH and BTMSPA. However, to make the samples still acidic, an excess of HCl was added beyond the quantity of amine present. In sample A6 (BTMSH), a quantity of dipropylamine was added comparable to the amount of amine in sample A7 (BTMSPA). The initial molar ratio of \(\text{SiOCH}_3: \text{H}_2\text{O}: \text{HCl: dipropylamine: methanol}\) was \(1: 1: 0.185: x: 12.7\) (\(x = 0.167\) for B6, \(x = 0\) for B7) in sample B6 or B7.

All solutions were prepared in sealed polystyrene vials. The solutions were aged at room temperature until the gel point, which was determined as the point at which no movement of the meniscus of the sample could be observed upon tilting the vial at 45° relative to vertical. More specifically, the gel point was defined as the time at which the meniscus did not move within one minute of being tilted.

*CTAB templated sol-gel synthesis.* The procedure to prepare CTAB-templated materials is based on the procedure of Kumar et al.\(^{13}\) CTAB, water, and concentrated ammonia were stirred together for 10 minutes before the dropwise addition of the precursor. The solution was aged at room temperature for 24 hours with stirring. The solution was then filtered and the as-synthesized sample was dried in air overnight. The surfactant was then removed by washing / ion exchange with acidic ethanol (5 ml 36.5 wt% HCl in 150 ml ethanol).
Six samples (C1 to C6) were prepared with the same compositions but with different precursors (TEOS, TMOS, MTMS, BTMSE, BTSH, and BTMSPA, respectively). Each sample had an initial molar composition of 1 SiOCH$_3$ (SiOCH$_2$CH$_3$): 0.13 CTAB: 2.4 NH$_3$: 138 H$_2$O.

**PEO-based non-ionic surfactant templated sol-gel synthesis.** The procedure for preparing C$_{12}$E$_{10}$-templated materials is similar to what was reported by Bossiere et al.\textsuperscript{14} C$_{12}$E$_{10}$, water, and HCl were first mixed together with stirring. After aging at room temperature for one day, the desired amount of solid NaF was added to the solution. The solution was then aged at 55 °C for three days with stirring. The solution was filtered and the C$_{12}$E$_{10}$ was removed from the sample by Soxhlet extraction with 150 ml ethanol as a solvent.

Five samples (N1 through N5, with TEOS, TMOS, MTMS, BTMSE, and BTMSH as precursors, respectively) were prepared with the molar composition of 1 SiOCH$_3$ (SiOCH$_2$CH$_3$): 0.12 C$_{12}$E$_{10}$: 0.059 HCl: 329 H$_2$O: x NaF (x = 0.06 for samples N1, N2, N4, and N5; x = 0.60 for sample N3). Because of the amine in BTMSPA, excess amount of acid was added in sample N6. The molar composition for this sample was 1 SiOCH$_3$ (SiOCH$_2$CH$_3$): 0.12 C$_{12}$E$_{10}$: 0.68 HCl: 329 H$_2$O: 0.60 NaF.

4.2.3. **Characterization.** Powder X-ray diffraction (XRD) patterns of the powder products were recorded in the Bragg-Brentano geometry using a Siemens 5000 diffractometer, with a step size of 0.02° and a scanning speed of 0.1 °/min. Each sample was scanned at 2θ from 1.5° to 7.5°. We utilized 0.15406 nm Cu K$_\alpha$ radiation and a graphite monochromator for the measurement. Nitrogen sorption was measured at 77 K with a Micromeritics Tristar 3000 automated nitrogen adsorption apparatus. Samples were degassed under flowing nitrogen at 120 °C for over four hours before the measurement. The KJS modified BJH method\textsuperscript{15} was used to estimate the pore size distributions for all samples.

4.3. **Results and Discussion**

4.3.1. **Comparison of products made by a non-templated sol-gel process under basic conditions**
Seven samples B1 to B7 were prepared under basic conditions. Gel times and product properties of these samples are compared in Table 4.1.

From our study of the sol-gel kinetics of these precursors (see Chapter 3), we know that as we move through the series of silanes in B1 through B7, the hydrolysis reactivity in basic condition follows the following pairwise trends: TEOS < TMOS, TMOS > MTMS, MTMS < BTMSE, BTMSE > BTMSH, and BTMSH < BTMSPA. The reactivities of TMOS, MTMS, and BTMSE are similar in magnitude, while the reactivity of BTMSH is closer to that of TEOS. Gel times measured for this series of samples (Table 4.1) do not follow the trend that would have been expected based on the differences in the hydrolysis reactivity. This indicates that the gel time is not determined merely by the reactivity of the silane toward the first hydrolysis step. However, some trends follow the reactivity to some extent. Both TEOS and TMOS have four functionalities, and TEOS is less reactive than TMOS. The gel time in B1 is longer than that in B2. However, because transesterification plays an important role in sample B1 (see Chapter 3), the difference in the gel times is not as large as would be expected based on the difference in the hydrolysis reactivities.

MTMS and BTMSE have similar hydrolysis reactivities to TMOS. However, while TMOS takes many months to form a gel, within several days, a precipitate was observed for sample B3, and a gel for sample B4. The large difference in the gel times surely could not be explained by the different reactivities of the silanes. This difference also could not be explained by the different functionalities of the precursors if they react by random polycondensation. The gelation conversion predicted by random branching theory would be 1/(f-1) where f is the functionality of the monomer. The gelation conversions would be expected to be 0.33, 0.50, and 0.20 for TMOS, MTMS, and BTMSE, respectively.

The reason that we didn’t obtain gel/precipitate very quickly with TEOS and TMOS is most likely due to the formation of cage-like silsesquioxane structures or siloxane rings. These structures gel at a much higher overall conversion than is predicted by random branching theory, and react extremely slowly to interconnect into a three dimensional network structure. When one of the alkoxy groups of TMOS is replaced with –CH₃ to form MTMS, the solubility of the cage-like nanoparticles formed is limited. When the concentration of cages or rings is large enough, they will crystallize or
precipitate from the solution. When BTMSE is used instead of MTMS, the siloxane cages or rings formed initially are easily connected to each other because of the pre-existing bridging ethylene chain. A three dimensional network structure is therefore much more easily formed. Thus, we find that structural effects in the arrangement of organic groups best explain the difference in gel times among samples B1 through B4.

Comparing samples B4 and B5, the hydrolysis reactivity of BTMSE exceeds that of BTMSH by almost an order of magnitude, and yet the gel time of BTMSE is significantly longer. A notable difference between the products is that while the BTMSE gel is transparent, the BTMSH gel is opaque. Since the bridging chain is short in sample B4 (C2), the sol remains homogeneous and transparent until gelation. When the bridging chain is as long as C6, the bridging chain is very hydrophobic and phase separation occurs during the polymerization process. An opaque product is therefore obtained. Phase separation may accelerate gelation in the case of BTMSH. In addition, ethylene-bridged silanes are capable of forming 5-atom carbosiloxane rings which delay gelation. Hexylene-bridged silanes do not readily form 9-atom carbosiloxane rings, so gelation can occur much more quickly. The length of the alkylene chain may also assist gelation since it is much easier to the nanoparticles to reach each other for a bridged silane with longer chain.

BTMPSA has six carbon atoms and one amine group in the bridging chain. The bridging chain length is slightly longer than that of BTMSH. However, because of the amine group, the hydrolysis coefficient of BTMSPA is much larger than that of BTMSH. However, the gel time of BTMSPA (sample B7) is much longer than that of BTMSH (sample B5). The reason might be due to the hydrophilicity of the amine group in BTMSPA. The amine group helps to keep the growing siloxane polymers soluble in the methanol solution, leading to the slow formation of a gel which is homogenous and transparent. Sample B6 rules out the possibility that the difference in gelation times is simply due to an inhibiting effect of the amine. When the amine is not incorporated into the chain but an equivalent amount of dipropylamine is present (B6), the hydrolysis kinetics and gel time is similar to those of the hexylene-bridged sample (B5).

Nitrogen adsorption isotherms of the products obtained after drying are compared in Figure 4.1. All samples have a fraction of their pores which are microporous. B4 has a
type I isotherm, is completely microporous, and has the highest surface area. B7 also has a type I isotherm and only contains micropores, but it has the lowest surface area. The gels made from the tetrafunctional monomers (B1 and B2) have a fraction of their pores which are mesopores, and hysteresis loops with multiple steps suggesting inhomogeneous pore networks. Their micro/meso-porous structure is not unusual for silica xerogels. Samples B3 and B5 have fairly low surface areas. Samples B3 and B5 have type II adsorption isotherms with H3 hysteresis loops. The hysteresis loop for sample B3 does not close at low relative pressures. The adsorption isotherms and hysteresis loops indicate that both samples are made up with aggregates of nanoparticles with little internal porosity. Sample B6 is surprising because while it is made with the same precursor as B5, it has a large hysteresis loop that suggests uniform mesoporosity. The dipropylamine must actually be serving as a mesopore template in this case. As Figure 4.1 shows, the mesopore size distributions for samples B1, B2 and B6 are fairly similar, while all other samples do not have appreciable mesoporosity. In general, for the materials with bridging organics, with an increase in the length of the bridging chain, the surface area decreases. When the bridging chain is longer, it will be more flexible, which allows a greater collapse of pores during drying. Because the bridging organic of BTMSE is short and rigid, a compact microporous structure is obtained. The surface area of BTMSH is smaller than what has been reported before. The reason may be due to the drying process. All samples here were dried in air without any special precautions. This treatment would exaggerate the collapse of the pores. The amine-functional bridged silane collapses the most because the gel is an elastic, homogeneous solid rather than a particulate gel.

4.3.2. Comparison of products made by a non-templated sol-gel process under acidic conditions

Seven samples A1 to A7 were prepared in acidic conditions. pH values in the solutions should be approximately the same if all amines (in samples A6 and A7) have been titrated by HCl. Gel times and total surface areas of all samples are compared in Table 4.2.
Similar to the products obtained in basic conditions (Table 4.1), transparent gels are observed for samples prepared from TEOS, TMOS, BTMSE, and BTMSPA. This indicates that the growing siloxane polymers from those precursors are more soluble than those prepared from MTMS and BTMSH. The trend in the gel times is similar to that in basic conditions. A1 has a similar gel time to A2 because of the transesterification reaction. A4 gels much faster than A2 because of the pre-existing bridging ethylene chain. With an increase of the chain length, the gel time is much shorter, but a non-homogenous product is obtained. Because of the limited solubility of the methyl groups, dense particles tend to be formed with MTMS as the precursor.

Reactants in sample A6 are more dilute than those in sample A5. This may cause the difference in the gel times between A5 and A6. It took much longer time to gel for sample A7 than sample A6. The kinetics of condensation of BTMSH and BTMSPA under highly acidic conditions are similar. Therefore, the difference in gel times is most consistent with expectation that amine in the bridging chain should increase the solubility of the growing siloxane polymers.

Nitrogen sorption plots of the acid-catalyzed non-templated samples are shown in Figure 4.2. Samples A1, A2, A4, and A5 have type I adsorption isotherms. All of them are microporous. Sample A6 is nonporous since only negligible surface area is obtained (Table 4.2). The surface are for sample A7 is also very low. However, sample A7 has a type IV adsorption isotherm with a H2 hysteresis loop, indicating this sample has a small amount of uniform mesopores. A narrow pore size distribution is observed for sample A7 (Figure 4.2). Similar to the samples prepared under basic conditions, the total surface area decreases as the bridging alkylene chain length increases.

For samples made in the non-templated sol-gel process, it takes long time to gel with TEOS or TMOS as the precursor. Because of the transesterification reaction, the gel time is only slightly shorter with TMOS than it is with TEOS. Products prepared from TMOS and TEOS in basic conditions are mesoporous, while they are microporous in acidic conditions. Gels are obtained relatively quickly with BTMSE. This indicates that BTMSE can be used as a substitute for TEOS or TMOS in some circumstances. Samples made from BTMSH have surface areas much lower than 560 m$^2$/g, as reported by Loy et al.$^9$ This is reasonable since gels are dried with supercritical CO$_2$ in Loy et al.’s work.
experiments, all samples are dried in air which will induce the collapse of pores. Because of the hydrophilic property of the amine group in BTMPA, homogeneous gels form which are susceptible to collapse upon drying. The amine also is hydrophilic and basic, so samples made from this precursor might not be stable in air. That may be the reason that the total surface areas of A7 and B7 are so small.

4.3.3. Comparison of products made by a cationic surfactant-templated sol-gel process

The CTAB templated sol-gel process in basic solution is a common process used to make ordered mesoporous materials, in particular materials similar to MCM-41. Ammonia or NaOH is normally added to adjust the pH value in this process. In basic solution, a silica precursor will be hydrolyzed to produce negatively charged silica species. These negatively charged silica species are then attracted to the headgroups of positively charged surfactant micelles. Condensation reactions happen among the locally concentrated silica species that have been attracted. The local density of silica species in this process should be much higher than it in the non-templated sol-gel system, which increases the condensation rates dramatically. Without the template, cage-like structures or rings are likely to form in the sol-gel process, which delays gelation. In the presence of the template, these structures will easily condense as they surround the template. Dense particles which are aggregates of CTAB and the condensed precursor are easily formed. This is the reason that precipitates form easily in a cationic surfactant templated process. Condensation in the absence of templates will be called “random condensation” in this chapter to distinguish it from localized condensation occurring among the species surrounding templates.

Six samples (C1 through C6) were prepared with the same compositions but with different precursors. Precipitates were obtained from all solutions. If a solution was prepared under the same conditions with TEOS as the precursor but without CTAB, no gel or precipitate was obtained after several days. This indicates that localized condensation is dominant over random condensation in the surfactant templated sol-gel process.

Product properties of all samples are shown in Table 4.3. Solutions of C1, C2, C3 and C4 became turbid within several minutes after adding the precursor. A gel was
formed immediately when BTMSH was used as the precursor (sample C5). For C6 (with BTMSPA), a large amount of precipitates formed at a very early stage of the process. After aging, sample C5 had a gel-like morphology while the others had powder morphologies. The gel-like structure indicates that this sample has a three dimensional network structure which may come from random condensation.

The nitrogen sorption isotherms of all CTAB-templated samples are shown in Figure 4.3. In basic solution, the hydrolysis reaction is the rate-limiting step for all of these samples (see Chapter 3). The hydrolysis rate of TEOS is slower than TMOS. However, no large difference was found in the precipitation times of C1 and C2, or the properties of the products. Both samples are ideal MCM-41 types of structures with type IV isotherms and narrow pore size distributions (Figure 4.3). This indicates that the effect of hydrolysis kinetics might be negligible in this case. For TEOS, TMOS, and MTMS, the localized condensation is expected to be dominant to form individual particles since these precursors prefer to form cages or rings in the non-templated process. However, the methyl group of MTMS disrupts the interactions with the CTAB and the formation of a network in the pore walls. Therefore, the surface area is reduced, the pores are expanded, and the uniformity of the pores is less (indicated by the large hysteresis loop in Figure 4.3). With BTMSE as the precursor, the bridging chain helps to create connections between silica sites. However, the length of the bridging chain is so short that the connected particles can aggregate together, to form large individual particles instead of a three dimensional network structure. The structure of the BTMSE sample is similar to MCM-41, but the pore size distribution is somewhat broader. The situation is different when BTMSH is used. The bridging chain is long, flexible, and hydrophobic. Random condensation can easily proceed even with the presence of CTAB. The lack of well-defined mesopores in sample C5 confirms that micelle templating did not work well in this case. In addition to the long bridging groups allowing non-localized condensation to occur, they may allow greater mixing with CTAB, discouraging the formation of an ordered aggregate. Instead, the sample has large, nonuniform mesopores as indicated by the hysteresis loop in Figure 4.3. It is interesting to see that small mesopores are again obtained with BTMSPA (sample C6). The amine group in the bridging chain may help to attract the surfactant headgroups through hydrogen bonding, or at least to prevent
interactions of surfactant tail with the bridging chain. The large amount of precipitates and the narrow mesopore size distribution of C6 indicate that CTAB associates well with BTMPA. The difference between C5 and C6 may again come from the amine group of BTMPA. C6 has a similar pore size to sample C4. Both of them are slightly smaller than those of C1 and C2. The difference in the pore sizes might be due to the shrinkage of pores of C4 and C6 during the drying process. Both of the samples have integral organics in the pore walls which may allow shrinkage during drying.

Both samples C3 and C5 have large hysteresis loops in their isotherms. Both samples also have broad distributions of large pores. The rest of the CTAB-templated samples in this series have reversible isotherms. All of them also have sharp inflections in their isotherms and narrow pore size distributions. The reason that the template didn’t work well with MTMS and BTMSH is likely to be the precursor structures rather than the kinetics. All precursors are expected to be hydrolyzed to produce negatively charged silica species before condensation. The difference in the kinetics may affect the formation rate of the silica/surfactant aggregates, but will not affect the formation of the aggregates. The poor ordering of C3 and C5 may arise for different reasons. MTMS has one alkyl chain, which limits the formation of silica walls around the surfactant. The as-synthesized material may not have enough silica to sustain the pores during removal of the surfactant. The low well-connected silica extent in MTMS/CTAB aggregates is illustrated with an extra sample prepared for comparison. This sample is the same as C3 except that half of the MTMS is used in the new sample. Little product is collected (less than 0.02 grams), and the as-synthesized product is flaky with light density. For samples made with the other precursors at the same molar compositions, at least 0.2 grams of samples were recovered by filtering. On the other hand, BTMSH has a long and hydrophobic bridging chain. The long bridging chain facilitates random condensation. However, the lack of mesopores is not just a result of the long chain; small mesopores are found in the product made with BTMSPA. The hydrophobic chain of BTMSH would be expected to interact with the tails of CTAB through dipolar and hydrophobic forces, reducing the driving force for micelle formation and allowing a disordered composite to form. This will disrupt the formation of the silica/surfactant aggregates and favor random condensation. Although both C3 and C5 don’t have narrow pore size distributions, their surface areas
are still much higher than what have been obtained in non-templated sol-gel process, which indicates that CTAB helps to form or stabilize large pores. When BTMSPA is used, the hydrophilic chain helps to promote co-assembly of the precursor with CTAB micelles and thus restricts the random condensation. However, there is still some evidence for the random condensation in sample C6. The large amount of product collected (1.44 g) indicates that part of the product was formed by the random condensation. Still, templating is indicated by the presence of narrowly distributed mesopores in C6 (inset of Figure 4.3). The surface area of C6 is much larger than what were obtained in the non-templated sol-gel processes (A7, B7). Although it does not have an extremely high pore volume, sample C6 is interesting because amines are incorporated homogeneously into the pore walls.

The long-range order of the pore structures of all samples were characterized with XRD. Sample C1 and C2 have exemplary 2D hexagonal structures (not shown). The XRD pattern of C4 has only one sharp peak which indicates this sample has a wormhole-like / disordered hexagonal pore structure. The XRD pattern of C6 also has one peak, indicating that this material has a wormhole-like pore structure. This is the first time that a material with wormhole-like structure was made by using BTMSPA as the sole precursor. XRD patterns of C3 and C5 do not show reflections, which is consistent with the absence of narrowly distributed pores in the nitrogen adsorption results. The \( d_{100} \) spacing of sample C1 is larger than that of sample C2 (Table 4.3). Since both samples have the same pore size and pore structure, the difference in the \( d \) spacing is because of the different thickness in the pore walls. Sample C1 has a thicker pore wall than sample C2. This suggests that slower hydrolysis reactivity is favorable to form thicker pore walls. The \( d_{100} \) spacing of C6 is much larger than that of C4, which is again larger than that of C2. Since the pore sizes of C4 and C6 are the same which is slightly smaller than that of C2, the incorporation of a bridging chain has increased the pore wall thickness. The longer is the bridging chain, the large pore wall thickness it has increased.

The investigation of CTAB-templated materials show that because of its limitation to form a network structure in the pore walls, MTMS has difficulty to co-assemble with CTAB to make a uniform mesoporous material. The long and hydrophobicity chain in BTMSH makes it unable to co-assemble with CTAB. There is no large difference found
under the synthesis conditions between materials made with the tetrafunctional silanes TEOS and TMOS. By using BTMSE, the pore size becomes smaller, but the surface area is still very large. The product made from BTMSPA is interesting, because it is usually presumed difficult or impossible to make materials with integral long-chain organic groups. Because of the solubility of the amine group, we were able to isolate a sample (C6) with some uniform mesopores and a fairly high surface area, which is ideal for the applications of this material as a selective basic catalyst, an adsorbent, or for further functionalization.

4.3.4. Comparison of products made by a non-ionic surfactant-templated sol-gel process

Non-ionic polymeric surfactants can be prepared in a very wide array of molecular weights, so a wide variety of large pores can be created which are useful for applications such as protein adsorption. Thus, there is a significant reason to understand the nonionic imprinting process in comparison to templating with cationic surfactants.

In a cationic surfactant-templated sol-gel process under basic conditions, hydrolyzed silica species are attracted to the surfactant micelles through electrostatic interactions. When a nonionic surfactant such as C_{12}E_{10} is used, the co-assembly is based on weaker hydrogen bonding interactions. In the two-step synthesis procedure with NaF as the condensation catalyst,\(^8\) the silica/ C_{12}E_{10} aggregates formed initially during the acidic hydrolysis step remain soluble. The addition of NaF induces the silica condensation and precipitation of particles.\(^14\) In the first step, the solution is normally aged for 1 day in highly acidic conditions which permits the complete hydrolysis of the precursor. The hydrolysis and condensations stages are thus separated. Because of this, the effects of varying kinetics of the sol-gel reactions on the product properties are expected to be limited. Differences in the products are more likely to be found due to the differences in the precursor structures.

Properties of samples N1 to N6 are compared in Table 4.4. Before the addition of NaF, all solutions were aged for 1 day at room temperature. The precursors are expected to be completely hydrolyzed since the hydrolysis reaction is very fast in acidic conditions.\(^19\) The condensation is expected to happen to some extent during this step, although it should be slow. Weakly condensed silica/PEO aggregates are still soluble if
they have enough –OH groups. However, for MTMS, the solubility of these aggregates is limited because of the Si-CH$_3$ group. This is the reason why we observed a turbid solution for sample N3 prior to the addition of NaF. For BTMSE, the situation is similar to TMOS except there is a short bridging chain connecting the weakly condensed aggregates. When the bridging chain is too long, as for BTMSH, the solubility of these aggregates again is limited by the hydrophobicity of the precursor. Moreover, these weakly condensed structures are very easily connected to each other to form a three-dimensional network structure because of the long bridging chain. As a result, a gel can form. BTMSPA has the similar bridging chain length as BTMSH. However, the amine group in the bridging chain helps to keep the weakly condensed structures dissolved in the C$_{12}$E$_{10}$/water solution. This is similar to what happens in the non-templated sol-gel process.

Upon the addition of a small amount of sodium fluoride (NaF/Si = 6 mol %), precipitates were observed for TEOS, TMOS, BTMSE, and BTMSH. No precipitates were observed for MTMS and BTMSPA after three days. BTMSPA has a hydrophilic chain which helps to dissolve the condensed material. By increasing the amount of NaF, the condensation is expected to increase. Precipitates were obtained for BTMSPA and MTMS by increasing the amount of sodium fluoride to NaF: Si = 60 mol %.

Isotherm plots and pore size distributions of the N-series samples are compared in Figure 4.4. Samples N1 and N2 have similar isotherm shapes. Both of them have hysteresis loops and sharp inflections in the isotherms. Sample N2 has a higher surface area than N1. Both of them have the same pore size which is understandable, since the same template was used. Sample N3, prepared with MTMS, has very low porosity because the interactions between C$_{12}$E$_{10}$ and the methyl groups are not favorable. The isotherms of N4 are reversible, indicating a highly uniform mesopore structure. N5 has a surface area similar to C5, but it does not have any mesopores. Both surface areas are much higher than what would have been obtained without any template (samples B5 and A5). However, all the samples made with BTMSH without adding dipropylamine lack narrow pore size distribution. The sample prepared with BTMSPA (N6) has a small surface area, but a broad distribution of large mesopores.
XRD patterns of samples N1 and N2 only have one sharp reflection (not shown), which indicates all the samples have wormhole-like pore structure. No peak is observed for sample N4, which is possibly because the first peak is out of the range of the XRD instrument. Only peaks after 1.5 ° (2θ) can be identified in our XRD instrument. No reflection is observed for samples N3, N5 and N6 as expected.

The investigation shows that there is no big difference in the use of TMOS and TEOS as the precursor. Both non-bridged alkane-functional precursors and bridged precursors with long bridging chains are not able to make mesoporous silica with narrow pore size distributions when combined with the non-ionic surfactant C_{12}E_{10}. Somewhat surprisingly, the sample prepared with BTMSE forms a composite material with a very narrow mesopore size distribution.

4.4. Conclusions

Six silanes were used to investigate effects of small, systematic change in the precursor structure on the gel times and product properties of materials prepared with and without pore templates. The gel time in the non-templated sol-gel process depends more on the structure of the silane than on the reactivity of the precursor measured at the start of the reaction (see Chapter 3). A long bridging chain favors rapid gel formation, although precipitation may occur. Ethylene-bridged silanes and amine-containing bridged silanes gel on a longer time scale, but they tend to remain dissolved in solution until the gel point or until they co-assemble with pore templates. Mesoporous materials are made with TMOS or TEOS in basic conditions. Materials made with BTMSE are microporous even in basic conditions. Samples made from TEOS, TMOS and BTMSE have narrow mesopore size distributions when prepared by cationic surfactant templating or nonionic surfactant templating. Pores made from BTMSE have smaller sizes than those from TEOS or TMOS. Samples made from MTMS and BTMSH are microporous even in the presence of a pore template. Samples made from BTMSH in templated processes have much higher surface areas than those made by non-templated sol-gel processes. However, the low surface areas of the non-templated samples A5 and B5 may be due to the uncontrolled ambient drying process that causes the collapse of pores. The sample made from MTMS by cationic surfactant templating has the highest surface area compared to
the samples prepared in other conditions. This indicates that the cationic surfactant templated process may be a good choice to make microporous materials from trialkoxysilanes. The sample made with BTMSPA in the cationic surfactant-templated process (C6) has a wormhole-like structure. The success of pore templating in sample C6 indicates that other bridged silanes with long hydrophilic chains may also be able to make materials with wormhole-like pore structures. For all samples made from bridged silanes, the surface area decreases with an increase of the bridging chain length. The interactions of the bridged silane with the template are very important in the templated process. The inability of bridged silanes with long chains to make mesoporous materials is more likely due to the hydrophobicity of the chain allowing uncontrolled mixing of the pore template with the silane, rather the co-assembly of the silane with micelles.

4.5. References


Table 4.1. Products of sol-gel reaction in basic conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>$k_{hl}$ (M$^{-1}$s$^{-1}$)</th>
<th>Gel time</th>
<th>Product morphology</th>
<th>$S_{BET}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>TEOS</td>
<td>0.293 ± 0.004</td>
<td>6 month</td>
<td>transparent gel</td>
<td>401</td>
</tr>
<tr>
<td>B2</td>
<td>TMOS</td>
<td>2.35 ± 0.03</td>
<td>5 month</td>
<td>transparent gel</td>
<td>428</td>
</tr>
<tr>
<td>B3</td>
<td>MTMS</td>
<td>1.97 ± 0.01</td>
<td>\</td>
<td>particles</td>
<td>261</td>
</tr>
<tr>
<td>B4</td>
<td>BTMSE</td>
<td>2.69 ± 0.03</td>
<td>72 hours</td>
<td>transparent gel</td>
<td>727</td>
</tr>
<tr>
<td>B5</td>
<td>BTMSH</td>
<td>0.305 ± 0.004</td>
<td>2.5 hours</td>
<td>opaque gel</td>
<td>106</td>
</tr>
<tr>
<td>B6</td>
<td>BTMSH</td>
<td>0.369 ± 0.007</td>
<td>2 hours</td>
<td>white powder</td>
<td>254</td>
</tr>
<tr>
<td>B7</td>
<td>BTMSPA</td>
<td>1.54 ± 0.02</td>
<td>18 hours</td>
<td>transparent gel</td>
<td>88</td>
</tr>
</tbody>
</table>

* (see Chapter 3)

Table 4.2. Products of sol-gel reaction in acidic conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>$k_{ac}$ M$^{-1}$s$^{-1}$</th>
<th>Product morphology</th>
<th>Gel time</th>
<th>$S_{BET}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>TEOS</td>
<td>/</td>
<td>Transparent gel</td>
<td>8 months</td>
<td>410</td>
</tr>
<tr>
<td>A2</td>
<td>TMOS</td>
<td>1.08 ± 0.09</td>
<td>Transparent gel</td>
<td>7 months</td>
<td>500</td>
</tr>
<tr>
<td>A3</td>
<td>MTMS</td>
<td>3.6 ± 0.2</td>
<td>Few particles</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>A4</td>
<td>BTMSE</td>
<td>1.05 ± 0.07</td>
<td>Transparent gel</td>
<td>60 hrs.</td>
<td>685</td>
</tr>
<tr>
<td>A5</td>
<td>BTMSH</td>
<td>0.18 ± 0.05</td>
<td>Opaque gel</td>
<td>22 min.</td>
<td>240</td>
</tr>
<tr>
<td>A6</td>
<td>BTMSH</td>
<td>0.41 ± 0.01</td>
<td>Opaque gel</td>
<td>20 hrs</td>
<td>2</td>
</tr>
<tr>
<td>A7</td>
<td>BTMSPA</td>
<td>0.22 ± 0.01</td>
<td>Transparent gel</td>
<td>17 days</td>
<td>37</td>
</tr>
</tbody>
</table>

(see Chapter 3).
### Table 4.3. Sol-gel reaction with CTAB as the template.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>As-synthesized product morphology</th>
<th>Product weight (g)</th>
<th>( d_{100} ) (nm)</th>
<th>( S_{BET} ) (m(^2)/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>TEOS</td>
<td>White powder</td>
<td>0.51</td>
<td>3.53</td>
<td>853</td>
<td>3.5</td>
</tr>
<tr>
<td>C2</td>
<td>TMOS</td>
<td>White powder</td>
<td>0.48</td>
<td>3.40</td>
<td>922</td>
<td>3.4</td>
</tr>
<tr>
<td>C3</td>
<td>MTMS</td>
<td>White powder</td>
<td>0.60</td>
<td>/</td>
<td>696</td>
<td>/</td>
</tr>
<tr>
<td>C4</td>
<td>BTMSE</td>
<td>White powder</td>
<td>0.76</td>
<td>3.71</td>
<td>1214</td>
<td>3.1</td>
</tr>
<tr>
<td>C5</td>
<td>BTMSH</td>
<td>Gel</td>
<td>0.99</td>
<td>/</td>
<td>475</td>
<td>/</td>
</tr>
<tr>
<td>C6</td>
<td>BTMSPA</td>
<td>White powder</td>
<td>1.44</td>
<td>5.52</td>
<td>358</td>
<td>3.1</td>
</tr>
</tbody>
</table>

### Table 4.4. Sol-gel reaction with PEO-based surfactant as the template.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>Solution before adding NaF</th>
<th>Weight of extracted sample (g)</th>
<th>( d_{100} ) (nm)</th>
<th>( S_{BET} ) (m(^2)/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>TEOS</td>
<td>Clear</td>
<td>0.15</td>
<td>5.38</td>
<td>732</td>
<td>4.3</td>
</tr>
<tr>
<td>N2</td>
<td>TMOS</td>
<td>Clear</td>
<td>0.15</td>
<td>5.07</td>
<td>879</td>
<td>4.3</td>
</tr>
<tr>
<td>N3*</td>
<td>MTMS</td>
<td>Turbid</td>
<td>0.07</td>
<td>/</td>
<td>74</td>
<td>/</td>
</tr>
<tr>
<td>N4</td>
<td>BTMSE</td>
<td>Clear</td>
<td>0.14</td>
<td>/</td>
<td>892</td>
<td>3.3</td>
</tr>
<tr>
<td>N5</td>
<td>BTMSH</td>
<td>Soft gel precip.</td>
<td>0.31</td>
<td>/</td>
<td>409</td>
<td>/</td>
</tr>
<tr>
<td>N6*</td>
<td>BTMSPA</td>
<td>clear</td>
<td>0.44</td>
<td>/</td>
<td>163</td>
<td>/</td>
</tr>
</tbody>
</table>

*NaF/Si =60 mol% in samples N3 and N6.*
Figure 4.1. Isotherm plots and pore size distributions for samples B1, B2, B4, B5, B6, and B7.
Figure 4.2. Nitrogen sorption data: (a) Isotherms for samples A1, A2, A4, A5, A6 and A7; (b) Pore size distribution (KJS modified BJH method) for sample A7.
Figure 4.3. Isotherm plots and pore size distributions for samples C1, C2, C3, C4, C5, and C6.
Figure 4.4. Isotherm plots and pore size distributions for samples N1, N2, N3, N4, N5, and N6.
Chapter 5. Mechanism of the Surfactant Templated Sol-Gel Process in Water/Ethanol Solution


5.1. Introduction

The Stöber process for the synthesis of colloidal silica has been known to the materials synthesis community for decades. In this process, tetraethoxysilane is hydrolyzed in ethanol/water/ammonia solution, and uniformly sized (essentially monodisperse) particles form by precipitation. Grün et al. carried out the same process in the presence of surfactant pore templates to synthesize mesoporous spherical silica particles. Shortly thereafter, several groups reported that in addition to being organized into periodic arrays, the pores in these materials are often oriented radially towards the edges of the particles. This is an ideal pore arrangement for providing accessibility to the interior of the particles for applications such as catalysis and selective adsorption. In spite of the potential applications, the mechanism of forming such an unusual structure is difficult to explain.

Prior studies of mesoporous materials synthesis mechanisms focused mainly on how long-range order develops, and led to the conclusion that the synthesis most likely occurs through cooperative assembly of silicate species and surfactants driven by Coulombic or hydrogen bonding interactions. Recent studies indicate that under acidic conditions, phase separation occurs prior to the onset of long-range ordering, and that this phase separation influences particle morphology. Contrasting this, in an alkaline solution, Regev used cryo-TEM to observe elongated cylindrical micelles early in reaction, which are more consistent with organized structure formation prior to precipitation. A TEM investigation of acid-neutralized samples suggested the opposite - that disordered aggregates form first in NaOH solution, which subsequently rearrange into ordered structures. However, none of these studies are directly applicable to Stöber synthesis conditions, and they do not explain how a radial pore orientation emerges.

The mechanism of morphology development in the Stöber process (in the absence of surfactants) has been studied in detail. The formation of uniform particles was
originally attributed to fast nucleation followed by growth by monomer addition.\textsuperscript{16,17} However, more recent research has indicated that this process is better modeled by the combination of an initial nucleation and aggregation mechanism that is followed by monomer or small particle addition.\textsuperscript{23,24} When surfactants are added to the Stöber process, the relative importance of nucleation, aggregation and growth to the co-assembly of surfactant/silica aggregates again becomes a question. Van Tendeloo et al. have proposed that the formation of radially oriented close-packed cylindrical pores can be explained by nucleation and growth.\textsuperscript{25,26} They suggested that a faceted Ia3d cubic (similar to MCM-48\textsuperscript{27}) aggregate forms early in the precipitation process. We will use MCM-48 as shorthand notation for structures with Ia3d cubic symmetry in this chapter. They proposed that hexagonally patterned silica/surfactant aggregates grow on the facets of the cubic seed to create a particle with an MCM-48 core from which cylindrical pores emanate.\textsuperscript{25,26}

When we attempted to apply this hypothesis to materials synthesized using the cationic fluorinated surfactant 1H, 1H, 2H, 2H-perfluorodecylpyridinium chloride (HFDePC) as a pore template in the presence of ethanol and ammonia (chapter 7), we found a conflict. The synthesized material has an x-ray diffraction (XRD) pattern indicating a 2D hexagonal close packed (HCP) pore arrangement, and it consists of spherical particles with radially oriented pores.\textsuperscript{28} However, the core region observed by TEM is very small and shows no indication of cubic ordering. This is consistent with the behavior of the surfactant; HFDePC does not form an Ia3d cubic phase because of the stiffness of the fluorinated chains.\textsuperscript{29,30} We could not rule out the possibility that HFDePC assembles in a unique way, so here we address the following issues for the surfactant for which this radially oriented pore structures were originally discovered, cetyltrimethylammonium bromide (CTAB):

1. Is the MCM-48 core model applicable to all spherical silica particles with radial pores?

2. If the MCM-48 core model does not apply to all particles, what is actually at the center of these particles? Is it a single aggregate, a cluster of aggregates or nonporous silica?
3. Is there evidence for MCM-48 particles early in reaction that would serve as seeds? Whether the seeds exist or not, how are the formation of spherical particles and the development of pore structure related?

4. The MCM-48 core model implies that ethanol works as a cosurfactant to induce the structure transformation from hexagonal to cubic.\textsuperscript{31} However, ethanol is also known to serve as a co-solvent for cetyltrimethylammonium bromide (CTAB).\textsuperscript{32} What is the actual role of ethanol in this case, and how does it affect the pore size and pore structure?

In this chapter, we will address these questions by detailed characterization of intermediate and final products of tetraethoxysilane (TEOS) hydrolysis in solutions of water, ethanol, ammonia, and CTAB. As we will show, our conclusions do not support the seeded growth mechanism proposed by Van Tendeloo et al.\textsuperscript{25} We will propose an alternative hypothesis that radial pore orientation originates at the surface of malleable particles. This mechanism is more consistent with the established role of aggregation in Stöber particle synthesis. Also, while ammonia has been described as the morphology catalyst in the Stöber process,\textsuperscript{2} a polar solvent such as ethanol also plays an important role in forming spherical particles.\textsuperscript{33} The roles of ethanol in mesoporous silica synthesis have been in dispute for some time.\textsuperscript{31,32,34,35} Roles as both cosolvent and cosurfactant have been suggested.\textsuperscript{31,32,36,37} Our results will be shown to be consistent with roles as a low-dielectric solvent and as a cosolvent for CTAB. We will discuss how these roles influence pore order and particle morphology.

5.2. Experimental Section

Samples were prepared based on the procedure of Liu et al.\textsuperscript{31} The initial reactants had the molar ratios 1 tetraethoxysilane (TEOS): 0.3 CTAB: 11 NH\textsubscript{3}: x C\textsubscript{2}H\textsubscript{5}OH: 144 H\textsubscript{2}O with x = 0, 10, 20, 40, or 58. The products will be called SP1 through SP5 corresponding to the order from x=0 to x=58. Particles were formed by mixing all reagents in the reverse order listed. The TEOS was added slowly over 30 seconds. After aging the solutions for two hours, white powder precipitates were filtered and washed with deionized water. Dried samples were calcined at 500 °C for 4 hours or twice extracted with acidic ethanol (150 ml ethanol with 3 ml of 36.5 wt% aqueous HCl) to remove the surfactant.
X-ray diffraction (XRD) patterns were recorded on a Siemens 5000 diffractometer using Cu Kα radiation (λ = 0.15406 nm) and a graphite monochromator. Diffraction data were recorded at 2θ values between 1.8° and 7.0° with a step size of 0.02° and a scanning rate of 0.1 degrees/min. Transmission Electron Microscope (TEM) images were collected with a JEOL 2010F electron microscope operating at 200 kV. Solidified samples were dispersed in an acetone solution and then deposited on lacey carbon grids. Nitrogen sorption measurements were performed on a Micromeritics Tristar 3000 system. All samples were degassed at 150 °C for 4 hours under flowing nitrogen prior to measurement. The BJH method with a modified statistical film thickness equation was used to calculate the pore size distributions from the adsorption branch of the isotherms. Cylindrical pore shape was assumed for the pore size calculations.

In addition to the fully cured samples, a series of samples were prepared for TEM by cold drying, to investigate the development of particle morphology and pore structure. In this method, a lacey carbon grid was placed on a tissue and pre-cooled with liquid nitrogen. A drop of solution was quickly removed from a reacting mixture at a certain time and dropped onto the grid. The temperature of the grid was kept as low as possible while avoiding the formation of ice crystals. The solution was quickly cooled on the grid, and simultaneously solution was drawn away by the tissue. While the thinned layer of solution remaining on the grid was still cool, the grid was quickly blown dry with forced air at room temperature. The dried sample was examined by TEM within 4 hours.

5.3. Results and Discussion

A seeded growth mechanism for spherical particles with radial pores was proposed by Van Tendeloo et al.25,26 They observed both hexagonal and square projections of pore arrays in the center of the solid particles by TEM and concluded that these arrays are different projections of an MCM-48 core. Furthermore, consistent with the monomer addition mechanism of Matsoukas and Gulari,16,17 they proposed that radial pores form by epitaxial growth of cylindrical surfactant/silica aggregates from the facets of the core nuclei. Isotropic growth from MCM-48 cores also explains the spherical shape of the particles. However, four questions related this mechanism still need to be addressed, as
outlined in the introduction. The discussion of our results will be organized to address those issues sequentially.

5.3.1. Are MCM-48 cores necessary?

As discussed in the introduction, we observed radial pores without an MCM-48 core when the fluorinated surfactant HFDePC was used as a pore template. With the doubt raised by this observation, we started to look at the structure of CTAB-templated particles in detail. We reproduced the spherical silica particle (SSP) sample of Van Tendeloo et al. (which we call sample SP5), and examined the pore structure by TEM. We did not find evidence for MCM-48 cores in the particles that we examined. For example, a hexagonal pattern is clearly seen in the center area of the particle in Figure 5.1a. After tilting this particle by 10 degrees (Figure 5.1b), part of the hexagonal pattern has changed to a layered pattern which is consistent with a side view of cylindrical pores rather than an MCM-48 structure. The layers are arranged in random directions in the middle of the particle which indicates that the center of the particle contains a cluster of aggregates instead of a single aggregate. Otherwise, all of the layers should be oriented in one direction. Thus, we find that at least some of the particles that have radially oriented pores do not show evidence for an MCM-48 core.

A cluster of randomly oriented cylindrical aggregates such as at the center of the particle in Figure 5.1 can give rise to many types of Moiré patterns in TEM, including both hexagonal and square dot patterns. It is conceivable that the evidence for projections of a cubic core observed by Van Tendeloo et al. was actually due to overlapping of two or more layered cylinders patterns. Also, if several differently oriented layers overlap at the center of the particle, we may observe electron diffraction spots or rings that also resemble projections of the Ia3d cubic structure, as observed by Lebedev et al. Because TEM has a very large depth of field, it is difficult to rule out overlapping cylinder projections. Still, we have no specific reason to doubt the structure assignment of Van Tendeloo et al. We can only say that for a sample of the same composition, we found many particles that do not have the appropriate relationship of pore projections necessary to identify an MCM-48 core. Therefore, we conclude that in
both HFDePC and CTAB templated particles, an MCM-48 core is not necessary for the observation of radially oriented mesopores.

5.3.2. What is at the center of the particles?

Given that MCM-48 cores are not essential for radial pore formation, we address whether there is any special “core” structure with a density differing from a “shell” on the outside of the particle. An Ia3d cubic structure would be expected to have a different overall density than a HCP structure. Therefore, our SSP sample was studied with X-ray mapping by energy dispersive spectroscopy. The result is shown in Figure 5.2. Figure 5.2a shows a dark field scanning TEM (STEM) image and Figure 5.2b shows the map of silicon and oxygen along a slice through the center of the particle. The latter intensity reflects the density of the element Si or O integrated along the z-axis. If the particle is hollow, the elemental density should be lower in the middle than in the edges as observed for particles with hollow cores. If it is a uniform solid, each elemental density should show a smooth half-ellipse profile. If there is a core of a different density than the rest of the particle, there should be a density jump which is reflected in the X-ray mappings as a sharp change in the slope of the curves. The curves in Figure 5.2b conform to a smooth half-ellipse, showing that there is no special core of significantly higher or lower density than the rest of the particles with radial pores. We therefore doubt not just that there is an MCM-48 core, but that there is any type of special “core” structure in these particles. We suspect, as mentioned above, that the appearance of a core is more the result of observing several randomly oriented domains at the center of the particle, but only one orientation near the edges. Even in a perfectly radial structure, the illusion of a core can be created by seeing projections along the pore direction at the center of the particle, but across the pores near the edge of the particle.

5.3.3. Are cubic seeds formed early in reaction?

While we did not find universal evidence for the presence of cubic cores (or any other core structure) in particles with radially oriented mesopores in the the SP5 product, it is still remotely possible that in spite of extensive searching, we failed to find properly oriented cubic cores. Therefore, to test directly the hypothesis of the formation of cubic
seeds which act as cores, we examined cold-dried TEM samples withdrawn from the earliest possible time until radial pores could be observed. If cubic seeds are part of the process of forming particles with radial pores, we expect to be able to isolate small MCM-48 particles.

Generally, there are two methods that have been used for the preparation of quenched reacting colloidal samples for TEM. In the first, cryo-TEM, one vitrifies the sample in liquid ethane and then observes the sample at liquid nitrogen temperature. Soft, fragile assemblies such as fractal aggregates and surfactant aggregates can be captured and observed if this method is scrupulously applied. However, sample preparation is relatively slow (requiring liquid film thinning before vitrification), and samples prepared in this method can not withstand a high energy electron beam. Therefore, it would be difficult to trace surfactant-silica aggregate formation over a few dozen seconds with this method. The second method is the drying method. In this method, researchers normally remove a liquid sample and blot it with a tissue, and then let the sample dry in air. This method is very simple and the sample prepared is stable enough to observe surfactant/silica aggregates with a high energy beam. The disadvantage is that reaction may continue to happen as the sample is dried on the grid. Fragile structures may also collapse during drying. Bearing in mind these limitations, we adopt an improved drying method to reduce the possibility of continued silica reaction during sample preparation. In this method, samples are cooled down to the temperature just above the freezing point, to slow reactions without introducing ice crystals that may tear fragile colloidal aggregates. Simultaneous with the cooling, most of the solution is blotted with a tissue to thin the sample, to remove most of the solvent, and to distribute colloidal aggregates uniformly over the surface of the grid. After blotting, the rest of the solution is dried quickly with a fan at room temperature. The combination of cooling, blotting and forced convection during drying should reduce artifacts, but if anything, the dried samples should be more dense than the structures in solution. In particles withdrawn during the Stöber process, Bailey found that drying produced dense particles with fuzzy edges early in reaction due to the collapse of ramified, weakly condensed silica clusters that could be observed by cryo-TEM.
To search for cubic seed particles, we study samples withdrawn during a synthesis batch of sample SP5. Samples were removed every ten second until 90 seconds elapsed. The synthesis solution became turbid approximately 60 seconds after the addition of TEOS. The samples were cooled and dried as described above, and representative TEM images are shown in Figure 5.3-5.5. After 10-20 sec, only weakly condensed, amorphous silica/CTAB aggregates with ill-defined structures are observed (not shown). The images appear to be made up of small (4-8 nm) dark spots uniformly suspended in a grey matrix. At high magnification (Figure 5.3a), the dark spots are found to give fringe patterns indicating that they are molecular crystals. Because the silica does not crystallize under these conditions, we interpret these spots as being CTAB aggregates (micelles or microcrystals). The sizes of these clusters are consistent with the sizes of CTAB micelles observed in solution by cryo-TEM and dynamic light scattering. In Figure 5.3a, we can see that these clusters are suspended in an amorphous matrix, most likely of silica.

After 50 sec of reaction, more distinct particles with rough edges are observed (Figure 5.3b). The structures of these particles are similar to the structures observed in dried Stöber samples early in reaction by Bailey et al. The appearance of these particles may be due to the collapse of the weak condensed silica/surfactant aggregates with ramified structures. From statistical analysis of a set of randomly selected particles, the size of the aggregates is around 50 nm and the standard deviation of the sample is 15 nm. At higher magnification (not shown), CTAB micelles are still observed throughout the particles, which show no sign of any long-range order.

After 60 sec of reaction, a new stage begins which is marked by the onset of turbidity. At this point, a bimodal distribution of particles is observed in the dried TEM sample (Figure 5.4a). The smaller particles are 24 ± 4 nm in diameter, and the large ones are 90 ± 23 nm. The smooth edges of the majority of the particles suggest that they did not collapse during the drying process of sample preparation. If they were, rough edges should be observed. However, some rough particles are still rarely observed, and their raspberry-like appearance suggests that large particles form by aggregation of several smaller clusters. One of the particles indicating the aggregation mechanism is shown in the inset of Figure 5.4a. Note that although spherical particles begin to appear that this
time, with dimensions comparable to the final particle size, no ordered surfactant aggregates can be found in any of the particles.

At 70 seconds, the sample consists mainly of large spherical particles with diameters in the range of 350 ± 30 nm (Figure 5.4b). A smaller number of small (41 ± 7 nm) particles are also present, but they also have smooth edges (inset of Figure 5.4b). CTAB micelles are still present, but now they appear to coat the particles (the dark spots in the inset of Figure 5.4b). The coating of micelles probably was not deposited during drying, because if it were, we would anticipate a uniform coating of the crystals all over the grid, which is not observed. These crystals indicate that the surfactant micelles might be attracted to surround the silica/surfactant particles in the liquid solution. This is reasonable since the silica/surfactant particles in solution are expected to be negatively charged because of the uncondensed Si-O\(^-\) groups. These negatively charged groups should attract the positive charged CTA\(^+\) micelles to surround the particles. Also at 70 sec, ordered patterns start to be apparent for some of the particles (although they are not shown due to poor contrast). This is consistent with the findings in acidic conditions and in acid-quenched NaOH solutions of initially amorphous silica/surfactant aggregates that form ordered micelle patterns as the particles age.\(^{13}\)

Ordered patterns were clearly visible in many particles for the sample collected after 90 sec. Figure 5.5a shows a particle with peanut shape and stripe features along its edge. This particle is not representative of the particle shapes in this sample; many spherical particles were also observed in samples removed and dried at this time. However, there are also many particles with shapes, such as this peanut shape, that appear to have formed by aggregation of two or more spherical particles. If the mechanism were nucleation and growth by monomer addition, then all particles would be expected to be spherical since the rate of growth should be the same in all directions. The stripes at the edges of the particles are also very interesting. They are all perpendicular to the edge. A similar pore structure was also identified in the calcined sample SP5a obtained by adding the TEOS precursor to the synthesis solution all at once and aging for two hours. Figure 5.5b shows a peanut-shaped particle that was isolated from this sample, which has mesopore channels arranged perpendicular to its edge. This calcined sample also contains many spherical particles with radially oriented pores. This suggests that during the process of
aggregation and particle reformation, the micelles are able to reorient such that they always stay perpendicular to the edges of the particles. This would be very difficult to explain in terms of an Ostwald ripening mechanism or a monomer addition mechanism, and we instead propose that the “large” (>100 nm) particles formed at the onset of turbidity are still liquid-like. In fact, they are disordered immediately after precipitation and ordered structures form only in the concentrated silicate/surfactant environment of these precipitated particles. We find no evidence for any MCM-48 cubic silica particles prior to or after the formation of the radially oriented micelles.

Moreover, particle size distribution of the samples collected at 60, 70, 90 seconds have two distinct maxima: one ≥ 100 nm and the other < 100 nm. There are few particles with intermediate sizes. The smaller particles may come from the collapse of the ramified weak dense structures during the drying process as suggested by Bailey et al.\textsuperscript{20} Because small particles are always present, they must be continuously generated by nucleation of small silica/surfactant clusters. However, it does not appear that smaller particles simply grow by monomer addition after the collapse of the low-density clusters. If they did, a continuous distribution of particle sizes should be observed. Instead, these clusters must aggregate together to form denser and larger particles, or aggregate with existing large, dense particles. The absence of particles with intermediate sizes supports the importance of aggregation. Preferential aggregation of small particles with large ones is predicted by DLVO theory, and is consistent with previous observations of the Stöber process.\textsuperscript{23}

The mechanism of the Stöber process with a cationic surfactant template as observed by TEM is summarized in Scheme 5.1 and can be described as follows. At first, silica/surfactant clusters form and may be weakly connected into low-density ramified aggregates. These aggregates become larger and denser as silica species continue to be generated by hydrolysis. When a large number of aggregates of sufficient size is present in solution, they become colloidally unstable and suddenly aggregate together to form large denser spherical particles and the solution becomes turbid. The negatively charged particles may continue to attract positively charged CTA\textsuperscript{+} micelles which surround the particles, and as small clusters continue to nucleate, they may add to the surface of these particles. After these large spherical particles have formed, the surfactants organize into
cylindrical micelles and form a close-packed layer aligned perpendicular to the outer edge of the particle. As particles aggregate together, and as they continue to grow, this perpendicular alignment is maintained. When the particles are still soft, this alignment should be thermodynamically driven by the preferential orientation of the micelles at the interface. The precise reason for this orientation is not clear, but it may be due to the interface between the silica/surfactant phase and the mixed ethanol/water solvent being equally attractive towards polar and nonpolar species. Interfaces that interact equally with polar or nonpolar species have been found in Monte Carlo simulations to induce perpendicular alignment of nonionic surfactant mesophases. It is possible that the particles can then continue to grow by addition of new primary particles, by epitaxial addition to the existing radial surfactant/silica aggregates. This suggests that if the particles vitrify too quickly, it may not be possible for the micelles to adopt their preferred orientation normal to the interface, which explains why these radial structures are not always seen.

5.3.4. What is the role of ethanol in determining pore structure and orientation?

Part of the explanation for the feasibility of an MCM-48 core in silica spheres with radial pores was that, by acting as a cosurfactant, ethanol induces a hexagonal-to-cubic transformation, leading to the cubic seeds from which radii emanate. Finding little support above for the necessity of an MCM-48 core in radially oriented silica particles, we also are forced to question the role of ethanol as a cosurfactant. There is little support for this idea in the surface science literature, so we explore the role of ethanol more thoroughly here.

In the materials synthesis literature, the role of ethanol is controversial. Roles as both cosolvent and cosurfactant for CTAB have been suggested by researchers making mesoporous silica. If ethanol works as cosurfactant, it has been suggested that it will swell the palisade layer and increase the diameter of the micelles (and therefore of the pores in the material). If it acts as cosolvent, it will reduce the micelle (pore) sizes by decreasing the aggregation number. In either case, the change of micelle size should be reflected in the pore size of the product. To examine this change, we
reproduced the series of ethanol-containing samples of Liu et al. which are prepared with all parameters identical, but with increasing ethanol in the series of samples SP1-SP5.

The XRD patterns of the calcined samples SP1, SP3, and SP5 are similar to what was reported by Liu et al as samples E0, E20, and E58. Samples SP1 and SP2 display three peaks indexed to a 2D HCP structure (Figure 5.6a and 5.7a, respectively). Sample SP3 displays an Ia3d cubic structure, perhaps mixed with a minority of HCP structure. This sample was difficult to reproduce. The cubic feature might be lost after removing of the surfactant. Sample SP5 has a 2D HCP pattern with broad peaks. However, sample SP4 is different than the (supposedly identical) sample E40 of Liu et al. Both the as-synthesized and calcined XRD patterns (Figure 5.9a) show that SP4 consists of a mixture of cubic and hexagonal structures, as shown by a weak shoulder to the right of the (100) reflection of the 2D HCP structure. Hexagonal patterns were confirmed for both as-synthesized and extracted samples of SP5 (Figure 5.10). As the ethanol content increases, the pore structure in the SP series transforms from hexagonal to cubic and back to hexagonal. No cubic-lamellar structure such as the one described by Liu et al was identified between the cubic (SP3) and hexagonal (SP5) structures. In fact, we saw some deterioration of the cubic structure in sample SP4 in favor of the HCP structure upon calcination, rather than loss of a “lamellar” structure in favor of a cubic structure. The difference between our samples and those of Liu et al. may be due to subtle differences in the aging and drying steps (which were not fully described in the paper of Liu et al.).

TEM images were collected for this series to confirm the conclusions from XRD patterns and to trace the transformation of the particle morphology. With increasing ethanol, we observe not only a pore structure transformation from hexagonal to cubic to hexagonal, but also a particle morphology change from irregular (Figure 5.6b) to elongated (Figure 5.7b) to spherical-like with facets (Figure 5.8b) to spherical (Figure 5.9b and Figure 5.1). SP1 consists only of rough irregular particles (Figure 5.6b). SP2 is made up of elongated cylindrical particles with cylindrical pores running parallel to the main axis of the particles (previously described as a tube-within-a-tube structure, Figure 5.7b). SP3 contains both spherical and (American) football-like particles (Figure 5.8b). Many of the particles are faceted, and projections corresponding to views of an Ia3d
cubic structure are evident (Figure 5.8c). Both SP4 (Figure 5.9b) and SP5 (Figure 5.1) consist of almost perfectly spherical, uniform particles. Some of the pores in SP4 are arranged radially, while others are arranged randomly. The structure of SP4 again casts doubt on the assumption of the need for an MCM-48 core to explain the formation of radial pores, even though the XRD pattern of SP4 is very similar to what has been described by Van Tendeloo et al. for an ideal sample with radial pores.\textsuperscript{25} The TEM images of this sample are more consistent with a mixed polycrystalline structure than with MCM-48 cores and HCP shells. Fig 5.9b shows both hexagonal and square pore arrays, neither located at the center of the particle. It appears that a mixture of cubic and hexagonal domains forms during the precipitation process, but not that one phase serves as a nucleus for the other.

Figure 5.11 shows a comparison of the pore size distributions of samples SP1, SP2, SP4, and SP5, all of which have HCP pore structures. The pore structure in SP1 was not very stable. The pore size was found to decrease a little bit for some samples depending on the calcinating conditions. This indicates that the condensation extent of the as-synthesized SP1 was relatively weak. This is consistent with the observation that the hexagonal pore structure collapsed after extracting CTAB with acidic ethanol (data not shown). The pore sizes of samples SP2, SP4, and SP5 are all the same, and are slightly smaller than the pore size of SP1. This change is most consistent with ethanol acting as a cosolvent for CTAB in this case. The trend is not consistent with the cosurfactant role proposed by Liu et al.\textsuperscript{31}

The observations for the SP1-5 series can be better explained in terms of ethanol’s roles as low-dielectric solvent and as a cosolvent for CTAB. A limited amount of ethanol (up to ~2.4 mol/L) decreases the critical micelle concentration (cmc) of CTAB.\textsuperscript{44} However, short chain alcohols such as ethanol and propanol do not act as true cosurfactants when they decrease the CMC. A study of a series of alkyltrimethylammonium surfactants shows that propanol does not change the free energy of micellization per alkylene, which suggests that the propanol is completely solubilized in the palisade region of the micelle.\textsuperscript{44} NMR relaxation studies of CTAB/ethanol/water mixtures support this conclusion.\textsuperscript{45} Also, the ionization degree of the micelles increases as ethanol or propanol is added, so the micelle aggregation number
decreases. The interpretation offered by Zana et al. is that short chain alcohols at low concentration reside in the palisade layer where they decrease the dielectric constant for interactions between headgroups and allow surfactants to leave the micelles. The micelles shrink, but the ionization degree increases. Therefore, within the continuous (solvent) phase, bromide counterions are better dissociated than in aqueous solution.

At higher concentrations (above 2.4 mol/L), the cmc increases as ethanol is added. This suggests that ethanol acts as a surfactant cosolvent when a large amount is present. Because the solubility of ethanol in alkanes is small, it is unlikely that a significant amount of ethanol enters into the hydrophobic core of the micelles. Instead, the ethanol decreases the hydrophobic force that drives micelle formation, which we expect to first decrease the size of the micelles and eventually to decrease their number. At the same time, the dielectric constant of the continuous solvent decreases as ethanol is added, which should increase the extent of counterion association. This should lead to a decrease in the surface area per surfactant in the aggregates, and therefore to an increase in the packing parameter. This is expected to favor low-curvature aggregates: first cylindrical micelles, and then bilayer structures such as the Ia3d cubic phase.

These observations of the effects of ethanol on micelle shape are consistent with what has been observed for concentrated CTAB mesophases as well. As ethanol is added to a hexagonal CTAB mesophase, the unit cell size decreases due a decrease in the surfactant aggregation number. However, at high concentration, the cosolvent properties of ethanol cause the destruction of long-range ordering, and only micellar solutions are observed.

Taking into account all of the observations of the effects of ethanol addition to aqueous CTAB solutions, we can explain the trends that are observed in materials synthesis. The sample with no ethanol present initially (SP1) actually contains a significant amount of ethanol due to hydrolysis. At least one mole is generated per mole of TEOS (corresponding to 0.33 mol/L ethanol) and as much as 1.3 mol/L may be present by the end of the reaction. These concentrations are in the range where ethanol decreases the cmc by partitioning into the palisade layer of the micelles, at the same time increasing the dissociation of counterions from the micelle surface. Because of good dissociation, the silicate ions generated by hydrolysis remain soluble in solution for a relatively long
time, and they co-assemble with the micelles after a significant amount of condensation has occurred. The co-assembly leads to a hexagonal phase, but with randomly oriented domains and irregular particle morphology.

The first sample with added ethanol (SP2) contains almost 3 mol/L of ethanol at the beginning, and may contain as much as 3.9 mol/L by the end of the hydrolysis reaction. This is well above the concentration where ethanol begins to act as a cosolvent, and to increase the cmc of CTAB. We expect the dielectric constant of the mixed solvent to have decreased in this solution, promoting more ion association between the headgroups and counterions. This means that the headgroups will not be as charged, and therefore better able to assemble into low-curvature structures (cylindrical micelles). The high degree of association should also mean that the silicate species begin to interact with the micelles sooner. This may slow their rate of condensation, and allow long, well-organized close-packed micelle structures to form, which result in elongated particles. In spite of a larger degree of silica-surfactant association, the silica: surfactant ratio should decrease because bromide is preferentially associated with CTAB compared to small silica species. The pore size of the product decreases, which is consistent with the lower aggregation numbers observed for CTAB micelles and hexagonal phases as ethanol is added.

With more ethanol (SP3), we expect the micelle aggregation number to decrease, and the degree of ion association to increase. This decreases the driving force for co-assembly of the silicates with surfactants, and therefore should lower the silica: surfactant ratio in the product. This decreases the headgroup area in the resulting product, which explains the transition from the 2D HCP to the Ia3d cubic structure.

When still more ethanol is added (samples SP4 and SP5), a transition is seen back from the Ia3d cubic structure to a 2D HCP structure. This is difficult to explain in terms of the known cosolvent and dielectric effects of ethanol. The only factor that could contribute to this transition is that the number of micelles may be starting to decline enough that the silica: surfactant ratio in the co-assembled product starts to increase again compared to sample SP3. However, the TEM observation of dried samples discussed in the last section suggests that phase separation happens early in the particle synthesis process. Because the particles are able to minimize their interfacial area by adopting a
spherical morphology, the process may initially be liquid-liquid phase separation rather than precipitation of a solid. Partitioning of species between solvent-rich and the silica/surfactant-rich phase may influence the surfactant microphase behavior. The silica-surfactant phase that precipitates from these solutions should be poor in ethanol, which helps to explain the reason for the regressive phase transition. Another important factor is that as the hydrophobic driving force for CTAB micellization decreases due to ethanol addition. Ammonium may become a more competitive counterion for the silica anions, which would increase the silica: surfactant ratio as well. Predicting the phase behavior of such a complex mix of dynamically evolving, hydrogen bonding and charged species is a difficult thermodynamic problem, but an increase in the silica: surfactant ratio due to the partitioning of species between solvent and silica/surfactant phases is a plausible explanation for the change from Ia3d cubic to 2D HCP structure.

While the precise nature of the transition from the cubic to the hexagonal phase can only be addressed by a better understanding of silica-surfactant-solvent phase behavior, we currently attribute our observations to the roles of ethanol as CTAB cosolvent and low-dielectric constant solvent rather than as a cosurfactant. Scheme 5.2 summarizes the implications of these roles, as described above. The observation of a similar effect of methanol on the pore structure transitions (from hexagonal to cubic to hexagonal)\textsuperscript{31} also supports this interpretation.

5.4. Conclusions

In this chapter, we directly investigated the mechanism of forming silica spherical particles with radially orientated mesopores. We examined both intermediate and final products formed during precipitation of silica and CTAB from solutions of ethanol, water and ammonia. We found no support for the hypothesis that Ia3d cubic particles form initially and act as seeds for the growth of radially oriented pores. We proposed an alternative explanation for the formation of these spherical particles that is more consistent with prior investigations of the Stöber process. Our hypothesis, supported by products isolated during the particle synthesis, is that particles form by nucleation of silica/surfactant clusters which aggregate into spherical particles. The radial orientation of the pores emerges due to the alignment of CTAB micelles at the interface between the
solvent and malleable silica/surfactant aggregates. We also found the roles of ethanol to be most consistent with being a CTAB cosolvent and a low dielectric constant medium. The transform of the pore structure from hexagonal to cubic and back to hexagonal with increasing ethanol content can be related to changes in the silica: surfactant ratio. Ethanol also influences the particle morphology by influencing the relative rates of precipitation, condensation and co-assembly of the particles. By promoting association between less condensed silicate species and surfactants, ethanol induces a morphological transformation from irregular particles to weakly faceted particles (elongated or cubic) to spherical particles. We hope that these hypotheses will inspire further theoretical and in-situ experimental investigations of the synthesis of these materials.

5.5. References
Figure 5.1. TEM images of the same particle from sample SP5 tilted (a) at 0 degrees and (b) at 10 degrees. The same region is boxed in both images.
Figure 5.2. Density profiles of a particle from sample SP5: (a) Dark-field STEM and (b) EDS map of silicon and oxygen across along the slide indicated by the dashed line.
Figure 5.3. TEM images of cold-dried samples withdrawn at early stages of the synthesis of sample SP5: after (a) 10 seconds and (b) 50 seconds.
Figure 5.4. TEM images of cold-dried samples withdrawn at intermediate stages of the synthesis of sample SP5: after (c) 60 seconds and (d) 70 seconds.
Figure 5.5. TEM images of anisotropic particles found in the SP5 synthesis solution (a) cold-dried after 90 seconds and (b) after aging for 2 hours and calcining. Arrows indicate the orientation of micelles at the interface of the particles.
Figure 5.6. Characterization of sample SP1: (a) XRD patterns of as-synthesized and calcined materials; (b) low magnification TEM image of the calcined sample; and (c) high magnification TEM image of the calcined sample.
Figure 5.7. Characterization of sample SP2: (a) XRD patterns of as-synthesized and calcined materials and (b) TEM image of the calcined sample.
Figure 5.8. Characterization of sample SP3: (a) XRD patterns of as-synthesized and calcined materials; (b) low magnification TEM image of the calcined sample; and (c) high magnification of the calcined sample (the square outlines a square close-packed region).
Figure 5.9. Characterization of sample SP4: (a) XRD patterns of as-synthesized and calcined materials and (b) TEM image of the calcined sample. The hexagon outlines a hexagonal close-packed region and the square a square close-packed region (associated with an Ia3d cubic crystallite).
Figure 5.10. XRD patterns of as-synthesized and calcined materials of SP5.

Figure 5.11. BJH pore size distributions of samples SP1, SP2, SP4 and SP5 from nitrogen adsorption isotherms.
Scheme 5.1. The proposed mechanism of forming spherical silica with radial mesopores with a high concentration of ethanol. Nucleation begins with small disordered clusters which aggregate into large particles, followed by micelle organization at the particle surface.
Scheme 5.2. Proposed local effect of ethanol on the silicon: surfactant ratio and the micelle structure: a) with only the ethanol (ellipsoids) generated by hydrolysis, b) with a small amount of added ethanol, c) with moderate added ethanol, and d) with a large amount of added ethanol. Headgroup and silicate charges are indicated. Absence of a charge indicates an uncharged species or counterion association.
Chapter 6. Dual Latex/Surfactant Templating of Hollow Spherical Silica Particles with Ordered Mesoporous Shells


6.1. Introduction

Hollow spherical particles with mesoporous shells are of growing interest for potential applications in drug delivery, controlled release, adsorption and catalysis. Such particles have been synthesized by using surfactants or block copolymers in the presence of emulsions or vesicles. Emulsified droplets of nonpolar fluids such as mesitylene, trimethylbenzene or kerosene work as templates for large voids while the surfactants or copolymers co-assemble with silica to create mesopores. Emulsions or vesicles have also been used to create hollow particles using bilayer-forming surfactants, sonicated cetyltrimethylammonium bromide (CTAB) solutions, or dilution and neutralization procedures. However, these procedures require very strict, time-sequenced control of the synthetic conditions and produce particles with a wide particle size distribution. Also, the hollow core size and shell characteristics (thickness and pore size) cannot easily and independently be controlled by these techniques.

Compared to liquid emulsions, polystyrene lattices are of well-defined, stable size and are widely available commercially. Latex spheres have been used before as pore templates for macroporous materials and in combination with surfactants to make dual-templated macro/mesoporous materials. However, lattices have primarily been used to generate ordered arrays of macropores within a monolith. There has been one report by Lu et al. of the synthesis of hollow spherical silica particles with a latex template, but the shells of the particles were microporous. With this approach, the hollow core size can be easily controlled by selecting latices of different sizes. The shell thickness can be adjusted by adjusting the silica to latex ratio. However, it is difficult to make ordered mesoporous shells by simply adding surfactants to the recipe of Lu et al. We were unable to produce particles with ordered mesoporous shells by using this method. This may not be surprising, as the method calls for a large amount of 2-propanol. Studies of
CTAB-templated particle synthesis at room temperature have shown that propanol inhibits the development of long-range order.\textsuperscript{13,14} An alternative approach may be to use methanol or ethanol as the cosolvent to produce hollow spherical silica with mesoporous shells. However, we found it difficult in our preliminary efforts to control the process well enough to make only hollow spherical particles. Most of the samples synthesized consisted of two kinds of spherical particles, some hollow and many solid mesoporous spherical particles. The likely reason is that the interactions among the silica/surfactant aggregates were strong enough to cause nucleation of new particles faster than the aggregates added to the surfaces of existing latex particles.

In this chapter, we report an alternative procedure to make hollow spherical particles with hexagonally ordered mesoporous shells by using unmodified polystyrene latices and CTAB as dual templates in a concentrated aqueous ammonia solution. The high concentration of ammonia encourages aggregation between small particles (CTAB/silica aggregates) and large particles (silica-coated latex), allowing us to prepare a sample consisting primarily of hollow particles with mesoporous shells. This simple, one-step synthetic procedure allows independent control of the core size, shell thickness and mesopore size in hollow mesoporous particles.

6.2. Experimental Section

6.2.1. Materials. Aqueous polystyrene latex microspheres with plain surface with diameters of 0.0489 $\mu$m (2.57 wt\%, 3.74 x 10\textsuperscript{14} particles/ml), 0.202 $\mu$m (2.62 wt\%, 5.95 x10\textsuperscript{12} particles/ml), 0.356 $\mu$m (2.7 wt\%, 1.14 x 10\textsuperscript{12} particles/ml), and 0.535 $\mu$m (2.79 wt\%, 4.06 x 10\textsuperscript{11} particles/ml) were purchased from Polysciences, Inc (Warrington, PA). Aqueous latex microspheres containing primary amine surface functional groups (0.500 $\mu$m, 2.50 wt\%, 3.64 x 10\textsuperscript{11} particles/ml) was also bought from Polysciences, Tetraethoxysilane (TEOS) (98\%) and CTAB (>99\%) were purchased from Sigma-Aldrich. Aqueous ammonia (29 wt\% NH\textsubscript{3}) was from Merck. 2-Propanol (HPLC grade) was bought from Fisher Scientific.

6.2.2. Synthesis. The base-case sample was synthesized in concentrated aqueous ammonia at room temperature. For this sample, 0.90 g aqueous polystyrene latex (0.35 $\mu$m), 0.09 g CTAB, and 9.0 g aqueous ammonia were mixed together with vigorous
stirring. After 30 min, 0.46 g tetraethoxysilane was added slowly. The solution was filtered after being aged at room temperature for 2 hours with stirring. The as-synthesized sample was dried in air and then calcined in air at 550°C for 4 h.

Several series of samples were prepared to explore the effects of process parameters. The T-series explores the effects of the CTAB : latex ratio. Samples T1, T2, T3, T4, T5, and T6 were prepared in the same way as the base case, but with CTAB: latex mass ratios of 0.09 : 0, 0.09 : 0.45, 0.09 : 0.9, 0.045 : 0.9, 0.009 : 0.9, and 0 : 0.9 respectively. Sample T3 is as the same as the base case. The latex microspheres in sample T6 were replaced with the amino microspheres (0.500 µm). The prepared sample is called T7. Samples A1, A2, and A3 were prepared to investigate the effect of ammonia. The only difference among these samples was that some of the aqueous ammonia was replaced with deionized water. The mass ratios of aqueous ammonia to water were 0.5:8.5, 4.5:4.5, and 9:0, respectively. Sample A3 is the same as the base case. The C-series illustrates the effect of the size of the latex microspheres. Samples C1, C2, C3, and C4 were prepared in the same way as the base case, but the latex microsphere diameters (reported by the supplier) were 0.0489 µm, 0.202 µm, 0.35 µm, and 0.535 µm, respectively. C3 is the same as the base case. All samples were collected by filtering except samples T6 and T7. Both of them were collected by centrifuging.

A drop of the aging solution of the base-case sample was taken onto a lacey carbon grid to observe the aggregation of particles in solution. To investigate if these aggregates can be broken into individual particles, the calcined base case sample was ultrasonicated for twenty minutes in 2-propanol solution. A drop of the dispersed solution was observed under TEM.

6.2.3. Characterization. Powder X-ray diffraction patterns were recorded in the Bragg-Brentano geometry using a Siemens 5000 diffractometer, with a step size of 0.02° and a scanning speed of 0.2° /min. Cu-Kα radiation and a graphite monochromator were used. The transmission electron micrographs were taken with a JEOL 2010F instrument. Samples were prepared for TEM by suspending the calcined powders on lacey carbon grids. Nitrogen sorption was measured with a Micromeritics Tristar 3000. The samples were degassed under flowing nitrogen at 120 °C for 4 hours before the measurement.
Samples for FTIR analysis were ground finely, mixed with KBr at a concentration of 1 wt% of the sample, and pressed into translucent pellets. Spectra were collected with a ThermoNicolet Nexus 470 spectrometer.

6.3. Results and Discussion

6.3.1 Synthesis and characterization of hollow particles with ordered mesoporous shells

The base case sample was synthesized by room temperature precipitation (as described above) and recovered by vacuum filtration. This filtering procedure is often used to recover surfactant-templated sol-gel materials, in spite of the submicron particle size. A yield as high as 75 wt% could be achieved by capturing aggregates on the filter paper. The rest of the silica was lost as soluble silicates and individual submicron particles. The yield was similar for the product made without latex (sample T1, discussed more below). The removal of templates in the base case sample was confirmed by FTIR. The spectrum of the calcined sample is the same as that of the fumed silica (see Chapter 8), indicating the complete removal of templates.

A representative low-magnification TEM image (Figure 6.1) shows that the calcined base case sample is composed of uniformly sized, hollow, spherical particles. A small fraction of the sample also consists of small solid nanoparticles such as the one indicated in Figure 6.1 and irregular silica sheets (not shown). Low-magnification TEM images and scanning transmission electron micrographs (Figure 6.2a) show that each particle has one hollow core. The diameter of the core is around 0.35 $\mu$m, which is consistent with the average size of the latex reported by the supplier. All of the hollow cores appear intact, which indicates that the sample is stable during calcination. The shells of the particles are $124 \pm 10$ nm thick, and contain 2D hexagonal close packed (HCP) cylindrical mesopores, as shown in the high magnification TEM image (Figure 6.2b). Based on the shell thickness, the density of the mesoporous silica in the shells is estimated to be $1.4 \pm 0.2$ g/cm$^3$. This density is reasonable considering that the density of amorphous silica is 2.2 g/cm$^3$. The white arrows indicate regions, near the edges of the particles, where hexagonal patterns from direct views along the pores are visible. In the center of the particles, far from the walls, stripe patterns are seen, as illustrated in the upper left corner of Figure 6.2. We attribute these stripes to an edge-on view of the cylindrical channels of
the HCP structure. The stripe patterns at the center of each particle and HCP patterns near the edges show that the mesopores in the shells lie parallel to the particle surfaces. This orientation may result from direct addition of silica-encapsulated cylindrical CTAB micelles\textsuperscript{15} to the particle surface. An alternative explanation is that disordered surfactant/silica aggregates first add to the latex surface, and then micelles grow and orient parallel to the latex and solution interfaces.\textsuperscript{16}

Aggregates are observed among most of the hollow particles (Figure 6.1). To investigate if the aggregation happens before or after filtering, a drop of the solution was taken onto a lacey carbon grid and observed under TEM. Large aggregates of hollow particles were observed (not shown). This shows that the aggregation happens in the solution. This is consistent with the filtering method that we used to collect the as-synthesized sample. All particles would pass through the filtering paper if they were not aggregated in the solution. When the calcined sample was ultrasonically treated in 2-propanol solution, lots of small aggregates of hollow particles were observed under TEM (Figure 6.3). These small aggregates were formed by several hollow particles. This shows that large aggregates (Figure 6.3) can be broken into small aggregates even individual particles has not been observed.

The x-ray diffraction pattern of the calcined base case sample (Figure 6.4) has only one sharp but broad reflection corresponding to a d-spacing of 3.9 nm, showing that the sample has a uniform, ordered pore structure. However, the (110) and (200) reflections that would be expected for hexagonal close-packed cylindrical pores are not observed. The most likely reason for the absence of higher-order reflections is that the ordered mesopores are found in thin, curved shells lacking large diffraction domains.

Nitrogen adsorption isotherms of the calcined sample are shown in Figure 6.5. It is a type IV isotherm with an inflection indicating capillary condensation, and no hysteresis. The pore size distribution was calculated with the modified BJH method as described by Kruk et al.\textsuperscript{17} The sample has a narrow mesopore size distribution with a peak diameter of 2.7 nm. This pore size is smaller than the pore size normally obtained with CTAB as the template in MCM-41 materials.\textsuperscript{18} The pore wall thickness is 1.8 nm based on the d spacing (3.9 nm) and the pore size (2.7 nm). This pore wall thickness is much higher than the wall thickness assumed in a typical MCM-41 material (\texttextsuperscript{19} 1.0 nm). α\textsubscript{s}-plot was
plotted for this sample (Figure 6.6). The total surface area is 481 m$^2$/g and the mesopore volume is 0.32 cm$^3$/g. The relatively low surface area and pore volume compared to MCM-41 materials$^{18,19}$ may be due to the thick pore wall of this material (1.9 nm). Based on this pore volume, the density of the mesoporous silica shells is calculated to be $[1/\rho_{\text{SiO}_2} + V_{\text{pore}}]^{-1} = 1.3$ g/cm$^3$. This is consistent with the density calculated from the particle dimensions observed by TEM.

**6.3.2 Effect of the CTAB/latex ratio**

A series of six samples was prepared to investigate the effect of the CTAB:latex ratio. The mass ratios of CTAB: latex solution were 0.09:0, 0.09:0.45, 0.09:0.9, 0.045:0.9, 0.009:0.9 and 0:0.9 for samples T1 through T6, respectively. Sample T3 is the same as the base case discussed in the previous section.

White particles were observed immediately after adding TEOS in samples T1 through T5. These particles could be easily recovered by filtration. Product yield as high as 75 wt% could be obtained for samples T1 through T4. The yield of product for T5 was only 27 wt%. A stable colloid solution was obtained for sample T6. No product was recovered by filtering. This sample was centrifuged for several hours to obtain part of the product in low yield. Compared to the other sample, the low yields of sample T5 and T6 suggest that CTAB enhances the extent of the condensation reaction. This is consistent with the role of CTAB as a template in the sol-gel process. A cationic surfactant such as CTAB co-assembles with hydrolyzed silica species to form aggregates, thus increasing the local density of the silica and enhancing the condensation rate.$^{20}$

Representative TEM images of the T-series samples are shown in Figure 6.7 and Figure 6.8. For sample T1, only irregular mesoporous particles with HCP cylindrical pore patterns (and no macropores) are identified. With the addition of a certain amount of latex (sample T2), hollow spherical particles as well as large mesoporous particles (not shown) are observed in the sample. All of the hollow spherical particles have HCP ordered mesoporous shells 140 ± 20 nm thick. The mesopores in both the hollow particles and the large solid particles are obviously created by CTAB micelles and the hollow cores are consistent with the latex size. For samples T3 through T5, enough latex is present that only a few small solid particles are observed. Most of the particles in these
samples are hollow spherical particles. As the amount of CTAB decreases, the ordering of the mesoporous shells became weaker (for instance comparing T4 to T5). The thickness of the shells of hollow particles in this series decrease from 124 ± 10 nm (sample T3) to 108 ± 13 nm (T4) to 55 ± 6 nm (T5). The decrease in shell thickness is slight in going from sample T3 to T4, but it is dramatic on going from T4 to T5. This is consistent with the dramatic drop in product yield after filtering between samples T4 and T5. The drop in the shell thickness and the yield at this point indicates that CTAB-silica aggregates are the species that add to the surface of the latex particles to form these hierarchical hollow particles.

In sample T6 (made entirely without CTAB), most of the particles are solid spherical nanoparticles (<100 nm in diameter), and only a few macroporous hollow particles with broken shells can be identified (Figure 6.8). The nanoparticles are similar to the types of particles that can be formed by the Stöber process, and they form independently of the latex particles. The hollow particles have very thin shells and are nonporous or microporous. The presence of few hollow particles and the small yield of sample T6 demonstrate that the attraction between silica and the latex particles is small. The small negative charge of the unmodified microspheres would be expected to limit their interactions with negatively charged silica species. Once a thin coating of silica has been deposited, the negative charge of the particles increases, inhibiting growth of the coating. One extra sample was prepared to show that even the interaction between positively charged amine-modified microspheres and the silica species is too weak to induce the level of precipitation observed in the CTAB-containing samples. This sample was prepared with amine-modified latex microspheres (0.50 um). One representative TEM image of this sample is shown in Figure 6.9. No hollow particles are identified. All particles observed are solid particles, which are obviously synthesized without the incorporation of latex microspheres.

Isotherms and pore size distributions of the T-series samples are compared in Figure 6.10. Samples T1 through T4 have sharp inflections in the isotherms. As the concentration of latex microspheres increases from T1 to T3, the pore size decreases. This is consistent with the observation of other researchers.11 As the CTAB concentration decreases with a fixed amount of latex (samples T3 to T5), the pore size broadens.
considerably. The lack of a narrow mesopore size distribution for sample T5 is consistent with the lack of long range pore ordering found by TEM.

This series of samples shows that the presence of CTAB/silica aggregates is necessary to form spherical hollow particles with mesoporous shells. The shell thickness can be controlled to some extent by changing the CTAB : latex ratio, but there is an optimal ratio favoring hollow particles with mesoporous shells. The presence of excess CTAB can result in the nucleation of new CTAB-silica aggregates that become mesoporous particles without hollow cores. Too little CTAB allows solid silica nanoparticles to form independent of the latex spheres.

6.3.3. Effect of ammonia concentration

In the Stöber process, ammonia has been described as a morphology catalyst for the formation of nonporous spherical particles.\(^{21}\) It helps to form spherical particles. The effect of ammonia concentration for CTAB/latex templated particles was investigated by preparing samples A1 through A3 with different amount of ammonia. The total volume of each of the solution was kept the same by adding deionized ultrafiltered water. All three samples were synthesized with the same total mass (9 g) of aqueous ammonia, but the concentrations of ammonia used to prepare the samples were 1.6 %, 14.5%, and 29%, respectively.

TEM images of samples A1 and A2 are shown in Figure 6.11. Sample A3 is the base case discussed above. Sample A1 is composed only of large irregular particles. Hollow spherical particles with very thin shells are arranged randomly inside of those large particles. Faint micelle-like patterns in the shells of the hollow particles can be discerned in the high-magnification micrographs of sample A1 (Figure 6.11), but no long-range mesopore structure is present. This indicates that the thin shells of the hollow particles may be generated by condensation of silica species with a minimal amount of CTAB on the surfaces of latex microspheres. HCP cylinder patterns are clearly observed throughout the large irregular particles. This suggests that large irregular particles were formed from CTAB-silica aggregates in a process separate from the microsphere templating. The latex microspheres coated with a thin shell of silica particles were then
captured inside the CTAB templated silica particles due to the condensation between the CTAB/silica particles and latex/silica particles.

As the ammonia content increases, mesoporous shells are formed at the outside of the latex microspheres. In sample A2, mesoporous shells are present on at least some particles, but the shell thickness is not uniform. In places, a rough, ramified structure coats the outside of the particles (Figure 6.11). The appearance of the shells would be consistent with CTAB/silica aggregates being attracted to the outer surface of the microspheres. The structure may be very fragile because of a relatively weak attraction between the aggregates and the microspheres. With even more ammonia (sample A3), the shape of the mesoporous shells is very smooth and the shells are thicker. In this series of samples, an increase of the ammonia increases the aggregation between the CTAB/silica aggregates and latex/silica particles leading to the formation of hollow spherical particles with mesoporous shells.

 Isotherm plots and pore size distributions of these samples are compared in Figure 6.12. All three samples have sharp inflections in their isotherms and narrow pore size distributions. The pore size distributions are very narrow for samples A1 and A2, perhaps because large domains form without latex microspheres present. When enough ammonia is used to promote good hierarchical mesopore / macropore structure formation (sample A3), the pore size distribution broadens somewhat and shifts toward smaller pores.

6.3.4. Controlling of the core size by using latex with different size

Unmodified latex microspheres with different sizes were used as templates to produce samples C1 (0.0489 µm), C2 (0.202 µm), C3 (0.356 µm), and C4 (0.535 µm). Sample C3 is the same sample as the base case. Representative TEM images for samples C1, C2, and C4 are shown in Figure 6.13. No separate spherical particles with single hollow cores are observed for sample C1. Hollow voids are instead dispersed randomly inside of large, irregular particles. The voids are close to the size of the original microspheres, however. At the surface of each void, striped patterns indicate that a single layer of well-oriented CTAB micelles may have been associated with the microspheres, leading to highly ordered parallel patterns around each void. Samples C2 and C4 both have spherical particles with hollow cores similar to the base case (Figure 6.1), but with
core sizes that vary according to the size of the latex microspheres. Ordered hexagonal pattern are observed in the shells of both samples. Figure 6.13 shows hexagonal and striped patterns in the shells of the particles for sample C2. Compared to samples C2 and C3, sample C4 (prepared with the largest microspheres) has rougher edges. It is also much more difficult to observe ordered patterns in the shells of C4 than the others. This may be because that the shells of C4 are thick. The thicknesses of the shells are 138 ± 25 nm (C4), 124 ± 10 nm (C3), and 62 ± 5 nm (C2). The decrease in shell thickness in this series can be explained by the increase in number density of microparticles as the size decreases. Sample C1 seems to continue trend, although separate hollow particles are not present.

The nonuniformity of the shells of sample C4 may be explained by a large potential energy barrier to aggregation of CTAB/silica aggregates with large latex particles. Because of the barrier, the CTAB/silica aggregates are large and well-condensed by the time that they add to the latex surface. Another contribution to their morphology may be a lack of mechanical stability during calcination. Smaller microspheres (C3 and C2) present less of a potential energy barrier, and therefore aggregate sooner, while the CTAB/silica aggregates are still maleable. The particles are therefore smoother. For the smallest microspheres (C1), the CTAB/silica aggregates should coat the latex quickly, but the CTAB/silica/latex particles may be colloidally unstable, leading to coalescence of the particles.

Nitrogen sorption data and pore size distributions of samples C1 through C4 are compared in Figure 6.14. All samples have sharp inflections in the isotherms. Sample C1 has pronounced hysteresis at high relative pressure due to the presence of large mesopores (the hollow voids) surrounded by smaller mesopores. Sample C2 also displays some hysteresis for the same reason. The size of the hysteresis loop is decreased because the hollow “core” size is at the outer limit of the mesopore size range. For samples C3 and C4, the cores are too large to cause hysteresis. Sample C1 has slightly larger primary mesopores in the pore size distribution than the other samples. For samples C2-C4 (which all consist of separate spherical particles), the mesopore size is constant but the mesopore volume decreases as the latex size increases.
6.3.5. Dual templating mechanism

The results found here point to the formation of the shells by deposition of CTAB/silica aggregates onto the surface of the latex microspheres. The quantity of shell material deposited appears to be dictated by the solution conditions. There is an optimal concentration of CTAB. Too much will induce the nucleation of new particles of CTAB/silica aggregate without microsphere incorporation. Too little CTAB will lead to a mixture of microspheres coated with a thin layer of silica, and silica nanoparticles. Based on prior studies of the Stöber process with added CTAB, it is likely that the CTAB/silica aggregates deposit onto the microspheres as a disordered liquid-like phase, and adopt HCP ordering as the particles age. The CTAB micelles in the shells align parallel to the surface of the shells due to interactions with the latex and with the solution.

Ammonia not only serves as a base catalyst for the sol-gel reaction, but also helps to form the particle morphology. When present at a high concentration, ammonia may encourage the aggregation between small CTAB/silica aggregates and large latex microspheres to create hollow spherical particles with smooth, uniform shells. A low concentration of ammonia causes small CTAB/silica aggregates to grow independent of the microspheres, leading to large mesoporous particles with thin-walled unstructured hollow silica particles.

The size of the microspheres controls the size of the hollow cavities left behind after calcination. In the series of experiments performed, the number density of particles also increased with decreasing latex size, leading to thinner walls. However, with the smallest microspheres (50 nm, sample C1), agglomerated mesoporous particles with many spherical voids formed, rather than separate particles. Colloidal instability explains this observation. Figure 6.15 illustrates the DLVO potential calculated at 300 K for spheres with sizes corresponding to the diameters of the C-series samples. For Figure 6.15, the Hamaker constant is assumed to be the average of the values for polystyrene and fused silica in water, 0.9 x 10^{-20} J. The ionic strength is calculated based on the dissociation of ammonia (pK_b = 4.76). The surface potential of the spheres under these conditions is not known, but with \( \Gamma_0 = \frac{\exp(ze\Phi_0 / 2kT) - 1}{\exp(ze\Phi_0 / 2kT) + 1} \), the barrier to
agglomeration for the smallest particles is \( \sim 2 \) kT. This barrier is small enough to allow agglomeration and coalescence of the particles. For equally-sized particles, the potential energy is proportional to particle size, so as latex particle size increases, the barrier to coalescence rapidly becomes large. Thus, separate hollow particles are obtained. The DLVO potential also has a stronger secondary minimum at \( \sim 9 \) nm for larger particles, which may induce flocculation but not complete agglomeration.

The dependence of the DLVO potential on particle size also helps to explain why the CTAB-silica aggregates may have coated the largest latex particles slowly, leading to rough shells (sample C4). For small CTAB-silica particles (radius \( R_1 \)) interacting with larger (silica-coated) latex (radius \( R_2 \)), the DLVO potential should scale as \( R_1 R_2 / (R_1 + R_2)^2 \). Assuming that \( R_1 \) remains constant for the C-series samples, as \( R_2 \) increases, the potential energy barrier increases, but not by more than a factor of two. Therefore, agglomeration of the CTAB-silica particles with silica-coated latex microspheres would be slowed as the latex microsphere radius increases, but not completely stopped.

With the above considerations in mind, we find that the best conditions for creating separate hollow mesoporous particles are (1) a moderate amount of CTAB, (2) a large concentration of ammonia, and (3) quantities of TEOS and CTAB that are appropriate to the thickness of the shell desired in the final product. The size of the hollow cores can be controlled by the latex microsphere size, as long as colloidal stability does not interfere with the dispersion of the composite particles.

6.4. Conclusions

A dual templating method has been demonstrated to make hollow spherical ceramic particles with ordered mesoporous shells. Under appropriate synthesis conditions, the particles possess a single large cavity that can be used as a reservoir, and a controlled shell porosity that would have natural applications where controlled release or infusion is needed. Synthesis in a highly concentrated ammonia solution with an appropriate CTAB-latex ratio promotes growth of silica/surfactant aggregates at the latex particle surface rather than nucleation of new particles. The core size can be controlled by using latex microspheres with different sizes. The materials, made under relatively mild
reaction conditions, are stable during calcination and reproducible. This method provides a convenient way to design hollow spherical mesoporous ceramic particles.

6.5. References

Figure 6.1. Representative low magnification TEM micrographs of the calcined base-case sample prepared by dual templating.

Figure 6.2. Representative (a) STEM image of one particle and (b) high magnification TEM image of a quarter of one particle of the calcined base-case sample. Arrows indicate hexagonal regions.
Figure 6.3. Representative low magnification TEM micrographs of the calcined base-case sample after ultrasonically treatment.

Figure 6.4. X-ray diffraction pattern of the base-case sample after calcination.
Figure 6.5. Nitrogen sorption data at 77 K for base-case sample after calcination.

Figure 6.6. $\alpha_s$-plot of the base-case sample after calcination.
Figure 6.7. Representative TEM images of samples T1, T2, T4 and T5 after calcination.
Figure 6.8. Representative TEM image for sample T6 after calcination.

Figure 6.9. Representative TEM image for sample T7 after calcination.
Figure 6.10. Nitrogen sorption isotherms and pore size distributions of samples T1 through T5.
Figure 6.11 Representative TEM images of samples A1 and A2 after calcination.
Figure 6.12. Nitrogen sorption isotherms and pore size distributions of samples A1 through A3 after calcination.
Figure 6.13. Representative TEM images of C1, C2 and C4 at varying magnifications.
Figure 6.14. Isotherms and pore size distributions of samples C1 through C4.
Figure 6.15. DLVO potential for silica particles of varying sizes in concentrated aqueous ammonia.
Chapter 7. Cationic Fluorinated Surfactants Templated Sol-Gel Process

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7.1. Introduction

Nanoporous ceramic materials are useful for both traditional industrial catalytic and separations applications, and for emerging nanotechnology applications such as nanoparticle synthesis and support. These materials are prepared by the growth of a metal oxide network in the presence of a pore template. If the pore template is a solvent which is removed by supercritical drying, the wet gel structure is preserved and a highly porous aerogel can be obtained.6 Silica aerogels are typically mesoporous, and depending on processing conditions have a broad pore size distribution centered around 10-30 nm.7-9 However, sol-gel ceramics are fragile, and the distribution of pore sizes and wall thicknesses in a conventional gel makes the structure vulnerable to collapse.6,9 Solvent drying under ambient conditions usually results in a xerogel with much less porosity and smaller pores, due to surface tension-driven collapse of the pores.10 At the other extreme of pore structure, crystalline zeolite molecular sieves with fine pores (2-15 Å in diameter) can be prepared by growing silica with other metal cations in the presence of small organic cations such as tetrapropylammonium.11 When larger cationic and nonionic surfactants are used as pore templates, mesoporous silicates with amorphous pore walls but well-defined pores are formed by micelle templating.12,13 In this method, the
surfactants act as pore templates by co-assembling with ceramic precursors due to Coulombic forces or hydrogen bonding prior to material formation. Upon surfactant removal, pores are left behind that mimic the size and ordering of micelles in lyotropic liquid crystals. The pore structure mimics the long-range order of lyotropic surfactant mesophases, and features such as pore size, pore shape and wall thickness can be manipulated by choice of headgroup charge, tail length, tail number, and different reaction conditions (such as pH, temperature, and surfactant:silica molar ratio).  

Large pores can be formed by using block copolymer amphiphiles and by swelling surfactant tails with nonpolar compounds such as trimethylbenzene. 

A wide variety of hydrogenated surfactants, acids, and block copolymers have been investigated as templates to make nanoporous ceramic materials. Fluorinated surfactants are intriguing as pore templates because their self-assembly behavior differs significantly from hydrocarbon surfactants. Because of weak intermolecular interactions, the fluorocarbon chains in these surfactants are significantly more hydrophobic. As a result, fluorinated surfactants self-assemble much more easily than analogous hydrocarbon surfactants. This feature translates into unusually low critical micelle concentrations. They aggregate in water at a critical micelle concentration generally equal to that of an analogous hydrocarbon surfactant of 50% greater tail length. This feature can be used to make nonporous silica with smaller pore size than those obtained from hydrogenated surfactants. Pore size is known to decrease as the surfactant tail length decreases, but in spite of this trend, no single-chain hydrogenated cationic surfactants with chain length shorter than eight carbons have been used as supramolecular templates for nanoporous silica. Fluorinated surfactants are also lipophobic, which may facilitate synthesis of functionalized materials. Fluorinated surfactants interact selectively with low-surface tension solvents (e.g. pressurized CO₂ and fluorocarbons), which may be used to facilitate extraction, recovery, and recycling the fluorinated surfactants. The large van der Waals radius of fluorine compared to hydrogen also makes fluorocarbons stiffer. This results in surfactants which favor aggregates with low curvature (such as cylinders, discs and bilayers) and novel “intermediate” mesophases including rectangular and mesh phases.
Fluorinated surfactants have been used several times to form ordered mesophase composites through complexation with hydrocarbon polyelectrolytes, as recently reviewed by Thünemann.\textsuperscript{31} However, it is only within the last two years that association of fluorinated surfactants with inorganic ceramic precursors for materials synthesis has been investigated. In the first study to employ a fluorinated surfactant for ceramic synthesis, it was mixed with a nonionic hydrocarbon surfactant.\textsuperscript{32} The surfactant acted as a thermal stabilizer to allow synthesis to occur at high temperature. However, the pore size was too large to have been controlled by the fluorocarbon chain length. It is unlikely that the fluorinated surfactant itself acted as a pore template and, in fact, Han et al. hypothesized that fluorinated surfactants alone are not suitable pore templates.\textsuperscript{32} This hypothesis was almost immediately disproven by several recent reports of the use of cationic and non-ionic fluorinated surfactants as templates for mesoporous silica.\textsuperscript{1,33,34}

One of the aims of this chapter is to investigate the feasibility of making materials with small pore sizes by using single-chain cationic fluorinated. An established method to control the mesopore size in templated mesoporous ceramics is by the choice of surfactant tail chain length.\textsuperscript{23,35,36} Pore size is known to decrease as the surfactant tail length decreases. Single-chain hydrocarbon cationic surfactant with chains as short as -C\textsubscript{8}H\textsubscript{17} have been used to make materials with small pore sizes.\textsuperscript{37-40} However, surfactants with tails this short do not assemble into ordered structures easily, and all of the materials made with this surfactant have amorphous pore structures.\textsuperscript{37-40} Single-chain cationic surfactants with shorter chains offer limited prospects to be used as templates for ordered mesoporous because they are more difficult to self-assemble.\textsuperscript{41} No cationic surfactants with chain length shorter than six carbons have been used as supramolecular templates for nanoporous silica. Hexyl and shorter surfactants are usually used as molecular templates for zeolites.\textsuperscript{11} For instance, hexyltrimethylammonium bromide has a well-defined critical micelle concentration,\textsuperscript{42} but Beck et al. found that under hydrothermal conditions, it acts as a molecular (rather than supramolecular) template to form zeolitic ZSM-5.\textsuperscript{41} To overcome this limitation, Ryoo et al. began using double-chain hydrocarbon cationic surfactants.\textsuperscript{39} The double-chain surfactant with C\textsubscript{8}H\textsubscript{17} tails in the chain produced a 2-D hexagonal pore structure with a pore size of 2.39 nm, and even smaller double-chained surfactants could be used.\textsuperscript{39} A small pore diameter (1.96 nm) was reported by
An alternative approach is to use fluorinated surfactants. These surfactants are well known for their low cmc (critical micelle concentration) compared to analogous hydrocarbon surfactants. For example, the 8-carbon fluorinated pyridinium chloride (C$_6$F$_{13}$C$_2$H$_4$NC$_5$H$_5$·Cl) has a cmc of 16.2 mmol/L, which is approximately equal to that of the C$_{12}$ hydrocarbon pyridinium chloride surfactant (15.5 mmol/L). The low cmc means that fluorinated surfactants self-assemble more easily in solution, which we hypothesize, will translate into easy co-assembly with ceramic precursors to make small-pore mesoporous materials.

The second aim of this chapter is to demonstrate the potential to make materials with novel pore structures by using fluorinated surfactants. Researchers have already shown that not only pore sizes, but also pore structures can be controlled by the surfactant structure. Different surfactants co-assemble with silicates to generate mesoporous silicas with pore structures mimicking common lyotropic mesophases. Silica products with wormhole-like, 2D hexagonal, Ia3d cubic, rectangular, tetragonal, orthorhombic, sponge, lamellar, and vesicle pore structures have been made with hydrocarbon surfactants. The materials with orthorhombic and tetragonal pore structures have been synthesized in films, in which stress and shrinkage during drying may contribute to the formation of the structure. In spite of this variety of pore structure, there are still several liquid crystal phase structures that have not been replicated in mesoporous silica. Fluorinated surfactants can possibly help to expand the range of structures available in templated mesoporous ceramics because they easily form novel phases such as mesh phases.

With these two aims in mind, a comprehensive investigation on the use of cationic fluorinated surfactants as pore templates is reported here. The surfactants are members of a homologous series of perfluoroalkylpyridinium chlorides with straight and branched chains (C$_n$F$_{2n+1}$CH$_2$CH$_2$NC$_5$H$_5$·Cl where n = 2, 4, 6, 8, 10 and (CF$_3$)$_2$C$_n$F$_{2n-1}$CH$_2$CH$_2$NC$_5$H$_5$·Cl where n = 5, 7). Of this series, the self-assembly behavior of the F$_6$H$_2$ (where F$_i$ is a perfluoroalkyl group with i carbons and H$_j$ is an alkylene spacer with j carbons attaching the fluoroalkyl group to the pyridinium head group), F$_8$H$_2$, and F$_{10}$H$_2$ straight-chain surfactants in aqueous solution were studied with cryo-transmission
electron microscopy (c-TEM). The F₆H₂ surfactant was found to form globular micelles near the critical micelle concentration (cmc). Both globular micelles and thread-like micelles were observed for the F₆H₂ surfactant at concentrations just above the cmc. The F₁₀H₂ surfactant was found to form bilayers at surprisingly low concentrations, which indicates this surfactant should be prone to form lamellar phases or vesicles. Small angle x-ray diffraction (XRD) showed that at high concentration in aqueous solution, F₈H₂ favors “intermediate” phases with low curvature. As the F₈H₂ concentration increases, lyotropic mesophases found included 2D hexagonal close packed (HCP) columnar phase, a rectangular phase, a trigonal mesh phase, a random mesh phase, and a lamellar phase. Together, these c-TEM and XRD studies show that the perfluoroalkylpyridinium chlorides exhibits a broader range of micelle shapes and mesophases as the tail length increases than is usually observed in hydrocarbon surfactants. As we will show, this structural variability is transcribed into the pore structures of templated ceramic materials.

7.2. Experimental Section

7.2.1 Materials. All fluorinated surfactants were prepared by Dr. Hans Lehmler and Dr. Sandyha Vyas of the University of Iowa. Structures of these surfactants are shown in Table 7.1. To prepare 1H, 1H, 2H, 2H-perfluorobutylpyridium chloride (HFBPC, F₂H₂), a solution of pyridine (7.2 g, 0.1 mol) and 1H,1H,2H,2H-perfluorobutyl iodide (6.8 g, 24 mmol) were stirred under reflux for 6 h. Diethyl ether (50 mL) was added to the cooled solution and the product separated from the ether phase as a dark brown, thick liquid. This liquid was separated, washed with diethyl ether, and crystallized from ethyl acetate to yield 7.6 g (87%) of the 1H, 1H, 2H, 2H-perfluorobutyl pyridinium iodide. The corresponding chloride hydrate (HFBPC) was obtained in an overall yield of 73% by ion exchange chromatography on Amberlite IRA-410 using methanol as mobile phase followed by crystallization from acetone. The other fluorocarbon surfactants (CₙF₂ₙ₊₁CH₂CH₂NC₅H₅·Cl, n = 4, 6, 8, 10; (CF₃)₂CₙF₂ₙ⁻₁CH₂CH₂NC₅H₅·Cl, n = 5, 7) were synthesized as described previously by alkylation of anhydrous pyridine with 1H,1H,2H,2H-perfluoroalkyl iodide followed by anion exchange. All surfactants have been fully characterized and checked for purity. 
Tetraethoxysilane (TEOS, 99+%%) was obtained from Gelest. Concentrated aqueous ammonia (29 wt% NH₃ in water, Merck), deionized ultrafiltered water, concentrated aqueous HCl (ACS grade, Fisher Scientific) and anhydrous ethanol (Aaper Alcohol) were used as received.

7.2.2 Synthesis. Samples were made in aqueous (heterogeneous) and ethanol-water (homogenous) solutions based on previously reported procedures. Compositions for materials synthesized in aqueous solution are shown in Table 7.2 and Table 7.3. One series of samples (UKAx, where x = 6, 8, 9b, 10, 11b or 12) were prepared with the only difference in the surfactant. The synthetic conditions including the stirring speed, TEOS addition speed, reactor vessel, and the scale of solution are the same among this series of samples. The only difference among these samples is the type of the surfactant as shown in Table 7.2. To prepare these samples, surfactant, water and concentrated aqueous ammonia were first mixed for one hour before the slow addition of TEOS. The mixed solution was aged with moderate stirring at room temperature for 24 hours and was then filtered and dried in air for 2 days.

Compositions of samples UK4-0, UK4-1, UK4-2, and UK4-3 are also shown in Table 7.2. To prepare these samples, the specified amount of HFBPC (F₂H₂), water and concentrated aqueous ammonia (29 wt %) were stirred for 30 minutes at room temperature. Then, TEOS was added slowly with stirring, and the solution was stirred for 60 minutes at room temperature before sealing the bottles and heating at 50 °C without stirring for three days. As-synthesized samples were collected by filtering and dried in air for 2 days.

Three samples were prepared with the same compositions by using HFDePC as the surfactant template, but with different stirring rates. They were indexed as FSV-S1 (~150 rpm), FSV-S2 (~300 rpm), and FSV-S3 (~450 rpm). The synthetic procedure is the same as that for UKA10.

Samples UKA10-1, UKA10-2, UKA10-3, UKA10-4, UKA10-5, UKA10-6, UKA10-7, and UKA10-8 were prepared to investigate the effect of HFDePC concentration on the pore structure and the particle morphology. To ensure that the size of the reactor vessel and the scale of solution did not influence the results, two series of samples were
prepared in different batch sizes, but with all variables held constant except the concentration of HFDePC. From the two series, a pair of samples (UKA10-3 and UKA10-4) with identical composition was prepared to confirm that the reactor scale does not influence the results. Compositions of these samples are shown in Table 7.3. The size of the beaker, the stir bar, stirring speed, and TEOS addition speed were kept the same among samples UKA10-1, UKA10-2, and UKA10-3. The synthesis conditions were the same among samples UKA10-4, UKA10-5, UKA10-6, UKA10-7, and UKA10-8. A fast stirring speed was used for all samples to obtain homogenous solutions. The synthetic procedure is the same as described for UKA10.

TEOS is not water soluble. Phase separation happens at the beginning of a surfactant templated sol-gel process in aqueous solution. The addition of ethanol will help to homogenize the solution. However, the presence of ethanol will also affect the pore structure and particle morphology as we discussed in Chapter 5. Ethanol/water system is used in this study to expand the possibility to synthesize novel nanoporous silica. The materials synthesis in water/ethanol solution followed a similar procedure except that ethanol was added to the initial solution before adding TEOS, and the aging time before the initial filtering was only 2 hours. Two series were prepared from aqueous ethanol. In the first (samples UKHx-1 where \(x = 6, 8, 9b, 10, 11b\) or 12), the mole ratios after adding TEOS were 0.30 surfactant: 143 H\(_2\)O: 56.7 C\(_2\)H\(_5\)OH: 9.8 NH\(_3\): 1.0 TEOS. In the second (samples UKHx-2 where \(x = 10\) or 12), the ratios were 0.075 surfactant: 82.7 H\(_2\)O: 27.3 C\(_2\)H\(_5\)OH: 9.8 NH\(_3\): 1.0 TEOS.

For any sample discussed in this chapter, the surfactant was extracted by washing the sample twice with acidic ethanol (5 ml concentrated HCl in 150 ml ethanol) before characterization.

7.2.3 Characterization. X-ray diffraction (XRD) patterns were recorded on a Siemens 5000 diffractometer. Transmission Electron Microscope (TEM) images were collected with a JEOL 2010F electron microscope operating at 200 kV. Nitrogen sorption measurements were performed on a Micromeritics Tristar 3000 system. All samples were degassed at 150 °C for 4 hours under flowing nitrogen prior to measurement. The BJH method with a KJS modified statistical film thickness equation\(^{56}\) was used to
calculate the pore size distribution (PSD) from the adsorption branch of the isotherms. Samples were assumed to have cylindrical pore shapes unless a slit pore shape was indicated. In this case, a modified BJH method for slit pores was adopted to estimate the pore size distributions (Appendix B).

7.3. Results and discussion

In a surfactant templated sol-gel process, there are normally three ways to remove the surfactant template in an as-synthesized sample. The first is to calcinate the as-synthesized sample at very high temperature. Hydrocarbon bonds can be oxidized completely under this condition and the surfactant leaves as gaseous products. The second is to extract the surfactant by an acidic or salt washing process. The third is to extract the surfactant in an organic solvent under reflux. The third process is normally used for nonionic surfactants and does not work well for cationic surfactants. Fluorine-carbon bonds are too stable except at extremely high temperature. Therefore, the first process is not desirable for fluorinated surfactants. Fluorinated surfactants are difficult to decompose completely by calcinating. Harmful gases including HF might be produced in the decomposition process. Moreover, fluorinated surfactants are very expensive. In the long run, it would be preferable to recover and recycle the surfactants. This is the reason that the acidic washing method was selected to remove all surfactants. Acidic washing exchanges cationic surfactants with hydronium ions. Other reagents such as ammonium nitrate could also be used for this purpose. But for consistency with our early work, we always use acidic washing.

The incorporation of fluorinated surfactants as templates and the removal of these surfactants by acidic washing were checked by infrared spectroscopy. An example will be discussed of the sample prepared with HFOPC as the template (UKA8). The composition of this sample is listed in Table 7.2. FTIR spectra of the surfactant, as-synthesized sample, extracted sample, and fumed silica are compared in Figure 7.1. The solid surfactant spectrum (Figure 7.1a) shows several bands in the range (1400 cm$^{-1}$ to 700 cm$^{-1}$) associated with fluorinated alkyl groups. Of these bands, the most prominent ones have been assigned to asymmetric CF$_2$ stretching (1247 cm$^{-1}$), CCC deformation (1207 cm$^{-1}$), and symmetric CF$_2$ stretching (1147 cm$^{-1}$). In the as-
synthesized material (Figure 7.1b) all of these bands may be present, but the 1147 cm\(^{-1}\) band is most clearly defined (indicated with an arrow). In the extracted product (Figure 7.1c), the 1147 cm\(^{-1}\) band cannot be observed, but there still is a shoulder at about 1200 cm\(^{-1}\). This shoulder is typical of high-surface area silica\(^{60,61}\) and, like the more prominent band at 1093 cm\(^{-1}\), is assigned to asymmetric Si-O-Si stretching.\(^{62}\) The spectrum of fumed silica (>99%, Aldrich) shown in Figure 7.1d has the same features as the extracted material, and confirms the assignment of the shoulder at 1200 cm\(^{-1}\) to silica. A clearer indication of the presence of the surfactant in the as-synthesized product (Figure 7.1b) is the narrow band at 1495 cm\(^{-1}\) that does not coincide with any other bands. This band has not been assigned to fluorocarbons\(^{59}\) and is more likely to be associated with pyridinium motion. After 2 extraction steps, this band is completely absent (Figure 7.1c). The information from FTIR shows that fluorinated surfactants are incorporated into the materials and can be removed completely by acidic washing.

The XRD pattern can be collected for an as-synthesized material to determine the pore structure before removing the template. However, this technique has limited success for as-synthesized materials templated by fluorinated surfactants. Because of the low electron density contrast between fluorine and silicon, intensities of the peaks are very weak. The low contrast is exemplified by comparing XRD patterns of the as-synthesized and the extracted samples of UKA8 (Figure 7.2). The as-synthesized sample (dashed line) shows poorly resolved peaks due to the poor contrast between silicon and the fluorocarbon surfactant. Therefore, only XRD patterns of extracted samples will be shown in this chapter.

In our investigations, we found that process parameters are very important to the pore properties of fluorinated surfactants templated materials. Optimized conditions in particular the stirring speed might be different based on different compositions. For example, a slow stirring speed is favorable to obtain a material with high surface area and large pore volume as the sample SS-1 (shown in Appendix C). However, the same stirring speed can not be used for samples with high surfactant concentrations. Inhomogeneous product will be obtained when the stirring speed is not fast enough (see section 7.3.4.4). For this reason, the stirring speed might be different for different sample. For all samples, slow TEOS addition speed is preferred. TEOS is added dropwise.
In this chapter, we will focus on the synthesis and characterization of nanoporous silica by using different cationic fluorinated surfactant as the template. We will discuss the effects of fluorinated surfactant structures on the pore structure and the particle morphology. In particular, we will investigate effects of the chain length on the pore structure. Effects of hydrogenated surfactants have been reported by using a series of cationic surfactants, alkyltrimethylammonium bromide (C_{n}H_{2n+1}N(CH_{3})_{3}Br, n = 8-16), as templates. The investigation shows that the pore size increases with an increase of the chain length. The pore structure changes from wormhole-like (C8) to hexagonal (C10-C16) for samples prepared in aqueous solution.

7.3.1. HFBPC templated sol-gel process

Materials synthesized with HFBPC (F_{2}H_{2}) as the template are discussed in this subsection. Four samples were prepared with the initial molar compositions listed in Table 7.2. All four samples were prepared under the same conditions, but the type of product differed significantly. For UKA4-0 (without HFBPC), no gel or precipitate was obtained after heating at 50 °C for more than a week. No gel or precipitate was observed for UK4-1 during the initial room temperature step either. However, a gel was obtained after heating this sample overnight at 50 °C. This gel was homogeneous and transparent, with a few suspended colorful crystals. It is unusual for a surfactant to induce gelation in a sol that otherwise would not gel. In an alkaline solution, anionic deprotonated silicate species are present, which interact with cationic surfactants through Coulombic and hydrogen bonding forces. This interaction is thought to promote the co-assembly of organized surfactant/silica aggregates. In the synthesis solution of UK4-1, these interactions still should occur, but the driving force for co-assembly is too weak to form an ordered surfactant/silica composite. Instead, the interaction between surfactants and silica creates somewhat hydrophobic aggregates that are drawn together more rapidly than the silica species would be alone. This accelerates the rate of aggregation of silica oligomers and nanoparticles present in solution, and may also accelerate silica condensation. Sample UK4-2 initially formed a soft gel at room temperature after 30 minutes, but within 50 minutes it converted into a gelatinous precipitate. For sample UK4-3, a precipitate was obtained within 30 minutes at room temperature. Apparently in
this sample, the driving force for co-assembly increases enough that silica-surfactant aggregates precipitate, as would normally be expected under these conditions.\textsuperscript{1,3} All of these samples were aged for 3 days at 50 °C before drying.

Nitrogen sorption data of UK4-1, UK4-2, and UK4-3 are shown in Figure 7.3. Sample UK4-1 has a Type IV adsorption isotherm with a narrow H1 hysteresis loop, which suggests that it is composed of uniform mesopores. This isotherm has features like those of some dried sol-gels and materials prepared with polymeric surfactants,\textsuperscript{65-67} but the hysteresis loop of UK4-1 is narrower than that of aerogels and xerogels. UK4-1 has a narrow pore size distribution centered at 11.1 nm. This is an exceptionally large mesopore size for a surfactant-templated material, and is consistent with the gel-like nature of this sample. The hysteresis loop of UK4-2 is more similar to a H3 hysteresis loop, suggesting that large mesopores are present in a matrix of smaller pores.\textsuperscript{68} The pore size distribution of UK4-2 is broader and weaker than that of UK4-1, which indicates that there are fewer large mesopores. In contrast to the first two samples, no large mesopores are indicated in the BJH pore size distribution of sample UK4-3. Because of the limitation of the instrument, a pore size distribution was not obtained in the microporous region, but the Type I isotherm of this sample (with textural porosity) is consistent with a microporous sample.

$\alpha_s$-plots\textsuperscript{69,70} of all samples are shown in Figure 7.4. Several linear regions can be identified. For UK4-1, the plot has typical features associated with mesoporous materials. The sharp inflection in the region ($1.3 < \alpha_s < 1.8$) indicates capillary condensation in mesopores. For samples UK4-2 and UK4-3, microporosity is indicated by a drop in the slope of the $\alpha_s$-plots at $\alpha_s$ values below 1. The pore texture characteristics of all samples are summarized in Table 7.4. The quantitative analysis of the $\alpha_s$-plots shows a decrease in mesopore volume in favor of micropore volume when going from sample to UK4-1 to UK4-3.

XRD patterns of all samples were collected, but no reflections were identified for samples UK4-1 and UK4-2. Only one reflection was observed for sample UK4-3, with a d-spacing of ~2.3 nm (Figure 7.5). This d-spacing is the smallest that we are aware of in any silica powder formed by supramolecular surfactant templating.\textsuperscript{39,40} In fact, this d-spacing is close to the smallest pore diameters that have been reported in such materials.
The presence of this reflection indicates that UK4-3 may have a wormhole-like pore structure. Assuming a cylindrical pore shape, the pore size of UK4-3 can be estimated from the equation 
\[ w_d = 1.213d_{100}\left(\frac{\rho V_p}{1+\rho V_p}\right)^{1/2} \]
where \( \rho \) is the density of the silica (2.2 cm\(^3\)/g) and \( V_p \) is the primary pore volume.\(^{39}\) The pore size calculated for UK4-3 is 1.6 nm. Normally, silica with pore size larger than 2.0 nm is obtained by the surfactant templated sol-gel process. The upper limit of the pore size available in zeolites is about 1.5 nm.\(^{21}\) The gap between the pore size of zeolites and mesoporous silica is difficult to span. Silica with pore sizes in the range of 1.3 nm ~ 1.8 nm have been reported before.\(^{56,63,71}\) However, the reported materials either have slit pore shapes or the reported sizes are questionable because the BJH method was used for pore size (and is known to underestimate pore sizes for diameters < 6.5 nm).\(^{68}\)

Representative TEM images of the samples are shown in Figure 7.6. Sample UK4-1 has a uniform foam-like pore structure with a pore size of about 12 nm. Sample UK4-2 is composed of a mixture of foam-like structure and dense silica (which may account for the microporosity in the adsorption results). In the sample UK4-3, only interconnected particles with wormhole-like pores with pore size much smaller than 10 nm are observed.

The characterization of this series of samples presented in Figures 7.3-7.6 gives a consistent picture of the structure changes in this series of samples as the HFBPC concentration increases. The pore size decreases by almost an order of magnitude, from 11.1 nm to 1.6 nm between UK4-1 and UK4-3, and the pore structure changed from foam-like to wormhole-like. These pore sizes sit both above and below the range of pore sizes available by surfactant templating with the entire series of alkyltrimethylammonium surfactants (ranging from C8-C16) that are soluble and able to co-assemble with silica at room temperature.\(^{72}\)

The dramatic change in pore properties with surfactant concentration can be related to the poor ability of HFBPC to self-assemble. The critical micelle concentration (cmc) of this surfactant has not been reported, but we would expect it to be greater than 0.17 mol/L (the cmc of 1H,1H,2H,2H-perfluorohexylpyridinium chloride\(^{73}\)). If it is similar to other fluorinated surfactants, HFBPC should have a cmc about equal to that of a hydrocarbon with a 50% longer chain (hexyl). Hexyltrimethylammonium bromide has been shown to have a clear cmc of about 0.5 mol/L, although it forms very small aggregates.\(^{42}\)
Comparing these numbers to the concentrations used for synthesis, for UK4-1 the concentration is 0.099 mol/L, which we expect to be below the cmc. There is a low driving force for micelle self-assembly, which translates into a low driving force for co-assembly with silica. Apparently, the interaction between HBuPC monomers and silicates is still strong enough to promote silica condensation and oligomer / nanoparticle aggregation, leading to a gel in the case of UK4-1. The presence of HFBPC during drying may also have contributed to the preservation of the pore structure, instead of the usual collapse of pores observed in silica gels dried under ambient conditions.

On the other hand, the concentration of HFBPC in the synthesis solution of UK4-3 is 0.86 mol/L, which is above the cmc of the analogous hydrocarbon. This concentration is apparently high enough to form micelle-silica aggregates that are able to precipitate. The pore diameter of this sample is consistent with the trend of decreasing pore size with decreasing alkyl length in perfluoroalkylpyridinium chloride templated silica. The next largest surfactant in this series (1H,1H,2H,2H-perfluorohexylpyridinium chloride) produces wormhole-like pores with a diameter of 2.19 nm (see section 7.3.2 below). The decrease in pore diameter to 1.6 nm is consistent with micelle templating by a shorter surfactant. The large pores of UK4-1 and UK4-2 were obviously not templated directly by micelles.

The effect of surfactant concentration on product structure for HFBPC differs significantly from that of another member of this series of surfactants, 1H,1H,2H,2H-perfluoroocetylpyridinium chloride (HFOPC). When the HFOPC concentration is varied under similar synthesis conditions, the same mesopore diameter is found, which is consistent with the micelle size (see section 7.3.3 below). The textural porosity varies, and is greater with a smaller surfactant concentration, but the mesopore diameter does not change. Even when the concentration of surfactant is as low as 6.2 mmol/L (well below the cmc of 16.2 mmol/L\textsuperscript{74}), the pore diameter is constant (see section 7.3.3 below). The difference in the trend for HFBPC can be attributed the smaller driving force for co-assembly of this surfactant, which leads to only enough interaction to induce gelation at concentrations below the cmc.

In this subsection, a partially fluorinated surfactant with extremely short chain (1H,1H,2H,2H-perfluorobutylpyridinium chloride) was employed to synthesize a series
of nanoporous silica samples. This surfactant may have the shortest tail among the surfactants that have been used as supramolecular templates in the sol-gel process. Porous silica with unusually large, uniform foam-like mesopores was obtained at low surfactant concentration. At a high surfactant concentration, a more typical wormhole-like pore structure was obtained, with a pore diameter of only 1.6 nm. This is the first example that we know of in which a surfactant helps to form gels with large mesopores without the addition of a micelle-swelling organic solvent. These observations illustrate that surfactants can play a role in inducing aggregation and gelation, in addition to their well-known molecular and supramolecular templating roles.

7.3.2 1H,1H,2H,2H-perfluorohexylpyridinium chloride (HFHexPC) templated sol-gel process

Two samples were prepared with HFHexPC (F₄H₂) as the template. Sample UKA6 was prepared in aqueous solution while UKH6-1 was prepared in ethanol/water solution. Precipitates were obtained for both of the samples.

XRD patterns of UKA6 and UKH6-1 are shown in Figure 7.7. Both of the patterns indicate a wormhole-like pore structure. The first reflection for UKA6 is much narrower than that of UKH6-1, suggesting that the pore size in UKA6 is more uniform than that in UKH6-1. TEM images of the two samples are shown in Figure 7.8. UKA6 consists of irregular particles. Wormhole-like pores are clearly observed in each of the particles. UKH6-1 consists of spherical particles. It is difficult to observe the presence of mesopores in this sample. This is consistent with the weak intensity of the first peak in the XRD pattern of UKH6-1. The spherical particle shape is due to the presence of a large amount of ethanol, which was addressed before (see Chapter 6).

Nitrogen sorption data and the pore size distribution (PSD) of UKA6 are shown in Figure 7.9. No obvious sharp inflection can be identified in the isotherm plots. However, a narrow pore size distribution with size 2.18 nm at the maximum is observed in the PSD of this sample. The lack of sharp inflection in the isotherm is due to the small pore size, which is near the boundary between micropores and mesopores. This makes the isotherm look like Type I, which is typical for microporous materials. Nitrogen sorption data and the pore size distribution of UKH6-1 are shown in Figure 7.10. This sample has narrow
pore size distribution with the size 2.19 nm at the maximum. By comparing the PSDs of UKA6 and UKH6-1, we can see that the peak intensity in UKH6-1 is much lower than that in UKA6. This confirms that there are fewer uniform mesopores in UKH6-1 than those in UKA6 as indicated by XRD and TEM.

For both of the samples, no ordered pattern was observed. Different conditions have been tried with HFHexPC as the template. No ordered pattern was obtained so far. This indicates that it might be impossible to produce porous silica with ordered pore structures from this surfactant.

7.3.3. HFOPC templated sol-gel process

Cationic fluorinated surfactants with four and six carbons in the chains have been employed to synthesize nanoporous silica in previous sections. No ordered pore structure was observed for any sample. In order to investigate the chain length restriction for ordered silica, we synthesized another fluorinated surfactant with increased chain length (F6H2). This surfactant was used as the template for nanoporous silica in both aqueous and ethanol/water solutions.

Before attempting to synthesize materials, we used polarization contrast optical microscopy to rapidly scan the phase behavior of HFOPC. HFOPC was reported to able to form globular micelles near its cmc.\(^\text{43}\) HFDePC has been reported to form hexagonal, mesh phase, and lamellar phase.\(^\text{30}\) Therefore, we could not be sure a priori whether our surfactant would be able to form conventional pore structures such as hexagonal close packed cylinders. Figure 7.11a shows the results of a flooding experiment, in which a solid crystal of surfactant was surrounded with deionized ultrafiltered water. The solid material was initially near the top center of the figure, so the concentration decreases moving away from the point. The micrograph was collected very shortly after the water was introduced. Moving outward, transitions are seen from a lamellar structure (near the center) to an isotropic liquid crystal phase (the black band) to a hexagonal close packed phase, to an isotropic micellar phase.

Samples were also prepared of well defined composition and allowed to equilibrate at room temperature (22 \(\pm\) 1 °C) for 72 hours. Figure 7.11b shows that a 50 wt% solution in water has a hexagonal close packed (HCP) structure, as indicated by the fanlike texture.
The 60 wt% solution also has a HCP structure (not shown). Figure 7.11c shows that a 70 wt% solution of HFOPC in water has a lamellar structure, indicated by the “streaky” appearance of the birefringence texture. This rapid screening study of the phase behavior of the surfactant suggests that it may be possible to prepare a material with HCP, isotropic liquid crystal, or lamellar structure.

With the confirmation that our surfactant is able to form ordered mesophases at room temperature, we discuss the synthesis. Samples UKA8 and UKH8-1 were prepared in aqueous and ethanol/water solution respectively. The XRD pattern of UKA8 is shown in Figure 7.12. The pattern clearly shows evidence for three diffraction peaks which are indexed according to a 2D hexagonal close packed (HCP) structure. The unit cell size for the 2D HCP structure is $3.28 \pm 0.01$ nm. The diffraction peaks are relatively broad, and from the Scherrer equation, we estimate a scattering domain size of approximately 13 nm. Contrasting this, MCM-41 prepared using octyltrimethylammonium bromide has a uniform pore size, but no evidence of higher-order diffraction peaks due to well-defined order $^{38}$.

TEM confirms the presence of cylindrical pores with 2D hexagonal symmetry. Figure 7.13 shows two representative images of UKA8 after surfactant extraction. Figure 7.13a shows a direct image of the 2D HCP structure. A Fourier transform of this region (inset) shows six spots characteristic of a 2D HCP structure. Figure 7.13b shows a region with layers of light and dark stripes. The Fourier transform of this region (inset) shows two spots characteristic of a lamellar structure. However, the image is also consistent with a 2D HCP cylindrical structure viewed from the edge of the cylinders. The spacing between layers is consistent with the 2D HCP (100) d-spacing measured by XRD. There is no indication from XRD or from TEM sampling that lamellar regions are actually present in our sample. The observation of small oriented domains in the TEM images is consistent with the broad XRD peaks observed in Figure 7.12.

The nitrogen sorption data for UKA8 is shown in Figure 7.14. This type IV isotherm has an inflection at $p/p_0 = 0.116$, suggesting that capillary condensation in uniform pores is occurring. To learn more about the pore structure, we prepared and analyzed an $\alpha_s$-plot according to the procedure of Sayari et al.$^{38}$
Analysis of the $\alpha_s$ plot determines features of the structure of these materials (Figure 7.15). We observe the same features as have been observed for other mesoporous silicates. A line fit through the data at low $\alpha_s$ passes through the origin, indicating that the product does not contain micropores larger than the size of a nitrogen molecule. Pore properties are reported in Table 7.5.

Availability of well-defined porous silica has recently led to improved methods for determining the size of cylindrical silica pores by nitrogen adsorption. A modified BJH approach (the KJS method) has been shown to give accurate estimates of pore size for MCM-41 materials. In Figure 7.14, we show the pore size distribution calculated using the KJS modified BJH method. The peak pore diameter, $d_{KJS}$, is given in Table 7.5. Consistent results are found using non-local density functional theory values, based on the position of the inflection in the isotherm ($d_{NLDFT}$), or from a simple geometric calculation based on the assumption of cylindrical pores.

Values calculated by the KJS modified BJH method, NLDFT, and geometric methods are all consistent with a pore diameter of 2.62 nm. This disagrees with the prediction of the often-used BJH method, 1.9 nm. The BJH method is known to underpredict pore diameters near the micropore-mesopore boundary so other estimates can be considered to be more reliable. A similar pore diameter was recently reported when a large amount of the cosurfactant butylamine was added to an MCM-41 synthesis solution, but the long range ordering of that material was limited (as indicated by only two diffraction peaks). The thickness of the pore walls of UKA-8 could be calculated from the pore size and cell parameter. Based on the pore size estimated above, this gives an approximate wall thickness of 0.7 nm.

To determine whether different pore structures could be obtained with HFOPC, a series of samples UKA8S-1, UKA8S-2, UKA8S-3, and UKA8S-4 were prepared with the only difference in the initial surfactant concentration (see Table 7.2). The sample UKA8S-3 is the same sample as UKA8.

Isotherm plots and PSD of these samples are compared in Figure 7.16. XRD patterns of these samples are shown in Figure 7.17. Pore properties are compared in Table 7.5. A hexagonal pattern was identified for UKA8S-1, UKA8S-2, and UKA8S-3 (Figure 7.17). This indicates that stable hexagonal structure could be formed in a large range of
surfactant concentration (6.2 mmol/L–59.0 mmol/L). Only one broad peak was observed in the XRD pattern of UKA8S-4. This pattern shows that this sample has a uniform pore size without good long range ordering. All samples have narrow pore size distributions. With an increase of the amount of surfactant, the PSD became sharper at first (from UKA8S-1 to UKA8S-3) and then broader (from UKA8S-3 to UKA8S-4). The increase of the sharpness from UKA8S-1 to UKA8S-3 is reasonable since there should be more surfactant/silica aggregates formed with the increase of surfactant. This leads to the creation of more uniform mesopores in the material. This explanation is supported by the trend of micropore volume. With the increase of surfactant, the micropore volume decreases (Table 7.5). Micropore volume can be attributed to porous silica formed without surfactant templating. The sudden loss of sharpness of the PSD from UKA8S-3 to UKA8S-4 indicates that the pore structure becomes less ordered. This is consistent with the observation from the XRD patterns (Figure 7.17). It is possible that lamellar pore structure was formed in UKA-8S4. The collapse of the lamellar structure would destroy the ordered pore structure and would lead to the formation more micropores. A large micropore volume was identified in UKA8S-4, which is consistent with the possibility that mesopores collapsed. The pore size of UKA8S-4 also supports this possibility. The size of UKA8S-4 is 2.38 nm, while that of UKA8S-3 is 2.62 nm. The small pore size in UKA8-S4 may be due to using an improper pore shape model to calculate the PSD. For this sample, a cylindrical shape is assumed. This is inconsistent with the pore shape that would be expected for a sample formed by the collapse of a lamellar silica-surfactant composite. The presence of slit pores in this case would decrease the estimated pore size.

We have found so far that several samples were prepared in aqueous solution that have ordered hexagonal structure. This is consistent with the hexagonal phase formed by HFOPC in aqueous solution. The possibility to form ordered structure in ethanol/water solution is also investigated here. UKH8-1 was prepared in ethanol/water solution. The XRD pattern of this sample shows only two peaks. (Figure 7.18) This pattern indicates that this sample either has a lamellar structure or a wormhole-like pore structure. No lamellar pattern was identified under TEM. Instead, all particles have wormhole-like pores. (Figure 7.19) This means that this sample doesn’t have long-range ordering similar to sample UKH6-1. For UKH8-1, all particles are spherical just as they are for UKH6-1.
Isotherm plots and pore size distribution (PSD) of UKH8-1 are shown in Figure 7.20. This sample has a high surface area and narrow pore size distribution. The pore size is 2.43 nm, which is smaller than the pore size of the sample synthesized using HFOPC in aqueous solution (UKA8, 2.62 nm).

In this section, we have shown by using a partially fluorinated octylpyridinium chloride surfactant, it is possible to synthesize silica particles with 2.62 nm, 2D hexagonal close packed cylindrical pores in aqueous solution. This structure can be obtained with a wide range of surfactant concentrations. The pore size was confirmed by several theoretical interpretations of the nitrogen adsorption data. The long-range 2D hexagonal ordering was confirmed by XRD and TEM. The hexagonal ordering is decreased by using an excessively large HFOPC: Si ratio, or by adding ethanol. The former can be explained by a hexagonal →lamellar transition. The effect of ethanol can be explained by a reduction in the aggregation number of the HFOPC micelles.

7.3.4. HFDePC templated sol-gel process

HFDePC can form several phase structures in aqueous solution. It has been identified to form micelles, hexagonal, rectangular and mesh phase with the increase of the surfactant concentration in aqueous solution.43

In this section, we will discuss materials prepared in different conditions using HFDePC, to investigate the possibility to obtain novel pore structures. Both aqueous and ethanol/water systems will be studied. Two materials with novel pore structures will be shown to form in aqueous solution. We will first address the preparation of these two materials, followed by discussion of the effect of surfactant concentration on the pore structure and particle morphology. One material synthesized in aqueous solution with the same conditions as UKA8 will be discussed for comparison with materials discussed in other sections. To investigate the effect of surfactant concentration on the pore structure, all process parameters and drying conditions will be kept the same to ensure that the difference in the pore structure is only due to the effect of surfactant concentration.
7.3.4.1 Synthesis of elongated particles with random mesh phase structure

In this subsection, we report a synthetic route to silica with a random mesh phase pore structure by liquid-phase one-step synthesis starting from a molecular precursor. Pore structures similar to mesh phase structures have been made by pillaring of clays and microporous solids.\textsuperscript{80-84} Like random mesh phases, the pillars between layers in these materials are randomly arranged. However, these materials are synthesized by swelling naturally occurring or synthetic layered minerals and then introducing metal oxide particles.\textsuperscript{81} Our one-step synthesis procedure instead produces particles by the direct co-assembly of surfactants and silica into an ordered mesophase.\textsuperscript{14}

A silica material, sample UK-2, was synthesized at room temperature by precipitation of tetraethoxysilane in the presence of HFDePC from an aqueous ammonia solution. The initial composition is reported in Table 7.3.

The XRD patterns of the as-synthesized and extracted samples are shown in Figure 7.21. Because the background is strong in our samples, we show for comparison (trace a) the XRD pattern of amorphous silica formed by precipitation of tetraethoxysilane in the presence of sodium dodecyl sulfate, followed by calcination. This sample has no reflections in the range of 20 in Figure 7.21, so only the background of the holder is shown. The pattern for the as-synthesized UK-2 (trace b) has low contrast because of the presence of fluorine (see Figure 7.2), but still indicates a single reflection. After extraction (trace c), the pattern has three distinct reflections. The two reflections at higher angles are indexed as (001) and (002) reflections of a layered structure with a layer spacing of 3.3 nm. The weak reflection at low angle is consistent with scattering from silica micropillars between the layers, but because of the strong background, there is significant uncertainty in the d-spacing. Based on the apparent peak position, we can place a lower bound on the average pillar spacing of 4.5 nm. We would not be able to see contributions to the XRD pattern from pillars spaced more than 6.1 nm apart under any circumstances, and contributions from pillars spaced between 6.1 and 4.5 nm apart may be underestimated because of the background. We will use STEM (below) to measure the pillar spacing more precisely. In any event, because we do not find a set of reflections that would indicate a periodic 3-dimensional arrangement of silica micropillars, the low-angle XRD reflection is interpreted as coming from a random mesh
phase (rather than trigonal or tetragonal). In related work with organic polyelectrolyte complexes with fluorinated surfactants, random mesh phase aggregates have been found frequently. 31

Another possible interpretation of the XRD pattern is a mixture of a lamellar phase (spacing 3.3 nm) and a wormhole-like phase (average pore spacing ≥ 4.5 nm). However, an ordinary lamellar structure would be expected to collapse upon heating, even if it were able to survive surfactant extraction. The thermal stability of this material was checked by heating two separate samples, one at 550 °C in air for 4 hours, and the other at 800 °C in air for 2 hours. Figure 7.21d shows that this sample was stable at 550 °C, which is consistent with a mesh phase but not with a lamellar phase. The mesh phase begins to collapse only upon heating at 800 °C (Figure 7.21e).

SEM images of sample UK-2 (Figure 7.22) show that the material is composed of elongated particles that are loosely aggregated into clusters (either in solution or during the process of drying a sample for electron microscopy). Low magnification TEM (Figure 7.23a) confirms the elongated particle morphology. Some of the particles are open at one end, as indicated by the small arrows in Figure 7.22. These particles are not hollow, but instead have shallow depressions at their ends. These appear to result from a “shell” of silica extending beyond the particle core – as a result of either the growth mechanism or of fracture. TEM and STEM images at higher magnification (Figures 7.23b/c) are consistent with a rough shell of amorphous silica surrounding particles with ordered cores.

High magnification TEM clearly shows the layered mesopore structure of these particles. Figure 7.23b shows that each elongated particle has a very well ordered layered pore structure. The region that appears to be amorphous in the lower left corner of Figure 7.23b is the result of several particles overlapping rather than a mixture of phases. When non-overlapping particles are visualized, they always have a layered, rather than wormhole-like, structure in TEM. The layered pattern is more clearly shown in the dark field STEM image of a single particle shown in Figure 7.23c. Remarkably, the slit-shaped pores in these particles are always found to be orthogonal to the main axis of the particle. Figure 7.23d shows a high magnification dark field STEM image, providing a close look at the layered structure. Silica pillars can be seen clearly between the layers.
The distance between the pillars was estimated by image analysis using all clearly resolved pillar spacings sampled from the entire width of the particle. The histogram of the spacing distribution is shown in the inset of Figure 7.23d. The distribution is broad, with a mean spacing of 6.3 nm and a standard deviation of 2.1 nm. These spacing estimates could be underestimated because Figure 7.23d is a 2D projection of a 3D structure, but this effect should be minimal because STEM provides clear contrast only within a shallow depth of field. The measured spacings are consistent with the position of the first XRD peak, within the described uncertainty. The distance between adjacent silica layers (3.1 ± 0.1 nm) is also consistent with the d-spacing for the (100) reflection of the mesh phase structure from XRD.

As a final confirmation of the mesopore structure, N\textsubscript{2} adsorption-desorption isotherms were collected for the extracted sample. The isotherm of UK-2 (Figure 7.24) is of type IV,\textsuperscript{85} while the isotherms of microporous, layered materials such as pillared clays are usually of type II, and sometimes display H4 hysteresis loops due to a platelet morphology.\textsuperscript{80,85,86} This confirms that our material is mesoporous (giving rise to the sharp inflection of the type IV isotherm) and does not have a platelet morphology (consistent with Figure 7.22). The upturn in adsorption at high relative pressure is probably due to nitrogen condensation within the clusters of particles illustrated in Figure 7.23a. This isotherm was converted to an alpha plot\textsuperscript{38} to determine pore texture characteristics. We determine a total surface area of $S_\text{t} = 765 \text{ m}^2/\text{g}$, external surface area of $S_\text{ext} = 338 \text{ m}^2/\text{g}$ and primary pore volume of $V_p = 0.44 \text{ cm}^3/\text{g}$. The pore size distribution (PSD) was calculated from the adsorption branch of the isotherm by the BJH method with a slit pore geometry and the modified adsorbed film thickness equation of Sayari et al (see Appendix I).\textsuperscript{38} The results, shown in the inset of Figure 7.24, indicate a slit pore width of 2.0 nm. This estimate is consistent with the slit pore width estimated from the average surface area and pore volume (~2.1 nm).

To summarize, after characterization by XRD, electron microscopy and nitrogen sorption, the material UK-2 has been found to have a novel mesh phase mesopore structure with large surface area and pore volume. It is composed of elongated particles with slit pores oriented orthogonal to their long axis, rather than the plate-like morphology that one would expect for a layered material. As we will discuss below, the
elongated particle shape is consistent with the tactoid shape adopted by many dispersed liquid crystals. This can be explained by the tendency of fluorinated surfactants to form bilayer fragments, such as disc-shaped micelles. Strong interactions between the elongated edge of disc micelles and exposed layers of a particle may promote the formation of elongated particles, rather than lateral growth. Our success using HFDePC to make a novel material further suggests that unexplored potential remains for other fluorinated surfactants to be used as pore templates for novel ceramic materials.

7.3.4.2 Synthesis of silica vesicles with mesoporous unilamellar shells

Vesicles are important self-organized structures that find increasing use in drug delivery and biomimetic applications. The bilayer shells of ordinary vesicles are fragile, and prone to dissolution and collapse as solution conditions change. If comparable solid structures could be formed using biocompatible materials such as silica, the resulting materials would be stable replacements useful for drug delivery, or for novel applications such as high-capacity gas adsorption. Vesicle-like hollow silica particles (which we will call “silica vesicles”) have been synthesized through sol-gel polymerization in the presence of nonionic and catanionic surfactants. In a few cases, cationic surfactants were also used to create silica vesicles. However, special processes were needed to create the vesicles, and most of them had multilamellar shells. Hubert et al. described the only example to date of direct coating of pre-existing unilamellar vesicles to generate single-walled silica vesicles in an extrusion process. The pore structure of the shells of these vesicles was not directly characterized, but they are expected to be microporous since they consist of solid concentric shells of silica. In this subsection, we report a novel material with ordered mesoporous single-walled vesicle structure which is prepared by co-assembly of silica with a fluorinated surfactant template. Fluorinated surfactants have begun to be employed as pore templates for ceramics, but there have not yet been reports of spontaneous formation of vesicle-like structures. By changing the shearing force during synthesis, we will show that elongated silica particles with multiple hollow chambers are obtained. This is the first time that this multi-chambered structure has been reported to our knowledge.
Three samples were prepared with the same composition using HFDePC as the surfactant template, but with different stirring rates. They were indexed as FSV-S1 (~150 rpm), FSV-S2 (~300 rpm), and FSV-S3 (~450 rpm). Slower stirring (< 150 rpm) resulted in incomplete hydrolysis of the tetraethoxysilane precursor, and a separate oily phase would remain unmixed even after 24 hours. All solutions changed from colorless to brown after the addition of ammonia. The brown color became darker with time. For FSV-S1, a single clear phase was formed after precursor addition, and no turbidity was observed until after 1 hour. For FSV-S2 and FSV-S3, both solutions became turbid within several minutes. FSV-S3 became turbid faster than FSV-S2.

A representative SEM image of sample FSV-S1 is shown in Figure 7.25. Most of the particles are intact spheres with diameters < 100 nm. Several particles (indicated by arrows) are broken, allowing one to see that they are hollow particles with relatively thick, rough shells. Representative TEM images of FSV-S1 are shown in Figure 7.26. Since TEM only shows two dimensional projections of the entire thickness of the sample, we need to imagine the real structures from these images. The dark double curve at the edge of each particle is consistent with each silica vesicle having one wall with a bilayer of dense silica (Figure 7.26a). Some of the particles have elongated or defective spherical shapes. A higher magnification image of a few particles (Figure 7.26b) shows more clearly that there is a uniform layer of pores within the wall of the vesicles (leading to the double-image at the edge of the TEM projection of each particle). Weak stripes and dot patterns can be seen in the shells of these silica vesicles, in the projection across the shells (towards the center of each particle). These patterns indicate that the walls of the silica vesicles are actually mesoporous. The mesoporous single-walled vesicle structure is further confirmed by dark-field STEM imaging. A representative STEM image is shown in Figure 7.27. Consistent with the SEM and TEM, Figure 7.27 clearly shows that each particle has a hollow single wall (the double white rings at the edge of each particle). The density of the projection from the interior of each particle is low because they are hollow. Weak stripe or dot patterns are observed within the shells of the hollow particles, confirming that the shells are mesoporous. These patterns suggest that the vesicle-like shells were formed by aggregation of silica with HFDePC micelles (cylinders or discs – see below for more discussion of this point).
Sample FSV-S2 was prepared at a higher stirring rate, and contains many single-walled spherical vesicles similar to those in Figures 7.25-7.27. Some particles, however, seem to be connected together to form elongated particles made up of several flattened silica vesicles. At an even higher stirring rate (sample FSV-S3), the sample is made up almost entirely of elongated particles made from flattened silica vesicles. An SEM image illustrating the elongated morphology of FSV-S3 particles is shown in Figure 7.28. Like FSV-S1, some of the particles are broken, and can be clearly seen to be hollow. A low-resolution TEM image of this sample (Figure 7.29a) shows that most of the particles are elongated and have multiple hollow chambers. Presumably, these chambers are formed by fusion of several silica vesicles in solution. A high magnification TEM image (Figure 7.29b) clearly shows that the elongated particles have mesoporous shells. Dark-field STEM (Figure 7.29c) confirms that these particles are hollow, and clearly shows the high-density silica walls that divide them into several chambers.

Nitrogen sorption data for the three samples are shown in Figure 7.30. All samples have type IV isotherms with large H3 hysteresis loops. This type of hysteresis loop has traditionally been associated with slit-like pores, but more recently has also been observed in structures consisting of voids surrounded by a mesoporous matrix or hollow particles with mesoporous walls. The sharp inflection in the desorption branch occurs because emptying of the smaller mesopores in the shells controls the evaporation of nitrogen from the large vesicle cavities. However, an exact pore size cannot be determined from this branch because there is a lower limit in the desorption pressure dictated by the properties of the adsorbing fluid. The pore size distributions (PSDs) from the adsorption branch of all samples are also compared in Figure 7.30. Peaks at the pore size corresponding to the expected surfactant micelle size (around 3.6 nm) are observed for all three samples. The PSD of FSV-S1 has two peaks in the small pore size region (<10 nm). The larger (5.2 nm) pore size is consistent with the spacing of the bilayer shells in the silica walls, as seen in Figure 7.27. With an increase of the stirring rate, the 5.2 nm pores disappear in favor of the 3.6 nm pores. FSV-S3 has only 3.6 nm pores. This trend is consistent with the transformation of the shells from porous bilayers to the uniform porous walls shown in Figure 29b.
The PSDs of samples FSV-S1 and FSV-S2 also contain weak peaks at much larger pore sizes. The maximum in the PSD at large mesopore size is at 60 nm for FSV-S1, and at 40 nm for FSV-S2. No clear large mesopore peak could be discerned in the PSD of FSV-S3. The 60 nm pores in the PSD of FSV-S1 is roughly consistent with the inner diameter of the silica vesicles indicated by STEM (Figure 7.27). The narrow large-mesopore PSD of FSV-S1 confirms the narrow size distribution of the silica vesicles in this sample. FSV-S2 is a mixture of single-walled silica vesicles and elongated multi-chambered particles. The narrow PSD may come from the former components. The lack of a clear peak in the large-mesopore range for FSV-S3 is probably due to a broader distribution of chamber sizes in this sample.

The formation mechanism of these silica vesicles is interesting to consider. The aggregation behavior of HFDePC was studied in detail by Wang et al., and no vesicles were found by cryo-TEM in aqueous solutions, even well above the critical micelle concentration. The addition of strongly adsorbing salt may help to form bilayers, but a simple salt solution (such as the ammonium hydroxide solution present prior to precursor addition) would be expected only to promote cylindrical micelle formation. Therefore, it is most likely that the vesicles are formed by the direct co-assembly of silica with HFDePC rather than coating pre-existing vesicles with silica. Such silica-induced vesicle formation has been observed directly by cryo-TEM in a catanionic templated mixture. The mesopore patterns in the walls of the vesicles are consistent with co-assembly of silica with cylindrical or disc-like HFDePC micelles. To support this interpretation, we prepared particles with the same molar composition, but using tetramethoxysilane (TMOS) as the precursor. The resulting particles have 2D hexagonal close-packed (HCP) cylindrical pores under TEM (data not shown), which demonstrates that the silica vesicles do not form by coating of pre-existing vesicles. The difference between the products may be explained by the difference in hydrolysis rates between the precursors. TMOS hydrolyzes quickly, and provides a large concentration of silicates to co-assemble with HFDePC into organized HCP particles. TEOS hydrolyzes more slowly, leading to a smaller concentration of silica species that co-assemble with HFDePC micelles into vesicle-like aggregates. We interpret the appearance of elongated multi-chambered hollow particles at higher stirring rates as being due to (1) a faster rate of TEOS
hydrolysis and (2) more frequent collisions between silica-surfactant aggregates. Both of these changes allow the vesicle-like particles to fuse prior to complete rigidification, while at a lower stirring rate they are able to solidify completely as discrete particles.

To summarize, we have reported the synthesis of novel spherical single-walled silica vesicles with mesoporous shells through a surfactant templated sol-gel process. The recipe of this sample is similar to one giving silica with a mesh phase structure (see section 7.3.4.1) except the surfactant concentration is much lower, and the stirring rate is controlled more exactly. The absence of vesicles in prior studies of the phase behavior of the surfactant in water (without TEOS) suggests that the silica vesicles form by co-assembly of fluorinated surfactant micelles with silica. As the shearing rate during synthesis is increased, the silica-surfactant aggregates merge to form elongated multi-chambered particles with mesoporous shells. This is the first example of such a structure that we are aware of.

7.3.4.3 Synthesis of UKA10

UKA10 was synthesized with the same conditions as UKA8 and UKA6. It represents a departure from the previous two samples because it consists of rod-like particles with a highly ordered layered pore structure oriented perpendicular to the main axis of the rods (Figure 7.31). The XRD pattern (Figure 7.32) and the TEM image for this sample are very similar to that reported for sample UK-2 (section 7.3.4.1), which was confirmed by STEM to have a mesh phase structure, with silica micropillars holding apart continuous silica layers.

The nitrogen sorption data for UKA10 is shown in Figure 7.33. The pore size distribution (PSD) for this sample was calculated based on a silt pore shape. The PSD for this sample is sharper than that for UK-2 (Figure 7.24). Pore properties of this sample are shown in Table 7.6. This sample has large mesopore volume (0.58 cm$^3$/g) and high surface area (850.7 m$^2$/g).

7.3.4.4 Effect of HFDePC concentration on the pore structure and particle morphology

When used as a pore template, HFDePC has been found to form novel particles by room temperature precipitation, namely, cigar-shaped particles with random mesh phase
pores (section 7.3.4.1) and hollow vesicle-like particles with mesoporous shells (section 7.3.4.2). The main difference between the conditions leading to these two structures is that the initial surfactant concentration leading to the vesicle-like structure is lower than that leading to the random mesh phase structure. This order of structures is unusual. When a cationic hydrogenated surfactant such as CTAB acts as the template, the general pore structure trend is from wormhole-like to hexagonal to lamellar as the surfactant concentration increases.\textsuperscript{100,101} Under certain circumstances, bicontinuous cubic structures form at conditions between those giving hexagonal and lamellar structures.\textsuperscript{102,103} To gain a better understanding of why unusual structures are found in HFDePC templated silica, we study here the concentration dependence of pore and particle architecture.

In this subsection, we will describe the preparation of a series of samples with the only difference being the surfactant concentration. We will show an unusual trend as the surfactant concentration increases. The pore structure will be shown to change from 2D close-packed cylinders to vesicle-like to random mesh phase to disordered. The corresponding particle structures will be found to change from round / uniformly mesoporous to elongated / hollow to elongated / uniform to round / uniform. Studies of specimens isolated from the solutions early in the synthesis process will show that these structures form spontaneously due to the preferred structure of the co-assembled silica-surfactant aggregates, rather than forming through an asymmetric growth process.

In a cationic hydrogenated surfactant templated sol-gel process, precipitates are usually obtained soon after the addition of TEOS.\textsuperscript{104} On the other hand, silica particles prepared with cationic fluorinated surfactants and TEOS often consist of suspended colloids instead of precipitates. This indicates either that condensation is not as extensive as with a hydrogenated surfactant, or that small particles are stabilized by fluorinated surfactants. A lower extent of condensation might be reached because, while interactions between silicate anions and the cationic surfactant are sufficient to induce particle formation, repulsion between the silica species and the surfactant tails may delay or prevent hydrolysis and condensation. On the other hand, the small particle size may be dictated by the high surface activity of the fluorinated surfactant.\textsuperscript{105}

Because of the contradictory interactions between the silica species and the head or tail of the fluorinated chains, the pore properties and particle morphology might be easily
affected by the process conditions. Investigations in our lab have shown that the pore properties of these materials are sometimes affected by stirring speed, TEOS addition speed, amount of solution, and reactor size. Even the drying conditions influence the pore properties. The effect of different stirring speeds on the particle morphology was previously investigated for vesicle-like particles prepared using HFDePC (see section 7.3.4.2). With very slow stirring, unilamellar vesicle-like silica particles are obtained. Increasing the stirring speed leads to agglomeration of the vesicles into elongated multi-chambered particles with porous shells.

To ensure that the differences observed in the pore structure and particle morphology is only due to the change of surfactant concentration, two series of samples were prepared. In each of the series, all reaction conditions were the same except the initial HFDePC concentration. One series (samples UKA10-1 to UKA10-3) was made with larger batches than the other series (samples UKA10-4 to UKA10-8). Samples UKA10-3 and UKA10-4 had the same composition.

Representative TEM images of samples UKA10-1 through UKA10-3 are compared in Figure 7.34. For sample UKA10-1, uniform mesoporous particles with ordered hexagonal patterns are observed. Most particles in this sample are found to be round (somewhat deformed spheres) by TEM. Both stripe and spot patterns are observed, corresponding to view across and along close-packed cylindrical pores, respectively. As illustrated by the particles in the lower left corner of Figure 7.34a, the cylindrical pores are highly curved due to the small particle size. The spot pattern in the upper right particle is not a perfect 2D hexagonal pattern, but instead is compressed in one direction, similar to a rectangular phase.  

Hollow cells are observed inside of the particles isolated for sample UKA10-2. These hollow cells appear to have been captured within larger solid particles. Ordered patterns are still evident in the walls of this sample. The particles in sample UKA10-2 are larger and more elongated compared to those in sample UKA10-1. Sample UKA10-3 consists of particles which are more elongated and which have multiple hollow cells arranged along their axes. No ordered pattern was observed in the shell walls, but they are mesoporous. The large hollow cells were shown to be formed by coalescence of vesicle-like silica particles in our preliminary study of this system (see section 7.3.4.2).
Thus in this series, TEM suggests that at the lowest HFDePC concentration the product has defective close-packed cylindrical pores, and increasing the concentration of HFDePC gradually induces the co-assembly of silica and HFDePC into hollow, vesicle-like structures which coalesce into elongated particles.

The change of the particle shape inferred from the TEM images is confirmed by SEM. Most of the particles in sample 1 are rough round particles under SEM (Figure 7.35). Sheet-like particles are also identified, but they are much rarer than the round particles. Elongated particles are confirmed in sample UKA10-3 under SEM, similar to those shown in Figure 7.28.

XRD patterns were collected for samples UKA10-1 through UKA10-3, but no reflections are observed for any of them. This is consistent with the small particle size and highly curved pore structures observed by TEM. The absence of reflections shows that there are no large, well-ordered domains in these samples, in spite of the short-range close packed order found by TEM.

Nitrogen sorption isotherm plots of the first three samples are reported in Figure 7.36. All three samples have weak inflections indicating the presence of uniform mesopores. Type H3 hysteresis loops are observed for samples UKA10-2 and UKA10-3. This type of hysteresis is associated with large meso- or macro-pores surrounded by walls with smaller meso- or micro- pores. This interpretation is consistent with the hollow cells observed inside of the particles in Figure 7.34. The hysteresis of sample UKA10-3 is larger than that of sample UKA10-2, which is consistent with a larger number of hollow cells in this sample. The mesopore size distributions for the three samples show pores of consistent diameter (~2.8 nm for samples UKA10-1 and UKA10-2, and ~3.2 nm for sample UKA10-3), and a decrease in mesopore volume as more hollow cells are produced in this series.

Representative TEM images for samples UKA10-5 through UKA10-8 are shown in Figure 7.37. Sample 4 has the same composition as sample UKA10-3 except that a larger amount of reactants was used to prepare the latter. Consistent with our expectation, the particles in both samples are very similar. Sample UKA10-4 consists of elongated particles with multiple hollow cells (TEM not shown). As the concentration of HFDePC increases, elongated particles with fewer hollow cells are observed in sample UKA10-5.
In sample UKA10-6, only uniform mesoporous elongated particles (tactoids) with silica layers oriented perpendicular to the particle axis are observed. This pattern was identified as a random mesh phase structure before (see section 7.3.4.1).¹ No hollow cells are apparent for this sample. In sample UKA10-7, a layered pattern is still observed, but the particles are shortened compared to those in sample UKA10-6. A disordered pore structure is observed for sample UKA10-8. The particles in this sample are aggregates of small, round nanoparticles. The particle sizes in this sample are obviously smaller than those in sample UKA10-7. So in this series of samples, TEM indicates that as the concentration HFDePC increases, first hollow vesicle-like cells disappear in favor of uniform mesh-phase pores, and then the elongated particles shorten until they become almost spherical.

SEM images of samples UKA10-4 and UKA10-6 confirm that these samples consist of elongated particles (see sections 7.3.4.1 and 7.3.4.2).¹,⁵ SEM images of samples UKA10-7 and UKA10-8 (Figure 7.38) show that both of samples have rough, spherical particles. These spherical particles flocculate together to form large aggregates. Smaller particles are observed in sample UKA10-8 than in sample UKA10-7. These observations are consistent with the findings from TEM.

XRD patterns were collected for samples UKA10-4 through UKA10-8. Two reflections with a d-spacing ratio of 2:1 were observed in the XRD patterns of samples UKA10-6 and UKA10-7. This pattern is consistent with a lamellar pore structure with randomly arranged pillars between adjacent silica layers. This structure is the same as the random mesh phase pore structure described before.¹ The lack of a weak low-angle peak representing scattering from pillars within the pore layers may be due to poor ordering of the pillars in the samples prepared under the current conditions. No reflections were observed for either as-synthesized or extracted sample UKA10-8. This is consistent with the disordered pore structure observed by TEM.

Isotherm plots and pore size distributions of samples UKA10-4 through UKA10-8 are compared in Figure 7.39. Sample UKA10-4 has a similar isotherm to sample UKA10-3. Both of them show a large H3 hysteresis loop indicating the presence of a large number of hollow cells. As the HFDePC concentration increases in this series, the hysteresis loop disappears and textural porosity is indicated by the upturn at high relative
pressure. The pore size distributions of all samples indicate comparable pore sizes (~3.2 nm), but the mesopore volume increases significantly on going from sample UKA10-4 to sample UKA10-7. The mesopore volume declines again in sample UKA10-8 due to its disordered pore structure. With the increase of HFDePC in this series, the evolution of the pore structure and particle morphology is the reverse of the trend for samples UKA10-1 through UKA10-3. Vesicle-like cells are lost in this series and elongated particles shorten into spherical-like particles as the HFDePC increases.

Of all the particle morphologies observed, the elongated mesh phase structures are the most difficult to rationalize in terms of known mesopore architectures. To better understand their formation mechanism, we examined cold-dried TEM samples. These samples were prepared by placing a drop of solution onto a liquid nitrogen-chilled (-2 °C) lacey carbon TEM grid resting on a lint-free absorbent tissue. The solution was quickly thinned by capillary suction of solvent into the tissue, and after thinning was dried by forced air. The samples were observed in the TEM instrument within 4 hours of preparation. We have to be wary of drying artifacts with this procedure, but we have previously been able to observe the development of micelle ordering in precipitated particles by this method (see Chapter 6).107

Cold-dried samples were prepared to examine the relationship between surfactant co-assembly and morphology development for sample UKA10-6. Four specimens were prepared with aliquots withdrawn from the synthesis solution 30 seconds, 2 minutes, 4 minutes, and 8 minutes after the dropwise addition of TEOS. The results are shown in Figure 7.40. After 30 seconds, surfactant-silica aggregates were present in the sample. A few silica vesicles (Figure 7.40a) were identified as well as a large number of uniform particles without any defined shape (Figure 7.40b). No ordered aggregates were observed at this time. The formation of these few vesicles may be due to a lower surfactant: Si ratio in local areas due to the insufficient stirring, which will be discussed in more detail below. No vesicle-like structures are identified in the product, so the structures isolated after 30 sec. must be soft enough to re-organize. In the next sample withdrawn (2 min, Figure 7.41), very few vesicle-like structures are still observed (Figure 7.41a). However, elongated particles with weak density contrast could already be observed everywhere on the grid. Layers can be identified in each of the weakly condensed particles, which are
oriented perpendicular to the particle axis (Figure 7.41b). The density contrast of the particles increases in the TEM sample isolated after 4 min due to increasing silica condensation (Figure 7.42a). The particles are still cigar-shaped, with surfactant layers oriented perpendicular to their axes. Particles collected after 8 min are still elongated particles, but the micelle structure is difficult to resolve (Figure 7.42b). The reason is most likely that the contrast between highly condensed silica and the surfactant mesophase is low. This experiment shows that the unusual orientation of the micelle layers perpendicular to the axis of these elongated particles emerges immediately after precipitation of the particles and only becomes more fully condensed with time. The elongated structure does not form by anisotropic growth, as we originally hypothesized. The elongated shape of the particles must simply be the thermodynamically favorable shape for this ordered, heterogeneous structure.

The same cold drying procedure was also applied for samples UKA10-1 and UKA10-4. No vesicle-like structure or particles with defined shape was observed for UKA10-1 at 30 seconds (Figure 7.43a). Small dense particles were identified after 2 minutes (Figure 7.43b). These particles became much larger and denser after 4 minutes (Figure 7.43c). No ordered pattern was identified for all these samples. Representative TEM images for UKA10-4 after 2 minutes, 4 minutes, and 8 minutes are shown in Figure 7.44. After 2 minutes, weakly dense particles were observed (Figure 7.44a). After 4 minutes, these particles became denser (Figure 7.44b). After 8 minutes, solid particles as well as hollow particles were identified (Figure 7.44c). The presence of hollow particles is consistent with the final particle morphology of this sample, which has elongated particles with multi hollow cells.

No ordered structure was observed for either UKA10-1 or UKA10-4 in the dried TEM specimens withdrawn after 2 minutes or 4 minutes. For sample UKA10-1, a slow rate of TEOS hydrolysis probably makes it difficult to isolate an ordered specimen with adequate electron density contrast for TEM. For sample UKA10-4, the structures may initially be too delicate to withstand drying. Only after 8 min. of reaction of sample UKA10-4 is the specimen stable enough to be able to isolate hollow structures similar to the final product.
As we mentioned earlier, it was important to use a high stirring rate for all of the samples to ensure a homogeneous distribution of reactants. Because fluorocarbons are both hydrophobic and lipophobic, TEOS is not as readily dissolved and hydrolyzed as it is with hydrocarbon surfactants. Therefore, process parameters such as stirring rate can influence the outcome of the process. We found in the preliminary report (section 7.3.4.2) that stirring can induce aggregation of individual vesicle-like particles into particles with multiple hollow cells. In the more concentrated solutions investigated here, gels can be obtained when the stirring rate is too low to homogenize the solution. To investigate the effect of inefficiency of stirring on the pore structure, sample UKA10-8S was prepared with the same composition as sample UKA10-8, but with larger amount of reactants (and therefore less intense mixing). The top of the solution formed a gel while the bottom was a colloidal dispersion. The layers were separated, filtered, and the surfactant extracted from each.

TEM images of these two samples are shown in Figure 7.45. The sample from the top (UKA10-8ST) contains uniform elongated mesoporous particles as well as a few hollow spherical particles. Both types of particles are coated with thick shells of amorphous silica. These particles appear similar to the types of particles obtained with lower HFDPC:Si ratios\(^1,5\) except that they have been coated with amorphous silica. The sample from the bottom of the vessel (UKA10-8SB) is composed of very small particles with disordered pores. The particle morphology is similar to that of sample UKA10-8.

The cause of the separation of the sample into two types of structures is likely to be the initial insolubility of the precursor, TEOS. Because TEOS has a density of 0.933 g/ml, it preferentially moves to the top of the solution until it is hydrolyzed. Therefore, near the top, the local ratio of HFDPC:Si is lower than the overall ratio. This leads to a distribution of uniform and hollow silica particles. The elongated colloidal particles easily gel because the top of the solution is not strongly sheared. After the gel forms, the remaining TEOS is not able to easily diffuse away, and instead it deposits to form the amorphous silica coating. The lower layer, on the other hand, is well mixed, and has a high HFDPC:Si ratio, which leads to a structure similar to the well-mixed sample 8.

The comparison of samples UKA10-8ST and UKA10-8SB shows that the stirring speed is critical to control the product quality in situations where the TEOS is slowly
hydrolyzed and not readily miscible with the surfactant. The importance of mixing also explains why a few vesicles were observed at the early stage of the reaction in sample UKA10-6. These vesicles may have formed due to insufficient mixing of TEOS oil droplets at early times. A low local HFDePC:Si ratio may have caused these vesicles to form. However, the condensation at this stage was weak enough that the vesicles reorganized into uniform mesh-phase particles with continued stirring. If the stirring were slower, vesicles would probably have been obtained, similar to those observed in sample UKA10-8ST.

To summarize the observations of HFDePC templated silica, the first sample consists of uniform particles with close-packed cylindrical mesopores. The concentration of HFDePC prior to adding TEOS (0.85 g/L) is less than the cmc of the surfactant (1.46 g/L). This indicates that silica-surfactant co-assembly is strong enough to induce micellization and ordering. The micelles are packed into a slightly compressed 2D hexagonal lattice (similar to a rectangular phase), which indicates that the cross section of the micelles may be somewhat asymmetrical.

As the concentration of surfactant is first increased (samples UKA10-1 to UKA10-3), hollow vesicle-like structures are favored. This is consistent with the tendency of fluorinated surfactants to form low-curvature structures such as disc micelles and bilayers. The mesh phases found in the phase diagram of HFDePC are made up of bilayer patches or disc micelles organized within a continuous water layer. Vesicle-like structures are presumed to form because the silica aggregates preferentially with the flatter surfaces of the micelles (where the headgroup density is highest). For micelles that are only somewhat flattened, this leads to co-assembly of HFDePC micelles and silica into sheets, which further organize into vesicle-like particles. The vesicles aggregate to form elongated particles with multiple hollow cells.

As the surfactant concentration increases further (samples UKA10-4 to UKA10-7), hollow cells are lost in favor of mesh phase-like pillared lamellar mesopores. This is consistent with the HFDePC micelles becoming more oblate as the concentration increases. Continued preference for silica at the flatter faces of the micelles would favor structures with more layering, such as the observed mesh phase structure. The layers in the particles are organized into elongated particles in which the surfactant layers are
perpendicular to the long axis of the particles. The formation of such tactoids is a well-known phenomenon in liquid crystal dispersions. A lamellar structure at an interface with an isotropic medium that has no strong preference for either layer would have a lower interfacial energy when the layers are oriented perpendicular to the interface than when they are parallel. Wulff showed that the orientation-dependent surface tension of a layered structure gives rise to elongation in the direction perpendicular to the layers. This is precisely what we see in sample UKA10-6, and similar shapes have been shown more recently to be favorable in small droplets of nematic and smectic liquid crystals. According to this explanation, the reason that sample UKA10-7 consists of particles with a smaller aspect ratio than sample UKA10-6 may be either (a) an increase in surface tension or (b) a decreased tendency for the liquid crystal director (in this case, the orientation of the surfactants) to align parallel to the droplet surface. Either of these changes could result from the aggregation of HFDePC into larger micelles which interact more strongly with silica.

The logical conclusion of this trend would be for the HFDePC to organize into perfect bilayers at the highest concentration. We found no evidence for formation of a lamellar structure, but the concentration did become high enough to allow a disordered bicontinuous pore structure to form (sample UKA10-8).

The unusual sequence of pore structures observed here is probably a consequence of the ability of this particular surfactant to organize into different types of micelles. The next-shortest surfactant in this series, HFOPC (see section 7.3.3), does not form materials with this much structural variety. 2D hexagonal close-packed cylindrical pores are observed across a wide surfactant concentration range from below the cmc to well above. On the other hand, the next-longest surfactant, HFDoPC (see section 7.3.5 below), strongly favors bilayers and it was therefore found to be difficult to form an ordered pore structure at any concentration. Hydrocarbon surfactants tend to undergo a transition directly from cylindrical micelles to bilayers (including bicontinuous cubic intermediate phases), which leads to the usual hexagonal \( \rightarrow \) cubic \( \rightarrow \) lamellar order of phases. The ability of HFDePC to form more oblate micelles as concentration increases may explain the observed hexagonal \( \rightarrow \) vesicle-like \( \rightarrow \) mesh phase \( \rightarrow \) disordered bicontinuous pore structure sequence.
A series of silica particles was prepared by precipitation from aqueous ammonia with different HFDePC:Si ratio. As this ratio increased, the pore structure changed from hexagonal cylinders to vesicle-like to random mesh phase to disordered bicontinuous pores. At the same time, the particle morphology changed from uniform round mesoporous particles to hollow elongated particles to uniform elongated particles to uniform round particles. This is the first time that we are aware of that this sequence of structural transformations has been reported for a surfactant-templated sol-gel process. The formation mechanism of elongated particles with random mesh phase structure was investigated. Elongated particles with highly ordered layers form quickly by co-assembly of silica and HFDePC, rather than by anisotropic growth of the particles. This indicates that unusual arrangement of slit-shaped pores perpendicular to the long axis of the particles is the thermodynamically favorable shape of the particles, which can be explained based on the shape of dispersed droplets of layered liquid crystals. We also investigated the effect of insufficient stirring on the pore structure at the highest HFDePC:Si ratio. Because the surfactant does not emulsify TEOS readily, insufficient stirring may lead to the formation of layers of sample with different structures. The upper layer has a lower HFDePC:Si ratio, and contains particles with mesh phase and vesicle-like structures. The lower layer has a higher HFDePC:Si ratio, and contains disordered meroporous particles similar to what one would expect based on the bulk HFDePC concentration. These findings show that because they favor low-curvature aggregates, certain fluorinated surfactants produce radically different types of structures than hydrocarbons do. However, we still can understand the structures formed based on the behavior of liquid crystal dispersions.

7.3.4.5 Spherical particles with radial pores synthesized in ethanol/water solution

All the above samples prepared with HFDePC (sections 7.3.4.1-7.3.4.4) were synthesized in aqueous solution. Efforts were also made to synthesize samples in water/ethanol solution to investigate the possibility to obtain ordered pore structures in the cosolvent system. As we discussed in the earlier sections, materials synthesized with HFHexPC (section 7.3.2) and HFOPC (section 7.3.3) lack long range ordering.
Sample UKH10-1 was synthesized in ethanol/water solution. The XRD pattern of UKH10-1 is typical for 2D hexagonal structure (Figure 7.46). TEM images (Figure 7.47) show that this sample has well-ordered radially oriented pores within spherical particles. At the center of Figure 7.47, one can see the 2-D hexagonal close packed cylindrical pores making up the radial structures in these particles. Both the XRD pattern and TEM image show this sample has the same structure as the spherical silica particle with radial pores prepared with a large amount of ethanol by van Tendeloo et al.\textsuperscript{115} However, unlike the CTAB-templated samples\textsuperscript{115}, UKH10-1 has a very small “core” region. We see no evidence for an Ia3d cubic “core” in the particles either, which is consistent with the absence of the “gyroid” phase from the phase diagram of HFDePC.\textsuperscript{30} The observation of good radial ordering of the pores of UKH10-1 brings into doubt the hypothesis that Ia3d cubic cores are responsible for radial pore formation in spherical silica particles. We propose instead that radial pores are formed by preferential orientation of the surfactant micelles normal to the particle interface. The investigation is discussed in Chapter 6.\textsuperscript{107}

SEM images were collected to confirm the spherical particle shape. A representative SEM image is shown in Figure 7.48. The circular projections found in TEM images are confirmed to be spherical particles based on the SEM images.

The nitrogen sorption data and PSD for UKH10-1 are shown in Figure 7.49. This sample has a type IV isotherm, which is similar to that for UKH8-1. The pore size is 2.72 nm estimated from the PSD, which is larger than the pore size of UKH8-1 (2.42 nm). This is expectable since the tail length in HFDePC is longer than that in HFOPC leading to the formation of micelles with larger sizes.

All materials prepared in ethanol/water solution so far have spherical particle shape (UKH6-1, UKH8-1, and UKH10-1). The spherical shape is attributed to the presence of large amount of ethanol. In Chapter 6, we showed that when CTAB is used as a template, the particle shape changes from irregular to elongated to spherical with an increase of ethanol. The formation of radial pores in sample UKH10-1 is attributed to the interactions of the silica/surfactant aggregates with the solution at the surface of the particles. No radial pore structure is obtained when other alcohols such as propanol and butanol are used for CTAB.
7.3.5 HFDoPC templated sol-gel process

In this subsection, a cationic fluorinated surfactant (HFDoPC) with C12 chain length was used as the template. Sample UKA12 was synthesized in aqueous solution. No peak is observed in the XRD pattern of the sample after extraction (not shown). This indicates that UKA12 has a disordered pore structure. TEM images of this sample confirmed the amorphous pore structure (Figure 7.50). UKA12 appears to be composed of crumpled sheets of silica. This appearance is consistent with the collapse of a lamellar structure during extraction. The heterogeneous density in UKA12 suggests that there was templating before surfactant extraction because pure silica precipitated under these conditions would be expected to form irregular particles of uniform density.

The nitrogen sorption data of this sample is shown in Figure 7.51. Pore properties of UKA12 are shown in Table 7.6. For UKA12, the total surface area is almost the same as the external surface area, suggesting that this sample is composed primarily of macropores. The pore size distribution for both this sample is very broad in the mesopore range, which confirms a lack of pore ordering in the extracted sample.

The reason might be the ease with which HFDoPC forms bilayers in aqueous solution. This suggests that layered pore structure which might be formed in the as-synthesized samples. These structures would be expected to collapse after removing the surfactant.

HFDoPC is found to form bilayers at surprisingly low concentrations in aqueous solution. This indicates that the cmc of this surfactant is low. The addition of ethanol will help to increase its cmc dramatically since HFDoPC is much more soluble in ethanol than in water. With using the ethanol/water system, it may be possible to synthesize silica with stable pore structures. Two samples were prepared in ethanol/water solution. Sample UKH12-1 was synthesized by using the same initial molar composition as UKH10-1.

The XRD pattern of UKH12-1 shows two weak peaks (Figure 7.52). Because of the background, the position of the first peak is not clear. The pore structure of this sample can not be clearly determined from this XRD pattern. TEM information is needed to determine the pore structure. The TEM image (Figure 7.53) of this sample shows that it is composed of sheet-like layers with weak stripe patterns and circular pores arranged within the walls of the particles. This indicates that the second peak (d-spacing of 1.0 nm)
is not likely to be from the same phase as the first peak in the XRD pattern; otherwise the pore structure should be more ordered. The appearance of the second peak could not be explained so far. TEM images show that this sample has both spherical particles and irregular particles. Under the same conditions, other samples (UKH6-1, UKH8-1, and UKH10-1) consist only of spherical particles. This indicates that both ethanol and the surfactant will affect the particle morphology in this process. Isotherm plots and pore size distribution of this sample are shown in Figure 7.54. This material has a broad pore size distribution. This is consistent with the poor ordering shown by its XRD pattern.

Because significant internal pore volume is observed for sample UKH12-1, it seems that the templating process worked better than for UKA12-1. The inconsistency between the pore diameter calculated from the pore texture characteristics ($w_d$) and from the KJS method ($w_{KJS}$) of UKH12-1 may be because assumptions in the method of evaluating $w_d$. The former is calculated by assuming uniform cylindrical pores, for which $w_d=1.213d_{100}(\rho V_p/(1 + \rho V_p))^{0.5}$ with $\rho = 2.2$ g/cm$^3$ for the density of amorphous SiO$_2$. We have found, for a series of HFOPC templated particles prepared with varying surfactant:Si ratio, that when the mesopores are not perfectly ordered, the pore width is underestimated by this equation. Another explanation for the unexpected small $w_d$ value for sample UKH-12 is that it indicates this sample may have a structure other than HCP. If it had a HCP structure similar to UKH10-1, the pore size of this sample should be larger since a template with a longer tail was used. The unexpected small pore size is consistent with the indication from XRD that this sample may have a defective lamellar or mesh phase structure.

A second sample UKH12-2 was synthesized in ethanol/water solution with better optimized compositions. The XRD pattern has three peaks (Figure 7.55). UKH12-2 is much more ordered than UKH12-1 as shown by the XRD pattern. Three peaks with d-spacings of 4.0 nm, 2.0 nm, and 1.0 nm are identified. It seems that this pattern indicates a lamellar structure. However, the missing (003) peak can not be explained. Moreover, the second peak is very broad. It may be a combination of two broad peaks merged together. In this case, this pattern may indicate a 2D hexagonal structure. The peak at 1.0 nm may come from another phase structure as for the sample UKH12-1. TEM images (Figure 7.56a) of this sample show that sample UKH12-2 has radial pores even though
they do not appear to be close-packed cylinders. Pores arranged in layers (Figure 7.56c) are observed from broken fragments of this sample, which is consistent with the lamellar or mesh phase XRD interpretation. The pore arrangement can be understood by looking at the center of the TEM image of a representative particle (Figure 7.56a), where we should be looking straight into the edge of the particle. While the particles with ordered pores in sample UKH10-1 show close-packed circles indicating a 2D hexagonal structure, thin linear pore segments are seen even near the very center of the particles of sample UKH12-2 (Figure 7.56a). Figure 7.56b also shows an image near the edge of the particles with higher transmission intensity, and suggests that there are many layers of material near the edge of the particles, giving them a rough appearance. The structure thus appears to be made up of silica layers arranged radially, somewhat like flower petals). This structure is consistent with the lamellar or mesh phase structure indicated by XRD.

7.3.6 1 H, 1 H, 2 H, 2 H- perfluoro-7-methyloctylpyridium chloride (HFMOPC), 1 H, 1 H, 2 H, 2 H- perfluoro-9-methyldecylpyridium chloride (HFMDepC) templated sol-gel process

All surfactants in the previous sections have straight fluorinated alkyl chains as tails. In this section, two cationic surfactants with branched chains are used as templates to study the effect of the branched methyl group on the pore structure.

7.3.6.1 Materials synthesized in aqueous solution

Samples were prepared in water or water/ethanol solutions under conditions similar to those used for other surfactants. Two materials UKA9b and UKA11b were synthesized with the same molar compositions as UKA6, UKA8, UKA10 and UKA12.

The XRD pattern of sample UKA9b (Figure 7.57) has two reflections that can be indexed to a lamellar or weakly ordered 2D hexagonal / wormhole-like pore structure. The XRD pattern of sample UKA11b (not shown) does not indicate any long range structural ordering.
Representative TEM images of samples for UKA9b and UKA11b are shown in Figure 7.58. Sample UKA9b (Figure 7.58a) consists of spherical particles with wormhole-like pores within each particle. This is an unusual morphology for particles synthesized in aqueous solution, where more often particles are rough and irregular. Compared to the other samples (UKA6, UKA8, UKA10), a spherical shape implies either that the surfactant-silica aggregates remained fluid for a longer time or that the surface tension of the surfactant-silica aggregates was higher. UKA11b lacks long range ordering by XRD, but has a short range ordering structure under TEM. Sample UKA11b (Figure 7.58b) consists of round, almost spherical, nanoparticles. The TEM image shows no indication of pore ordering, but a few of the particles appear to be broken in the sample, and they may be hollow. There also are large flat sheet-like structures. Both of these structures are consistent with a distribution of vesicle-like aggregates in this sample.

Isotherm plots and pore size distributions of UKA9b, UKA8, UKA11b, and UKA10 are compared in Figure 7.59. Because UKA10 has a mesh phase pore architecture, its PSD was calculated based on a slit pore shape. The isotherms of samples UKA8, UKA9b and UKA10 have sharp inflections, indicating capillary condensation in uniform pores. Consistent with this observation, these materials have narrow pore size distributions (Figure 7.59). The pore size distribution for UKA11b is very broad and the pore volume is low, which suggests that either an ordered silica-surfactant aggregate did not form, or it collapsed during extraction and drying. Properties of all samples are shown in Table 7.6.

The effect of branching is seen for sample UKA9b. Surfactants HFMOPC and HFOPC have eight carbon atoms in the main chains. The difference in the chain length should be small. However, sample UKA9b (2.72 nm) obviously has a larger pore diameter than UKA8 (2.62 nm) but weaker ordering. The branching in the surfactant therefore appears to have expanded the core of the micelles, but to have made micelles that more easily undergo fluctuations to create disordered, wormhole-like pores. Similarly, comparing sample UKA10 and UKA11b, the addition of one branching CF$_3$ group eliminates the long-range mesh phase ordering observed in sample UKA10. This leads to a sample with no discernable ordering by XRD or TEM, and a relatively low pore volume.
7.3.6.2 Materials synthesized in water/ethanol solution

Two samples UKH9b-1 and UKH11b-1 were synthesized in water/ethanol solution with the same molar compositions as UKH6-1, UKH8-1, UKH10-1, and UKH12-1.

The XRD pattern of UKH9b-1 is shown in Figure 7.60. The XRD pattern suggests that, similar to UKA9b, sample UKH9b-1 may have wormhole-like pore structures. No long range ordering was found by XRD for UKH11b-1 (not shown).

The TEM images of sample UKH9b-1 (Figure 7.61a) show that they have amorphous wormhole-like pore structures within spherical particles. Weakly ordered pattern, however, is observed at the edges of the particles (Figure 7.61a). This indicates that this sample has short range ordering. Sample UKH11b-1 (Figure 7.61b) consists of spherical particles without any ordered pore structure.

The isotherms and pore size distributions of samples UKH8-1, UKH9b-1, UKH10-1, and UKH11b-1 are shown in Figure 7.62. Most of the samples have large surface areas and narrow pore size distributions. The pore texture properties calculated with αs-plot are shown in Table 7.7. UKH8-1 (2.42 nm) has a smaller pore size than UKA8 (2.62 nm). Similar to UKA9b-1 and UKA8, UKH9b-1 (2.56 nm) has a larger pore size than UKH8-1. UKH10-1 has an ordered hexagonal structure, which is different than UKA10-1. The branching effect is similar to that of the samples synthesized in aqueous solution. The addition of a branching chain has either increased the pore size (from 2.42 nm in UKH8-1 to 2.56 nm in UKH9b-1) or destroyed the ordered pore structure (hexagonal in UKH10-1 to disordered UKH11b-1).

7.4. Conclusions

A homologous series of cationic fluorinated surfactants has been used to make silica powders with ordered mesopores. Experiments were performed to explore the possible pore sizes and structures that can be obtained by using these surfactants as templates. Two series of samples (UKAx series and UKHx-1 series with x is the carbon numbers in the surfactant tail) were prepared in water or ethanol/water solutions with the only difference in the type of the surfactant. For the series synthesized in aqueous solution, sample UKA4-3 was included for the comparison. UKA4-3 was synthesized under
different conditions compared to the others. This pore size of this sample, however, still reflects the effect of surfactant size on the pore size. Because the KJS (modified BJH) method has been proven to be accurate for uniform cylindrical pores, we take the pore width estimated by this method \( w_{KJS} \) as the best estimate of pore size for this series. The pore properties of the samples synthesized in aqueous solution are compared in Table 7.6. Sample UKA4-3 has the smallest pore size (1.60 nm) that has yet been made with surfactants. The pore width increases as the surfactant tail length increases at first (UKA6 and UKA8) but it decreases for sample UKA10. This is because both UKA6 and UKA8 have cylinder-based pore structures while UKA10 has slit pores. With HFDePC as the template, a material UKA10-1 was synthesized with hexagonal pattern (Figure 7.34a). The pore size of UKA10-1 is 2.68 nm, which is larger than the pore size of UKA8 (2.62 nm). This is consistent with the trend that the pore size increases with an increase of the carbon numbers in the straight chain. With an increase of the chain length, the pore structure transforms from wormhole-like to hexagonal to random mesh to disordered.

The pore properties of the samples synthesized in ethanol/water solution are compared in Table 7.7. UKH6-1 has the same pore diameter (2.19 nm) as UKA6. UKH8-1 (2.42 nm) has a smaller pore size than UKA8 (2.62 nm). UKH10-1 has an ordered hexagonal structure, which is different than UKA10. The pore size of UKH10-1 is 2.72 nm, which is larger than that of UKA10. Because the pore structure is similar in the series from UKH6-1 to UKH10-1, the pore size increases steadily in this series. Like the UKAx heterogeneous series, the UKHx-1 series shows that with increasing fluorocarbon chain length, the pore size increases and the pore structures transform from wormhole-like to hexagonal to defective lamellar.

As the tail length increased, larger pores were observed for samples synthesized in both aqueous solution and ethanol/water solution. However, there were inconsistencies in this trend as changes in the pore architecture occurred from wormhole-like to hexagonal to random mesh phase to lamellar. This order of pore structure appearance was found as the chain length increased for both aqueous and ethanol/water synthesis solutions. The difference was the tail length at which the transitions occurred. For example, HFDePC first formed a layered structure in the aqueous samples, while only HFDoPC formed layered pores in aqueous ethanol. These results show greater sensitivity
of pore structure to surfactant length for fluorinated surfactants than is observed in hydrocarbon surfactants. In addition, as was recently observed for hydrocarbon surfactants, particle synthesis in solutions with a large ethanol concentration lead to spherical, uniform particles with radially oriented pores, including an unusual radially oriented slit-shaped particle structure for sample UKH12-2.

Because HFDePc can form a variety of phases in aqueous solution, lots of attention has been focused on the synthesis of materials with this surfactant. Novel pore structures of random mesh phase structure and vesicles with unilamellar layers are prepared. By increasing the initial surfactant concentration, we are able to see that the pore structure changes from hexagonal to vesicles to random mesh phase to disordered with the corresponding particle morphology changing from spherical-like to elongated to spherical-like for the first time.

In summary, we find that the unusual self-assembly properties of fluorinated surfactants carry over into pore templating. Because of facile self-assembly, HFBPC produced particles with unusually small, uniform pores. Because fluorinated surfactants prefer low-curvature aggregates and unusual intermediate phases, we were able to isolate both standard (wormhole-like, 2-D hexagonal) and novel (random mesh phase, vesicles, radial) pore structures. The other advantage of these surfactants (the ability to interact selectively with low-surface tension solvents) will be explored in future contributions. We will also be investigating methods for recycling these surfactants.

7.5. References

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9237.
### Table 7.1. Fluorinated surfactants and their structures

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### Table 7.2. Initial Compositions of all samples synthesized in aqueous solution.

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</tr>
<tr>
<td>UKA8S-3</td>
<td>(UKA8)</td>
<td>1 TEOS: 0.166 HFOPC: 2.46 NH₃: 154 H₂O</td>
</tr>
<tr>
<td>UKA8S-4</td>
<td>HFOPC</td>
<td>1 TEOS: 0.333 HFOPC: 2.46 NH₃: 154 H₂O</td>
</tr>
<tr>
<td>UKA10</td>
<td>HFDDePC</td>
<td>1 TEOS: 0.166 HFDDePC: 2.46 NH₃: 154 H₂O</td>
</tr>
<tr>
<td>UKA12</td>
<td>HFDDoPC</td>
<td>1 TEOS: 0.166 HFDDoPC: 2.46 NH₃: 154 H₂O</td>
</tr>
<tr>
<td>UKA9b</td>
<td>HFMOPC</td>
<td>1 TEOS: 0.166 HFMOPC: 2.46 NH₃: 154 H₂O</td>
</tr>
<tr>
<td>UKA11b</td>
<td>HFMDDePC</td>
<td>1 TEOS: 0.166 HFMDDePC: 2.46 NH₃: 154 H₂O</td>
</tr>
</tbody>
</table>
Table 7.3. Samples prepared with HFDePC as the template in aqueous solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass composition</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HFDePC: H₂O: NH₃: TEOS</td>
<td></td>
</tr>
<tr>
<td>UK-2</td>
<td>0.30 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Moderate stirring</td>
</tr>
<tr>
<td>FSV-S1</td>
<td>0.087 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Slow stirring</td>
</tr>
<tr>
<td>FSV-S2</td>
<td>0.087 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Moderate stirring</td>
</tr>
<tr>
<td>FSV-S3</td>
<td>0.087 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Fast stirring</td>
</tr>
<tr>
<td>UKA10-1</td>
<td>0.1 g: 116.36 g: 1.78 g: 8.72 g</td>
<td>Fast stirring</td>
</tr>
<tr>
<td>UKA10-2</td>
<td>0.14 g: 116.36 g: 1.78 g: 8.72 g</td>
<td>Fast stirring</td>
</tr>
<tr>
<td>UKA10-3</td>
<td>0.78 g: 116.36 g: 1.78 g: 8.72 g</td>
<td>Fast stirring</td>
</tr>
<tr>
<td>UKA10-4</td>
<td>0.087 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Fast stirring</td>
</tr>
<tr>
<td>UKA10-5</td>
<td>0.23 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Fast stirring</td>
</tr>
<tr>
<td>UKA10-6</td>
<td>0.30 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Fast stirring</td>
</tr>
<tr>
<td>UKA10-7</td>
<td>0.50 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Fast stirring</td>
</tr>
<tr>
<td>UKA10-8</td>
<td>0.80 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Fast stirring</td>
</tr>
<tr>
<td>UKA10-8ST</td>
<td>0.80 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Slow stirring, top gel</td>
</tr>
<tr>
<td>UKA10-8SB</td>
<td>0.80 g: 12.92 g: 0.20 g: 0.97 g</td>
<td>Slow stirring, bottom solution</td>
</tr>
</tbody>
</table>

Table 7.4 Pore properties of samples prepared with short-chain fluorinated surfactant HFBuPC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>d (nm)</th>
<th>S_t (m²/g)</th>
<th>S_ext (m²/g)</th>
<th>V_pme (cm³/g)</th>
<th>V_pmi (cm³/g)</th>
<th>w_BJH (nm)</th>
<th>w_d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UK4-1</td>
<td>/</td>
<td>438</td>
<td>65</td>
<td>1.13</td>
<td>0</td>
<td>11.1</td>
<td>/</td>
</tr>
<tr>
<td>UK4-2</td>
<td>/</td>
<td>758</td>
<td>/</td>
<td>/</td>
<td>0.09</td>
<td>17.8</td>
<td>/</td>
</tr>
<tr>
<td>UK4-3</td>
<td>2.31</td>
<td>819</td>
<td>/</td>
<td>/</td>
<td>0.21</td>
<td>/</td>
<td>1.6</td>
</tr>
</tbody>
</table>

a d = XRD (100) interplanar spacing; S_t = total surface area; S_ext = external surface area; V_pme = primary mesopore volume; V_pmi = primary micropore volume; w_BJH = pore size estimated from BJH method; w_d = primary mesopore/micropore size calculated using w_d = 1.213d_{100}(ρV_p/(1+ρV_p))^{1/2} with ρ equal to 2.2 cm³/g and V equal to V_pme or V_pmi.
Table 7.5. Pore properties of UKA8 and UKA8S series of samples
All the parameters have the same meanings as in Table 7.4 except that \( w_{KJS} \) is the pore size estimated from the KJS modified BJH method\(^\text{72}\), \( d_{\text{NLDFT}} \) is the pore size calculated from the Non-Local Density Functional Theory (NLDFT).\(^\text{76}\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d_{100} ) (nm)</th>
<th>( S_t ) (m(^2)/g)</th>
<th>( S_{\text{ext}} ) (m(^3)/g)</th>
<th>( V_{\text{mic}} ) (cm(^3)/g)</th>
<th>( V_p ) (cm(^3)/g)</th>
<th>( w_{KJS} ) (nm)</th>
<th>( d_{\text{NLDFT}} ) (nm)</th>
<th>( 4V_p/(S_t-S_{\text{ext}}) ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UKA8S-1</td>
<td>2.74</td>
<td>795</td>
<td>223</td>
<td>0.021</td>
<td>0.40</td>
<td>2.59</td>
<td>/</td>
<td>2.80</td>
</tr>
<tr>
<td>UKA8S-2</td>
<td>2.76</td>
<td>793</td>
<td>171</td>
<td>0.014</td>
<td>0.43</td>
<td>2.57</td>
<td>/</td>
<td>2.76</td>
</tr>
<tr>
<td>UKA8 (UKA8S-3)</td>
<td>2.83</td>
<td>970</td>
<td>39</td>
<td>0.005</td>
<td>0.61</td>
<td>2.62</td>
<td>2.60</td>
<td>2.62</td>
</tr>
<tr>
<td>UKA8S-4</td>
<td>2.85</td>
<td>764</td>
<td>20</td>
<td>0.032</td>
<td>0.44</td>
<td>2.38</td>
<td>/</td>
<td>2.36</td>
</tr>
</tbody>
</table>

Table 7.6. Pore texture parameters of the samples made in aqueous solution.
All the parameters have the same meanings as in Table 7.4 and Table 7.5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d_{100} ) (nm)</th>
<th>( w_d ) (nm)</th>
<th>( w_{KJS} ) (nm)</th>
<th>( V_p ) (cm(^3)/g)</th>
<th>( S_t ) (m(^2)/g)</th>
<th>( S_{\text{ext}} ) (m(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UKA4-3({^\text{&amp;}})</td>
<td>1.60</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>UKA6</td>
<td>2.60</td>
<td>2.20</td>
<td>1.91</td>
<td>0.43</td>
<td>884.2</td>
<td>23.7</td>
</tr>
<tr>
<td>UKA8</td>
<td>2.83</td>
<td>2.60</td>
<td>2.62</td>
<td>0.61</td>
<td>981.5</td>
<td>40.0</td>
</tr>
<tr>
<td>UKA9b</td>
<td>2.81</td>
<td>2.62</td>
<td>2.76</td>
<td>0.66</td>
<td>943.0</td>
<td>76.2</td>
</tr>
<tr>
<td>UKA10({^*})</td>
<td>3.20</td>
<td>1.80</td>
<td>1.95</td>
<td>0.58</td>
<td>850.7</td>
<td>150.5</td>
</tr>
<tr>
<td>UKA11b</td>
<td>/</td>
<td>/</td>
<td>3.34</td>
<td>0.08</td>
<td>590.2</td>
<td>348.8</td>
</tr>
<tr>
<td>UKA12</td>
<td>/</td>
<td>/</td>
<td>2.89</td>
<td>0.08</td>
<td>512.4</td>
<td>470.3</td>
</tr>
</tbody>
</table>

\& UKA4-3 synthesized under different conditions compared to the others.

\* Calculations based on slit pore geometry assumption rather than cylindrical pores.

\( w_d \): Primary mesopores size calculated from \( w_d=d_{100}(\rho V_p/(1+\rho V_p)) \) for slit pore shapes with \( \rho=2.2 \text{ g/cm}^3 \);

\( w_{KJS} \): For sample UKA10, the modified BJH method for slit pores was used (Appendix I).
Table 7.7. Pore texture parameters of the samples made in ethanol-water solution.

All the parameters have the same meanings as in Table 7.6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>d_{100} (nm)</th>
<th>w_d (nm)</th>
<th>w_{KJS} (nm)</th>
<th>V_p (cm^3/g)</th>
<th>S_l (m^2/g)</th>
<th>S_ex (m^2/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UKH6-1</td>
<td>2.85</td>
<td>2.18</td>
<td>2.19</td>
<td>0.27</td>
<td>576.7</td>
<td>22.9</td>
</tr>
<tr>
<td>UKH8-1</td>
<td>2.66</td>
<td>2.36</td>
<td>2.42</td>
<td>0.52</td>
<td>875.0</td>
<td>23.6</td>
</tr>
<tr>
<td>UKH9b-1</td>
<td>2.81</td>
<td>2.56</td>
<td>2.56</td>
<td>0.59</td>
<td>897.0</td>
<td>28.1</td>
</tr>
<tr>
<td>UKH10-1</td>
<td>2.96</td>
<td>2.76</td>
<td>2.72</td>
<td>0.66</td>
<td>977.1</td>
<td>25.4</td>
</tr>
<tr>
<td>UKH11b-1</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>0.14</td>
<td>320.9</td>
<td>15.5</td>
</tr>
<tr>
<td>UKH12-1</td>
<td>4.00</td>
<td>2.22</td>
<td>3.32</td>
<td>0.12</td>
<td>215.8</td>
<td>40.1</td>
</tr>
</tbody>
</table>
**Figure 7.1.** FTIR spectra of KBr pellets pressed with 1 wt% of (a) the pure surfactant, HFOPC, (b) sample UKA8 as synthesized, (c) sample UKA8 after extraction, and (d) fumed silica. The arrows indicate surfactant bands in the as-synthesized product that are absent after extraction.

**Figure 7.2.** XRD results for sample UKA8 as-prepared (lower) or after extraction (upper).
Figure 7.3. Nitrogen sorption isotherms of all samples (UK4-1 up-shifted by 400 cm$^3$/g, UK4-2 up-shifted by 200 cm$^3$/g) and their BJH pore size distributions.
Figure 7.4. Alpha plots for all samples used to determine pore texture characteristics reported in Table 7.3.
Figure 7.5. XRD pattern for UK4-3, prepared with a high concentration of surfactant.

Figure 7.6. Representative TEM images for all samples (UK4-1, UK4-2, and UK4-3).
Figure 7.7. XRD pattern for UKA6 and UKH6-1.

Figure 7.8. Representative TEM images for UKA6 and UKH6-1.
Figure 7.9. Isotherm plots and PSD for UKA6.

Figure 7.10. Isotherm plots and PSD for UKH6-1.
Figure 7.11. Polarization contrast micrographs of HFOcPC solution in water at room temperature. (a) Low-magnification view immediately after flooding a single particle of solid surfactant with deionized water, (b) 200x magnification view of equilibrated sample of 50 wt% surfactant, and (c) 200x view of equilibrated sample of 70 wt% surfactant.
Figure 7.12. XRD pattern of UKA8.

Figure 7.13. Representative transmission electron micrographs of UKA8. The views illustrate (a) a 2D HCP region and (b) a striped region consistent with the 2D HCP structure viewed from the edge of the cylindrical pores. The insets show Fourier transforms of the images.
Figure 7.14. Isotherm plots and PSD for UKA8.

Figure 7.15. $\alpha_s$-plot for UKA8.
Figure 7.16. Isotherm plots and PSDs for UKA8S series of samples: (a) Isotherm plots; (b) PSDs.
Figure 7.17. XRD patterns for UKA8S series of samples.

Figure 7.18. XRD pattern for UKH8-1.
Figure 7.19. Representative TEM image for UKH8-1.

Figure 7.20. Isotherm plots and PSD for UKH8-1.
Figure 7.21. XRD patterns: (a) for amorphous silica and for sample UK-2; (b) as-synthesized; (c) after surfactant extraction; (d) after extraction and heating at 550 °C in air for 4 hours; (e) after extraction and heating in air at 800 °C for 2 hours.
Figure 7.22. Representative SEM image for UK-2 (the arrows indicate some of the particles with openings at one end where the particles appear to have broken).
Figure 7.23. Representative TEM images for UK-2  (a) low magnification image of particle cluster, (b) intermediate magnification image of particles, (c) dark field STEM image of a single particle, and (d) high magnification STEM image (inset: histogram of measured interpillar distances from the STEM image).
Figure 7.24. Isotherm plots and PSD (inset) of UK-2.

Figure 7.25. Representative SEM image of FSV-S1. The small white arrows indicate the openings of broken particles.
Figure 7.26. TEM images of FSV-S1: (a) low magnification; (b) high magnification.

Figure 7.27. STEM images of FSV-S1
**Figure 7.28.** Representative SEM image of sample FSV-S3. White arrows indicate broken particles which indicate that the particles are hollow.

**Figure 7.29.** Electron micrographs of sample FSV-S3. (a) Low magnification TEM, (b) high magnification TEM, and (c) dark-field STEM.
Figure 7.30. Nitrogen adsorption isotherms (left) and KJS modified BJH pore size distributions (right). Isotherms for FSV-S2 and FSV-S3 were offset vertically by 225 and 450 cm$^3$/g, respectively. PSDs for FSV-S2 and FSV-S3 were offset vertically by 0.05 cm$^3$/(g-nm) and 0.1 cm$^3$/(g-nm), respectively.
Figure 7.31. TEM image for UKA10.

Figure 7.32. XRD pattern for UKA10.
Figure 7.33. Isotherm plots and PSD for UKA10.

Figure 7.34. Representative TEM images for: (a) UKA10-1, (b) UKA10-2, and (c) UKA10-3. The scale bars are all 50 nm wide. The hexagon indicates the deformed hexagonal unit cell of the pores.
Figure 7.35. Representative SEM image of sample HFDePC-1.

Figure 7.36. I. Isotherm plots: a. UKA10-1, b. UKA10-2 (upshifted 100 cm$^3$/g), c. UKA10-3 (upshifted 200 cm$^3$/g); II. Pore size distributions for all samples: a. UKA10-1; b. UKA10-2; c. UKA10-3.
Figure 7.37. Representative TEM images for samples UKA10-5 to UKA10-8.
Figure 7.38. Representative SEM images of samples 7 and 8.

Figure 7.39. Nitrogen sorption isotherm plots (I) of a. sample UKA10-4, b. sample UKA10-5 (upshifted 100 cm$^3$/g), c. sample UKA10-6 (upshifted 200 cm$^3$/g), d. sample UKA10-7 (upshifted 300 cm$^3$/g), e. sample UKA10-8 (upshifted 500 cm$^3$/g). II. Calculated pore size distributions of all samples.
Figure 7.40. Representative TEM images of UKA10-6 collected at 30 seconds.

Figure 7.41. Representative TEM images of UKA10-6 collected at 2 minutes.
**Figure 7.42.** Representative TEM images of UKA10-6 collected after (a): 4 minutes; (b) 8 minutes.

**Figure 7.43.** Representative TEM images of UKA10-1 collected after (a): 30 seconds; (b): 2 minutes; and (c) 4 minutes.
Figure 7.44. Representative TEM images of UKA10-4 collected after (a): 2 minutes; (b): 4 minutes; and (c) 8 minutes.

Figure 7.45. Representative TEM images of samples UKA10-8ST and UKA10-8SB. A layered pattern is outlined with a rectangle for sample 8ST.
Figure 7.46. XRD pattern for UKH10-1.

Figure 7.47. Representative TEM image for UKH10-1.
Figure 7.48. SEM image for UKH10-1.

Figure 7.49. Isotherm plots and PSD for UKA10.
Figure 7.50. Representative TEM image for UKA12.

Figure 7.51. Isotherm plots and PSD for UKA12.
Figure 7.52. XRD pattern for UKH12-1.

Figure 7.53. Representative TEM image for UKH12-1.
Figure 7.54. Isotherm plots and PSD for UKH12-1.

Figure 7.55. XRD patterns for UKH12-2.
Figure 7.56. Representative TEM images for UKH12-2.
Figure 7.57. XRD pattern for UKA9b.

Figure 7.58. Representative TEM images for (a): UKA 9b; (b): UKA11b.
Figure 7.59. Isotherm plots and PSDs for UKA8, UKA9b, UKA10, and UKA11b.

Figure 7.60. XRD pattern for UKH9-1.
Figure 7.61. Representative TEM images for (a): UKA 9b; (b): UKA11b.

Figure 7.62. Isotherm plots and PSDs for UKH8-1, UKH9b-1, UKH10-1, and UKH11b-1.
Chapter 8. Synthesis of Inorganic and Organic-Inorganic Hybrid Vesicular Particles Using a Partially Fluorinated Surfactant

8.1. Introduction

Hollow spherical particles consist of a shell of solid material surrounding hollow cores. If the walls are permeable, these types of particles have potential applications in catalysis, absorption, and drug delivery. If the shells are nonporous, their permeability depends on the partitioning of solutes into the shell. In this chapter, we will discuss hollow particles with porous shells. These particles can be divided into two categories depending on the characteristics of the shell. The first type of particle consists of hollow particles with uniform porous shells. By uniform, we mean that the pores are distributed uniformly throughout the shell (although there is a difference in the density of the particles between the walls and pores, of course). Particles with this morphology can be synthesized by using latex microspheres as templates (see Chapter 6). Microporous or mesoporous silica is coated at the outside of microspheres, and removal of the latex creates a hollow core. The other type of hollow particle has bi- or multi-layer shells. This structure is similar to the structure of vesicles formed by surfactants in that, as one moves out radially from the center of the particle, multiple layers of some component are encountered. For example, in a phospholipids vesicle, the phorphorous headgroup is found in two layers, one inside or the particle and one outside. An example of a material with this structure is FSV-S1 (see Chapter 7), which has a bilayer of dense (microporous or nonporous) silica in the shells. A single layer of empty space or low density (mesoporous) silica is sandwiched between the two dense layers. Because of the empty (low density) layers, the hollow cores in mutilayered vesicular silica are easier to access than those in solid-shelled silica with a similar shell thickness. Mutilamellar vesicular silica also has advantages under conditions where the silica is to be dissolved; may layers allow doses of the contents of the particle to be gradually released, rather than the entire core at once.

Vesicular silica is normally synthesized by the co-assembly of surfactant micelles and hydrolyzed silica species. Vesicular silica with multilayers was first reported by Pinnavaia et al by using a bolaform amine amphiphile as the template. This material has
shells as thick as several hundred nanometers. Vesicular silicas with much thinner shells (~ 3nm – 70 nm) were synthesized by researchers from the same group by using gemini amine surfactants as templates. Both of these multilamellar vesicular silicas have been reported to have high thermal stabilities. The same vesicular structure can be synthesized by using catanionic surfactants as templates. In this case, vesicles with multilayers are formed due to the electrostatic interactions between a cationic surfactant and an anionic surfactant, and silica fills in the spaces between the bilayers. Cationic hydrogenated surfactants are not supposed to spontaneously form vesicles in aqueous solution. In order to prepare vesicular structures using these surfactants, special treatments have to be used to generate the vesicles. In contrast to hydrogenated surfactants, partially fluorinated surfactants are prone to form low-curvature structures such as discs, bilayers, and vesicles. We first reported the formation of vesicular silica with mesoporous shells by using the partially fluorinated surfactant HFDePC as the template, although in that case the walls seem to be formed from packed micelles rather than bilayers of surfactant (see Chapter 7).

Organic-inorganic hybrid materials are desirable for a variety of applications partially because of the uniform distribution of the organic sites (see Chapter 4 for more discussion of this). However, no vesicular organic-inorganic materials have been reported to be generated from solution as far as we know. The closest inorganic-organic hybrid structure reported previously is an onion-like multilayered structure prepared by evaporation-induced self-assembly by Brinker and co-workers. One of the aspects of the synthesis that we will explore in this chapter will be the possibility of using the stability of lipophobicity of a partially fluorinated surfactant to allow the formation of ordered organic-inorganic hybrids.

In this chapter, we will first report a route to synthesize vesicular silica with multilamellar structures by using a newly synthesized partially fluorinated surfactant as the template. The effect of different alkoxide groups on the particle morphology will be discussed. The synthesis of organic-inorganic hybrid materials with multilamellar vesicular structures will be reported, and the effect of the type of bridging organic will be explored.
8.2. Experimental Section

8.2.1 Materials. The partially fluorinated pyridinium bromide monohydrate surfactant, C_{8}F_{17}C_{10}H_{20}NC_{5}H_{12}Br·H_{2}O (F_{8}H_{10}), was prepared by Dr. Hans Lehmler and Dr. Sandhya Vyas of the University of Iowa. The synthesis of the surfactant required many steps, and will be the subject of a future manuscript from Dr. Lehmler’s group. Tetramethoxysilane (99+%, TMOS), tetraethoxysilane (99+%, TEOS), tetra-n-propoxysilane (95%, TPOS), and tetra-n-butoxysilane (97%, TBOS), bis(trimethoxysilyl)ethane (95+%, BTMSE), bis(triethoxysilyl)ethane (95+%, BTESE), bis(triethoxysilyl)octane (95+%, BTESO), bis(3-trimethoxysilylpropyl)amine (95%, BTMSPA), bis(3-triethoxysilylpropyl)amine (95%, BTESPA) were purchased from Gelest and used as received. Other reagents and solvents are the same as those in Chapter 3 and Chapter 7.

8.2.2 Synthesis. To synthesize a material, the surfactant F_{8}H_{10} was first dissolved by heating with DIUF water at 50 °C for 15 minutes. After cooling down to the room temperature, a transparent gel-like solution was obtained. Air bubbles were captured in the gel-like solution due to stirring. Aqueous concentrated ammonia was added to the solution. After 1 hour of stirring at room temperature, a silica precursor was added dropwise into the stirring solution. Due to the slow reaction rate of the precursor and the small particle size, the as-synthesized sample prepared with TBOS was collected by centrifuging after aging the solution for 3 days. The others were collected by filtering after aging for 1 day. The extraction of surfactant was carried out in acidic ethanol following the extraction procedure in Chapter 7.

Ten samples will be discussed in this chapter. Their names are derived from their precursors. Samples TM, TE, TP, TB, BME, BEE, BEO, BMPA, and BEPA are prepared from TMOS, TEOS, TPOS, TBOS, BTMSE, BTESE, BTESO, BTMSPA, and BTESPA, respectively. Sample TE-M is prepared from TEOS, but with the presence of methanol. The initial molar composition of all samples discussed in this chapter is 1 Si: 0.116 surfactant: 155 H_{2}O: 2.49 NH_{3}: x CH_{3}OH (x = 4 for sample TE-M, and x = 0 for the others).
8.2.3 Characterization. XRD, TEM, and nitrogen sorption were used to characterize the samples according to the sample preparation and analysis methods described in Chapter 7. For nitrogen sorption, all samples were degassed at 120 °C for 4 hours under flowing nitrogen before starting the analysis.

8.3. Results and Discussion

8.3.1 Syntheses of silica particles from tetraalkoxysilanes with $F_8H_{10}$

Four samples TM, TE, TP, and TB were synthesized with TMOS, TEOS, TPOS, and TBOS as the precursors, respectively. The as-synthesized samples were collected by filtering for TM, TE, and TP. No sample was collected for TB by filtering after aging the solution for 1 day. Oil droplets were observed after this solution was centrifuged overnight. This indicates that the hydrolysis in this solution was not completed. The aging time of the TB was therefore extended to 3 days to ensure completion of the hydrolysis.

Representative TEM images of all tetraalkoxide-derived samples are shown in Figure 8.1. Ordered patterns suggestive of a cubic pore structure are identified in sample TM. A pattern similar to the (4 3 2) projection in a gyroid-like structure is identified in the TEM images for sample TM. This pattern may also be observed in other cubic structures such as body-centered cubic structure, but not in a hexagonal structure. No hollow particles are observed. Well defined hollow particles with multi-lamellar shells are observed in sample TE. This vesicular structure is similar to those reported by Tanev and Pinnavaia. Most hollow particles have 5 to 13 silica layers in the shells. All particles in sample TP have hollow cores. The shells are much thinner than those in sample TE. Most particles only have one layer of uniform thin shell. Hollow spherical particles with thick shells are identified in sample TB. All particles have only one layer of solid thick shell. Weakly layered patterns are observed in the shells, indicating that the shells are mesoporous.

XRD patterns of some of selected members of this series are shown in Figure 8.2. The XRD pattern for sample TM has one sharp (1 0 0) peak and possibly two weak higher-order peaks at positions. The resolutions of these peaks, however, are not strong enough to define the pore structure. This material may have a cubic pore structure as
indicated by its TEM images. The characterization of the pore structure for sample TM will be studied further. One sharp peak is observed in the XRD pattern for sample TE. This peak is located at the (1 0 0) reflection of the lamellar structure indicated by TEM. No peak is observed for samples TP or TB (not shown). The absence of any peak is consistent with the lack of long-range order in the TEM images. No ordered patterns can be identified in the shells for sample TP (Figure 8.1). Only weakly layered patterns are indicated in sample TB (Figure 8.1).

Nitrogen sorption data of all samples are shown in Figure 8.3. All samples have type IV adsorption isotherms with hysteresis loops (Figure 8.3). All desorption isotherms drop at the relative pressure corresponding to the lower limit of adsorption-desorption hysteresis (P/P₀ at around 0.4). This desorption most likely occurs due to cavitation rather than being controlled by the size of the pores. Sample TM has a H₂ adsorption-desorption hysteresis loop. This indicates that this material either has large pores with narrow mouths (ink-bottle pores) or relatively nonuniform channel-like pores. The TEM images show that this material is more likely to have channel-like pores (Figure 8.1). There is a sharp inflection in the adsorption isotherm in sample TM. This sharp inflection indicates that this material has mesopores with a narrow pore size distribution, which is confirmed by its pore size distribution (PSD, Figure 8.4). Sample TE has a larger hysteresis loop than sample TM. The large loop indicates that this sample has large hollow cores surrounded by smaller pores, as discussed in Chapter 7. There is an inflection in the adsorption isotherm, which is consistent with the narrow pore size distribution of mesopores for sample TE (Figure 8.4). No inflection is observed in the adsorption branches of samples TP or TB. Consistent with this observation, both of them do not have narrow pore size distributions in the small mesopore range (2 to 10 nm). Both the hysteresis loops in samples TB and TP feature almost horizontal adsorption-desorption branches. This feature is normally attributed to narrow slit-like pores. This is not consistent with the observation from TEM, which shows that both samples TP and TB have hollow cores. The feature, however, has recently been attributed to large pores embedded in a matrix with pores with much smaller size. This interpretation is consistent with our observation for samples TP and TB. The absence of a peak in the PSDs of these two samples is probably because the shells are microporous. For
microporous samples, the filling of the pores in the shells occurs at a pressure too low to
determine by the modified BJH method.

Through the characterization in Figures 8.1-8.4, we have found that samples
prepared under consistent conditions with different tetraalkoxysilanes have a variety of
structures. The only difference among the samples is the alkoxide group: TM, TE, TP,
and TB have methoxide, ethoxide, propoxide, and butoxide groups, respectively. There
are two factors that contribute to the pore structure differences found with different
alkoxide groups. First, the size of alkoxide group is well known to affect the kinetics of
the sol-gel reaction. Under basic conditions, the hydrolysis is the rate-limiting step (see
Chapter 3). The bulkier the size of the alkoxide, the slower the hydrolysis rate (see
Chapter 3). This means that the hydrolysis rate should follow the order of TM > TE > TP
> TB. This is consistent with the observation of an oil phase when sample TB was stirred
only for 24 hours, indicating the existence of the un-hydrolyzed silane. No oil phase was
observed in other samples prepared with the same conditions. In a surfactant templated
sol-gel process, pore structures are formed as a result of the co-assembly process between
hydrolyzed silica species and the surfactant micelles (see Chapter 1). The co-assembly
process is controlled by the availability of hydrolyzed silica species for co-assembly. At a
specific time, the presence of more hydrolyzed silica species means that more silica will
aggregate with the surfactant micelles, which may change the particle morphology and
the pore structures. The second possible effect of the type of alkoxide is a co-surfactant
effect. During the templated sol-gel process, alcohols will be produced from the silanes.
A small amount of some long-chain alcohols are known to be as co-surfactants, and
methanol and ethanol are low-dielectric solvents with favor dissociation of surfactants
(see Chapter 5). Interactions between the alcohols and the surfactant micelles may induce
the transition of pore structures and particle morphology, as shown in Chapter 5 for
ethanol. Methanol, ethanol, propanol, and butanol will be produced from TMOS, TEOS,
TPOS, and TBOS, respectively. Methanol may destroy the vesicular structure by
reducing the micelle aggregation number, while the others help the formation of hollow
structures.

In order to further investigate the effect of alkoxide groups on the vesicular pore
structure, an extra sample TE-M is prepared with TEOS as the precursor and methanol in
the solution. The main difference between TM and TE-M is the difference in the precursor. The difference between TE-M and TE is the addition of methanol in sample TE-M. TEM images of sample TE-M show that this sample has a vesicular structure similar to that in sample TE (Figure 8.5). TE-M contains the maximum amount of methanol that could have been produced if the precursor were TMOS. The alcohol effect on the pore architecture is expected to be similar. However, no vesicular structure is observed in sample TM (Figure 8.1). This comparison indicates that of the two effects of the type of alkoxide, the hydrolysis rate of the precursor has the largest influence on the difference in the pore structures between sample TM and TE-M. The methanol in sample TE-M is not completely inactive, though. The addition of methanol in sample TE-M reduces the number of layers in the shells. The hollow particles in TE-M (Figure 8.5) obviously have fewer layers (2-6 silica layers) than those in TE (5-13 silica layers) (Figure 8.1). The comparison of the isotherm plots for TE and TE-M (Figure 8.6) also shows that the addition of methanol reduces the pore volume and the surface area for sample TE. Pore volumes measured at the relative pressure $P/P_0$ of 0.81 are 0.68 cm$^3$/g and 0.55 cm$^3$/g for samples TE and TE-M, respectively. The BET surface area for sample TE is 633 m$^2$/g, while the value is 597 m$^2$/g for sample TE-M. A much broader pore size distribution is observed for sample TE-M than that for sample TE. The loss of narrow pore size distribution in TE-M is consistent with the observation from TEM images, which show that the vesicular structure in sample TE-M has fewer layers in the shells (Figure 8.5).

The addition of methanol into the sample TE has reduced the shell numbers. However, the vesicular structure is still obtained. This shows that the production of methanol from TMOS in sample TM should not destroy the formation of the vesicular structure. The lack of hollow particles in sample TM is likely to be from the different hydrolysis rates between TMOS and other precursors (TEOS, TPOS, and TBOS). The fast aggregating process in sample TM may prevent the formation of stable vesicles in solution, instead favoring the formation of particles with a large amount of silica, which organize into a cubic pore structure.

TEOS appears to provide an optimal hydrolysis rate for the production of multilamellar particles (samples TE and TE-M). The slow hydrolysis of TPOS and
TBOS allows hollow vesicular particles to form, but they favor the formation of particles with uniform microporous shells. It is likely that both precursors nucleate hollow structures with a small quantity of hydrolyzed silane, and that graduate continuous nucleation causes addition to the surface of the particles, resulting in uniform shells.

8.3.2 Syntheses of materials from bis(trialkoxy)silyl)ethane

In this section, we explore the synthesis of multilamellar vesicular organic-inorganic hybrids. We hypothesize that the fluorocarbon components of the surfactants form stable bilayers with lipophobic cores. These cores would be less prone to disruption by organic modifiers than an hydrocarbon surfactant aggregates. The bridged silanes BTMSE and BTESE are used as the precursors. Both of them have the same ethylene group in the bridging chain. The difference between them is the type of alkoxide group. Samples BME and BEE were prepared under the same conditions as samples TM and TE.

Representative TEM images of BME and BEE are shown in Figure 8.7. No hollow particles are observed in sample BME. This confirms that methoxide groups do not favor the formation of vesicular structure. Most particles in this sample have relatively weak orderings (Figure 8.7a). However, highly ordered patterns are identified for some particles (Figure 8.7b). The ordered pattern may be attributed to a cubic pattern based on the projection shown in Figure 8.7b. This pattern is similar to the (3 1 1) projection of a gyroid-like cubic structure, which may also be observed in a body-centered cubic structure. TEM images of BEE (Figure 8.7c) show that this sample has a vesicular structure. Intact spherical hollow particles with multiple layers are observed. Most of the particles have 2 to 6 silica layers in the shells. The shell thickness is similar to that in sample TE-M (Figure 8.5), but thinner than that in sample TE (Figure 8.1).

XRD patterns for samples BME and BEE are shown in Figure 8.8. Only one weak peak is observed for either sample. The XRD patterns indicate that both samples have weaker ordering than samples TM and TE, and no further assignment of the long-range symmetry can be made based on these patterns.

Nitrogen adsorption isotherm plots and pore size distributions of samples BME and BEE are shown in Figure 8.9. Isotherm plots and the pore size distribution for sample BME are similar to those for sample TM (Figure 8.3). The nitrogen sorption indicates
that sample BME may have a similar pore structure as sample TM. This is consistent with the observation from TEM. Both BME and BM have non-vesicular pore structures. Sample BEE has an adsorption isotherm similar to samples TE, TP, and TE-M, which indicates the presence of hollow particles. The pore size distribution for sample BEE is broad (unlike sample TE). The replacement of TEOS with BTESE has weakened the ordering in the mesopores according to the XRD patterns and nitrogen sorption data. The weakening may be because of fewer layers in sample BEE than in sample TE. This is similar to the difference between sample TE-M and TE. In that case, it was the addition of methanol that reduced the level of ordering in sample TE-M.

In this section, two bridged silanes with ethylene groups have been used as precursors for materials prepared with $F_{8}H_{10}$. Similar to the difference between samples TM and TE, the sample (BME) prepared with the methoxysilane has a non-hollow structure, while the sample (BEE) made with the ethoxysilane has a vesicular structure. This is the first time as we know that vesicular organic-inorganic hybrid material has been produced from solution through a surfactant templated process.

8.3.3. Syntheses of materials from BTESO

Vesicular organic-inorganic hybrid materials have been synthesized in section 8.3.2 from a silane with short bridging chain. It is relatively common to incorporate short or stiff organic segments into surfactant-templated processes. However, long and flexible organic chains are much more difficult to coax into an organized form. Capitalizing on the possible stability of the fluorocarbon core of the micelles present during the synthesis of these particles, we developed the idea to attempt to incorporate longer bridging chains in the walls of a vesicular structure. Long bridging chains will give us more options to control the pore properties, swelling with organic solvents, and interactions with hydrophobic solutes than the short chains do.

In this section, we will synthesize a material BEO with BTESO as the precursor. An octylene chain is exceptionally flexible, and an organized mesoporous material has not been prepared with this chain. Most particles in sample BEO are non-hollow (Figure 8.10a). These particles appear to be composed of crumpled shells formed from hollow particles. A few hollow particles are, indeed, are observed in this sample (Figure 8.10b).
Still, the walls appear to be deformed for many of the particles which can explain why Figure 8.10a appears to show a collection of collapsed hollow particles. TEM images of the as-synthesized sample were collected to clarify the pore structure. One representative TEM image (Figure 8.11) shows that the crumpled shells have appeared before the removal of the surfactant. The layered patterns observed in the Figure indicate the formation of layered silica/surfactant micelles aggregates in solution. The crumpled shell-like particles in the as-synthesized sample indicate that while the long bridging chains are capable of forming vesicular structures, they are very flexible, and may collapse in solution even before drying occurs.

No peak is observed in the XRD pattern of BEO (consistent with the absence of long-range order). Isotherm plots for sample BEO are similar to those of other hollow particles (e.g., samples TE, TP, and BEE). This proves that a portion of the particles in this sample are indeed hollow particles with porous shells. The specific pore volume of the sample is not exceptionally large, however, because of the presence of collapsed particles. The adsorption-desorption isotherms for BEO are not reversible at the low pressures ($P/P_0 < 0.4$). The irreversibility can be attributed to either the swelling of the adsorbent or a chemisorption process. Since nitrogen is inert to the silica, it is more likely that the pore structure in sample BEO is not stable at low pressures. This indicates that the octane chains may swell at low relative pressure.

In this section, a silane with long bridging chain (C8) has been used as the precursor. Only part of the material has hollow features. This shows that while multilamellar vesicle particles with large organic bridges can be formed using $F_8H_{10}$, there is a limitation to the chain length that can be used to form stable vesicular structures.

8.3.4. Synthesis of materials from BTMSPA and BTESPA

Organic-inorganic hybrid materials containing amine groups are desirable for various applications because of the amines (see Chapter 1). The synthesis of ordered structure using BTMSPA or BTESPA is challenging. Because of the flexibility of the bridging chain, it is easy for the precursor to condense without surrounding the surfactant micelles (see Chapter 4). Even when ordered pore structures can be synthesized in the as-prepared samples, the pore structures collapse easily upon the removal of surfactants. It would be
interesting to synthesize hollow particles with mesoporous shells containing amines. The hollow structure may be stable if the shells are thick enough.

In the previous sections (8.3.1, 8.3.2, and 8.3.3), we demonstrated that the F₈H₁₀ templated sol-gel process can be used to synthesize vesicular structures with different precursors. In this section, we will study the possibility to obtain vesicular structures with amines in the bridging chains. Two samples BMPA and BEPA are synthesized as the same conditions as sample TE and BEE. TEM images show that both of them do not have vesicular structures (Figure 8.13). Weakly layered patterns are observed in sample BMPA. Wormhole-like pores are observed in sample BEPA. Compared to the irregular shapes in sample BMPA, most particles in sample BEPA are spherical-like. The spherical-like shape is consistent with the spherical shapes obtained from other ethoxysilanes (TE and BETE).

No peaks are observed in the XRD patterns of samples BMPA and BEPA, which is consistent with the poor ordering observed in the TEM images. The nitrogen sorption data is reported for both samples in Figure 8.14. Isotherms of sample BMPA are similar to those in samples TM and BME. A triangular hysteresis loops (type H2) is observed. This indicates that sample BMPA has channel-like pores with nonuniform diameter. The isotherms in sample BEPA are reversible, indicating low porosotiy and a lack of hollow particles.

The investigation in this section shows that the amines in the bridging chain disrupt the formation of multilamellar vesicular particles. BTESPA has a bridging chain shorter than that in BTESO. Since sample BEO contains some vesicular particles, we would have expected that hollow particles can be produced with BTESPA as the precursor. The lack of any hollow particles in sample BEPA shows that the amines have changed the interactions between the hydrolyzed silica species and the surfactant micelles resulting in the formation of solid mesoporous particles. The particle morphology in sample BMPA is consistent with other samples prepared with methoxysilanes. This further confirms that methoxide groups are not favorable for vesicular structures even when functional groups like amines are included in the bridging chains.
8.4. Conclusions

To summarize, a new partially fluorinated surfactant F$_8$H$_{10}$ has been used as the template. Spherical hollow particles with different shell structures have been formed with different silanes, including multiple layers, single layers, and solid mesoporous shells.

We find that all materials synthesized with methoxysilanes lack hollow structures. All materials synthesized with ethoxysilanes, but with non-functional bridging chains, contain hollow particles. The addition of amines into the bridging chain destroys the hollow structure, leading to the formation of spherical solid particles.

8.5. References

Figure 8.1. Representative TEM images of TM, TE, TP, and TB.
Figure 8.2. XRD patterns for samples TM and TE.
Figure 8.3. Isotherm plots for samples TM, TE (up-shifted 200 cm$^3$/g), TP (up-shifted 450 cm$^3$/g), and TB (up-shifted 700 cm$^3$/g).

Figure 8.4. PSDs for samples TM, TE, TP, and TB.
Figure 8.5. Representative TEM image of TE-M.

Figure 8.6. Nitrogen sorption data for samples TE and TE-M: (a). Isotherm plots; (b). PSDs.
Figure 8.7. Representative TEM images for: (a) BME with weak ordering; (b) BME with highly ordering; and (c) BEE.
**Figure 8.8.** XRD patterns for samples BME and BEE.

**Figure 8.9.** Nitrogen sorption for samples BME and BEE: (a) Isotherm plots for BME and BEE (up-shifted 250 cm$^3$/g); (b) PSDs.
Figure 8.10. Representative TEM images for sample BEO

Figure 8.11. Representative TEM image for the as-synthesized BEO
Figure 8.12. Nitrogen sorption for sample BTESO: (a) Isotherm plots; (b) Pore size distribution (PSD).
Figure 8.13. Representative TEM images for samples BMPA and BEPA.

Figure 8.14. Nitrogen sorption for samples BMPA and BEPA: (a) Isotherm plots; (b) Pore size distributions (PSDs).
Chapter 9. Preparation of Highly Dispersed Iron Oxide Nanoparticles in Amine-Modified SBA-15

9.1. Introduction

Highly dispersed nanosized metal oxide particles are of particular interests in catalysis, optics, magnetics, and medicine.\textsuperscript{1-4} For these applications, the product activity is determined not only by the size and crystallinity of the nano-scale particles, but also by the dispersion of these particles on a porous support. Mesoporous silica has been widely used as a support since it has high surface area, adjustable pore size, controllable pore structure, and is chemically inert. However, loading of metal oxides into these supports can be difficult to control. Iron (III) nitrate is a classic precursor used to prepare iron oxide particles. In solution, the first step in oxide synthesis is usually to precipitate iron hydroxide particles by raising the pH of the solution. The iron hydroxide can subsequently be transformed to the oxide by calcination. This process generates particles with a wide distribution of sizes and irregular shapes. The reason may be the rapid, uncontrolled precipitation and agglomeration that occur after adding a base such as concentrated aqueous ammonia. For supported oxides, the nitrate can also be loaded directly onto the support and converted to the oxide by calcination at high temperature, but the level of loading that can be achieved is limited.\textsuperscript{5}

Here, we demonstrate an improved process to prepare dispersed nano-sized iron oxide by using amine-modified SBA-15 as the support. When placed in aqueous solution, the amine groups should be rapidly protonated, to generate hydroxide species locally. The hydroxide reacts quickly with ferric ions to produce iron (III) hydroxide. At the same time, some of the ferric ions may form complexes with silanols at the surface of the material. By either mechanism, widespread rapid nucleation at the surface of the pores of the support is expected to lead to the formation of small, well dispersed nanoparticles within the uniform cylindrical pores of SBA-15. Previously, amine-functionalized silica supports have been used to generate supported CdS particles by complexation and reaction,\textsuperscript{6} but in the present case, the mechanism for particle formation does not rely on direct amine complexation of the metal, and can be generalized for many types of dispersed metal oxide nanoparticles.
9.2. Experimental Section

9.2.1. Materials. Tetraethoxysilane (TEOS) and (3-trimethoxysilylpropyl)diethylene-triamine (TMPDTA) were purchased from Gelest. Ferric nitrate nonahydrate (Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O) and silver (I) nitrate were purchased from Sigma. Pluronic® surfactant P123 was obtained from BASF, and has average composition HO-(C\textsubscript{2}H\textsubscript{4}O)\textsubscript{20}-(C\textsubscript{3}H\textsubscript{6}O)\textsubscript{70}(C\textsubscript{2}H\textsubscript{4}O)\textsubscript{20}-H. All chemicals used were of the highest available purity.

9.2.2. Synthesis. SBA-15 mesoporous silica was synthesized based on the original procedure reported by Zhao et al.\textsuperscript{7} P123 was dissolved in deionized water with heating. After cooling down to room temperature, a measured quantity of concentrated aqueous HCl (36.5 wt\%) was added. TEOS was then added to the acidic solution with stirring. The mass ratios used were 1 g P123: 32.04 g deionized water: 7.96 g concentrated HCl (36.5 wt\%) : 2.17 g TEOS. The solution was stirred at room temperature for 30 minutes before it was aged at 80 °C for 3 days without stirring. The as-synthesized sample was collected by filtering the solution and was then calcined in air at 550 °C for 4 hours to remove the surfactant. Amine functionalization was begun by dispersing 0.5 g of calcined SBA-15 in 50 g of toluene with 0.1 g of TMPDTA. The mixed solution was then refluxed for 1.5 hour. After filtration of the solution, the modified SBA-15 was dried overnight at 110 °C. The amine-modified material will be called MSBA-15. Before loading iron hydroxide, 0.20 g of MSBA-15 was ultrasonically dispersed in 4.0 g of acetone. A ferric nitrate solution was prepared with 3.0 g deionized water and 8.0 g ferric nitrate nonahydrate. The ferric nitrate solution was heated to 70-80 °C to ensure a rapid reaction inside the pores. The dispersed MSBA-15 solution was then added dropwise to the aqueous iron nitrate solution. After stirring overnight, the mixed solution was filtered. The filtered loaded sample was dried in air for 2 days, and then was washed several times with copious ethanol to remove excess ferric nitrate, until the washing ethanol was colorless. After washing, the sample was calcined at 300 °C in air for 2 hours to produce loaded MSBA-15. The iron oxide loaded, modified SBA-15 sample will be designated as LMS.
9.2.3. Characterization. Nitrogen sorption at ~77 K was performed with a Micromeritics Tristar 3000. All samples were degassed under flowing nitrogen at 110 °C for 4 hours before the measurement. XRD patterns were recorded with Siemens 5000 X-ray Diffractometer. Data were recorded in the 2θ range from 1.6° to 60° with a step size of 0.02 degrees and a speed of 0.5 degrees/min. Transmission electron micrographs were taken with a JEOL 2010 F transmission electron microscope at 200 kV. TEM samples were prepared by depositing dried powders onto lacey carbon grids. Magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer. The temperature dependence of the magnetization was measured using field cooling from room temperature (310 K) to 4 K in applied magnetic fields of 5000, 500 and 100 Oe. The magnetic hysteresis was measured at room temperature and 15K. The loading of iron was measured with an ICP optical emission spectrometer, and independently by energy dispersive x-ray analysis (EDX).

9.3. Results and Discussion

Several steps in the loading procedure are crucial to the controlled formation of supported metal oxide nanoparticles. The initial dispersion of silica in acetone is important to help distribute the silica homogeneously during addition to aqueous ferric nitrate. The drying step after iron hydroxide precipitation is critical to achieving a high level of loading. Without this step, the loading obtained was less than 2 wt%. The reason might be that partially hydrolyzed iron compounds form initially due to the limited availability of hydroxide ions. These partially hydrolyzed compounds are still soluble and therefore easily washed away unless the samples are dried. The washing step is necessary to remove the extra ferric nitrate. If this is not done, large crystalline particles of iron oxide are observed after calcination. The amine modification is important because without it, we find much lower loading of iron in the product.

The original ferric nitrate solution is reddish brown, and it is difficult to directly observe the formation of ferric hydroxide. The effect of the amine group in MSBA-15 was instead confirmed by performing several experiments with silver nitrate in place of ferric nitrate. Silver nitrate is expected to also form a hydroxide precipitate under basic conditions. However, the nitrate solution is colorless, while the hydroxide precipitate is grey or
brown. Two samples were prepared using the same loading procedure as the iron (III) nitrate, but with 0.05 g SBA-15 or MSBA-15, 1.0 g acetone, 0.75 g water, and 2 g silver (I) nitrate. The SBA-15 or MSBA-15 was ultrasonically dispersed in acetone, and in a separate vessel silver nitrate was dissolved in water and heated to 80 °C. When MSBA-15 was added to the heated silver nitrate solution, the colorless solution turned dark brown immediately, indicating the formation of silver hydroxide. The color of the mixed solution became darker with time. The solution mixed with SBA-15 did not change its color noticeably. Initially, the solution was pale grey. After aging both solutions without stirring for 2 weeks, dark brown/grey precipitates were observed with MSBA-15 while light grey precipitates were observed with SBA-15. The difference in the color between the two solutions demonstrates that the amine groups induce the precipitation of silver hydroxide. Presumably, the amines have a similar effect in the ferric nitrate solutions.

Nitrogen sorption isotherms and pore size distributions of samples SBA-15, MSBA-15, and LMS are compared in Figure 9.1. Sharp inflections in the isotherms at about the same relative pressure are observed for all samples. All samples have narrow pore size distributions centered at between 7 and 7.5 nm. The decrease in the pore size of MSBA-15 compared to SBA-15 is consistent with amines lining the surface of the pores. The peak pore size of LMS is the same as SBA-15, which is consistent with the amine groups being removed during calcination. However, the total surface area and pore volume of LMS are smaller than SBA-15 because of the incorporation of iron oxide particles inside the pores, reducing the pore volume.

XRD patterns of LMS show no reflections over the range of angles studied. The absence of reflections at low angles is due to the large d-spacing of the SBA-15 structure. The 2D hexagonal order of the silica support is confirmed by TEM, however. The absence of high-angle reflections indicates that the loaded iron oxide particles are amorphous or present as extremely small crystallites. TEM and STEM images were collected for the LMS sample. In the TEM mode, long range 2D hexagonal order is apparent, but it is difficult to specifically identify the iron oxide particles. No lattice fringes from crystalline iron oxide could be observed with high resolution TEM. This shows that virtually all of the iron oxide nanoparticles are
amorphous. By comparison, a sample prepared without the ethanol washing step after loading contains many large crystalline iron oxide particles. Because of its improved resolution and elemental contrast, darkfield STEM is used to observe the particle size and dispersion in the pores. One representative STEM image is shown in Figure 9.2a. The bright spots in the image are confirmed to be iron oxide particles by an EDX composition scan across one of the rows of iron oxide particles (Figure 9.2b and 9.2c). In the EDX profile, the density of iron is lowest at the edge and highest in the center of the selected particle. This confirms that this particle is an iron oxide particle; otherwise the density of iron should not change at different positions across this particle. Also, Figure 9.2b shows that these particles are very well dispersed in a pattern corresponding to the close-packed cylindrical pore structure of the SBA-15 support. The average size of the particles is around 4.0 nm. Consistent estimates of the loading of iron in the LMS are found by EDX and ICP to be 11 wt%. This loading is higher than most of the loadings reported in silica-supported iron oxide materials.\textsuperscript{1,2,8,9}

The amorphous structure of our loaded Fe\textsubscript{2}O\textsubscript{3} particles is different from the crystalline structure reported by other researchers preparing supported iron oxide nanoparticles.\textsuperscript{10,11} This amorphous structure may impart special properties to the loaded nanoparticles.\textsuperscript{12} The particle size (4.0 nm) is similar to the particle size reported by Ninjbadgar et al. and by Hyeon et al. but their particles were crystalline \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3}.\textsuperscript{11,13}

The measured magnetic properties of the LMS sample are shown in Figure 9.3. The magnetization is normalized by the loading of the iron oxide particles estimated from EDX and ICP. The loaded particles are found to be superparamagnetic at room temperature. A small hysteresis loop is observed at 15 K. The saturation magnetization at this temperature is about 17.0 emu/g. The low saturation magnetization is consistent with the magnetic properties of nanosized \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3} particles reported by Morales et al.\textsuperscript{14,15} The small particle size and the amorphous structure of the present sample might be the reason for the low saturation magnetization.\textsuperscript{14,15} The blocking temperature of LMS is below 4 K (not shown), which is much lower than that of reported nanocrystalline Fe\textsubscript{2}O\textsubscript{3} particles with similar sizes.\textsuperscript{11,13} Surface effects are probably responsible for the decrease in blocking temperature, since the particles are very fine, and are uniformly distributed over the silicon dioxide surface of the pores.\textsuperscript{11}
9.4. Conclusions

In this chapter, a new method was applied to load iron oxide nanoparticles in the cylindrical channels of mesoporous silica SBA-15. Amine functional groups were grafted onto the surfaces of the pores to induce localized precipitation of metal hydroxides inside of the pores. Calcination of the hydroxide leads to the formation of iron oxide. The concept of localized hydrolysis was demonstrated to produce iron oxide nanoparticles ~4 nm in diameter that do not block access to the pores. Iron loading as high as 11 wt% has been achieved, and even higher loading levels may be possible by this method. The loaded nanoparticles are amorphous and are very well dispersed over the surface of the pores after synthesis and calcination. SQUID measurements show that these particles are superparamagnetic at room temperature, which is consistent with their nanoscale size. An unusually low blocking temperature is found in the loaded sample, probably due to surface effects associated with the fine particle size and interactions with the support. These findings are promising indications that the loaded samples may have unusual properties for catalysis and for magnetic applications in medicine.

9.5. References


Figure 9.1. Nitrogen sorption isotherms and pore size distributions calculated with a modified BJH method for SBA-15 after calcination, amine-modified SBA-15 (MSBA-15) without calcination, and iron oxide-loaded SBA-15 (LMS) after calcination.
Figure 9.2. Representative dark-field STEM images and density profile of LMS: (a) STEM showing many bright iron oxide nanoparticles (several indicated with arrows); (b) STEM image with one bright particle selected for an EDX profile; (c) EDX profile of iron along the slice indicated by the solid line in (b).

Figure 9.3. Hysteresis diagrams of LMS at 310 K and 15 K.
Chapter 10. Conclusions and Opportunities for Future Work

10.1. Conclusions for previous work

This thesis has described studies of aspects of the synthesis, characterization and applications of sol-gel derived nanoporous silica and organic-inorganic hybrid materials. The synthesis and characterization of a number of silica-based porous materials made with a variety of organic modifiers and with a variety of pore templates has been described. The kinetics of the sol-gel reaction and the mechanism of the Stöber particle synthesis process in the presence of a surfactant were investigated. The use nanoporous silica as an active matrix for the formation of supported metal oxides was demonstrated.

The primary activity for this research was to synthesize well-defined nanoporous silica particles using cationic fluorinated surfactants as templates. In Chapter 1, we stated two main goals in the use of fluorinated surfactants as templates based on their self-assembly characteristics. One was to prepare silica with novel pore structure. In Chapters 7 and 8, we successfully demonstrated that these surfactants can be used to create particles not only with the usual pore structures found in mesoporous silica such as hexagonal and wormhole-like pores, but also with novel pore structures including random mesh phase tactoids, particles with multiple hollow chambers, and vesicular silica particles with either mesoporous shells or multilamellar shells. The unusual pore structure formed by some surfactants, especially 1H,1H,2H,2H-perfluorodecylpyridinium chloride, is consistent with the stiffness of fluorinated surfactants and their tendency to form aggregates with low curvature including discs and bilayers. Unusual sequences of structure transformations were found for this and other surfactants as the concentration was increased. The other main goal in using fluorinated surfactants was to synthesize silica with extremely small pores. This was achieved convincingly with the synthesis of supramolecularly templated silica with 1.6 nm diameter pores. This pore size fills in the gap between the pore sizes available in zeolites (<1.5 nm) and those that had been available in mesoporous silica prepared with hydrocarbon surfactants (>2 nm). The next step in this research would be to synthesize ordered silica with this pore size.

As the first group to use cationic fluorinated surfactants as pore templates, we have carried out comprehensive studies on the use of these surfactants as templates, some of
which is presented in the main text and some of which is outlined in the appendices. We investigated effects of process parameters and drying conditions on the pore structure. We concluded that cationic fluorinated surfactants templated sol-gel process is sensitive to the reaction and drying conditions. Long-range pore order is best achieved by a moderate stirring rate and drying conditions that give the silica time to condense fully before the solvent is gone. The addition of solvents to the process is a common route to control the pore size and the pore structure. We are the first group to employ fluorocarbon solvents in this process. Fluorocarbon solvents may be incorporated into surfactant micelles to expand the pore size.

In our research, we obtained spherical particles with radial pores from aqueous ethanol with the use of HFDePC as the template. This casts doubts on the proposed mechanism for the formation of these particles in the published literature. In Chapter 5, we proposed and demonstrated the validity of an alternative mechanism for this process. In this mechanism, small disordered silica/surfactant aggregates are formed initially. These small aggregates then aggregate together to form large particles which are still ordered. An ordered structure emerges only after the formation of these large silica-surfactant aggregate particles. We have found evidence that the radial alignment of the pores in the particles is produced by preferential orientation of cylindrical micelles normal to the particle/solution interface, and realignment of the micelles during aggregation and aging. A related mechanism is probably followed for many surfactant-templated particles prepared at room temperature, and may be generalized to explain the synthesis of other nanoporous materials, including zeolites.

The work with particles with radially oriented pores (Chapter 5) and with vesicular silica particles (Chapters 7, 8) sparked an interest in preparing other high-capacity porous particles. This led to a study of the use of latex micropsheres combined with a cationic surfactant as dual templates for porous silica (Chapter 6). This chapter presented the first example of using a stable latex core together with CTAB to prepare hollow spherical silica with hexagonally ordered mesoporous shells. The process mechanism was investigated by adjusting the relationship between the initial composition and the product structure and dispersion. This work leads us to conclude that the shell thickness and core
size can be independently controlled by the choice of the latex size. However, colloidal stability places limits on the types of particle that can be produced.

Another major part of this dissertation addresses the synthesis of organic-inorganic hybrid materials by using bridged silanes as precursors. BTMSPA with an amine group in the bridging chain has attracted our attention due to its potential usefulness as a site for adsorption, catalysis, and chemical modification. As part of studying the behavior of this silane, we investigated effects of the initial sol composition on the gel time (reported in the Appendices). In particular, we explored the role of solvent in detail. We need not only to consider its polarity, but also its specific functional groups to evaluate its influence on kinetics. This is the first time that the influence of solvent on gelation was related to the combined contributions from its polarity and its functional group.

In spite of many informative investigations in the 1990s, the kinetics of the sol-gel reactions of organically modified alkoxy silanes are not completely understood. Until this thesis, only one study by Vainrub et al. has been carried out on the comparison of a non-bridged silane with its corresponding bridged silane. Also, a study comparing the reactivity of bridged silanes with different chain lengths and different chain structures was not reported. In Chapters 2 and 3, we compared the kinetics in both acidic conditions and basic conditions of a deliberately selected series of silanes. These silanes possess differences representing the types of differences found among all silanes. Contributions from the organic group size, functionality, bridging chain, bridging chain length, and bridging chain functionality on the kinetics were discussed in detail. Basically, all the contributions could be explained based on inductive or steric factors. Bulky precursors will retard the reaction while the inductive factor might be different according to different reaction conditions. In basic conditions, the reaction will be fast if the electron density in the silicon is low. In acidic conditions, the reverse trend is observed. In Chapter 4, we synthesized materials based on the same set of silanes as were used for the kinetic investigations. Some of the structural features of the resulting materials could be understood in terms of the kinetic trends, but others could not. Structural factors related to the prevalence of cyclization in sol-gel polymerization also play a role in determining the gelation and pore properties of the products.
A last aspect of these materials that was a small part of this thesis is the application of the materials as a support for active nanoparticles. We introduced a new method of controlled precipitation of metal oxides. The surfaces of SBA-15 were functionalized with amines and used to precipitate iron hydroxide from a nitrate solution. The localization of amines at the pore wall also localized the formation and deposition of iron at the pore walls. The result was loaded materials with a high loading of uniform, accessible nanoparticles. The product had superparamagnetic properties consistent with the nanoparticle size, and could have medical imaging or catalytic applications.

To summarize, this thesis addressed several aspects of the sol-gel process for making organically modified and surfactant templated porous materials. We studied the kinetics of the precursors, investigated the mechanism of particle formation, and synthesized materials. We have contributed to the understanding of how ordered porous particles can be formed by the sol-gel process. This thesis pioneered the use of fluorinated surfactants as pore templates. We have proven that these surfactants have advantages in this research area for the formation of small or unusual pore structures. The next step to expand the usefulness of these surfactants will be to design a highly CO₂-philic fluorinated surfactant and work to demonstrate that the surfactant can be extracted and recycled after the synthesis of ordered silica. This will be one of the most important achievements to rationalize the use of fluorinated surfactants as templates. The success in this idea will bring a new concept to commercialize ordered mesoporous materials by removing one of the cost barriers to large-scale production of these structures.

10.2 Opportunities for Future Investigation

As described above, many accomplishments have been achieved in the course of this dissertation. However, several possible directions were not successful, some were not fully explored, and some could serve as areas for future investigation. The first of these is the use of amine-functionalized mesoporous silica for pH-responsive release of fluorescent dyes. This project has actually had some promising preliminary results showing that sulforhodamine-B can be successfully loaded, retained in the particles under acidic conditions, and released from the particle by raising the pH of the solution.
However, the investigation is not complete and needs to be reproduced and the release profile with respect to pH needs to be quantified still.

We have tried different reported conditions for the preparation of silica samples different than what was described here. We found that it was difficult to prepare ordered silica under several conditions (the materials may have uniform pores but not long-range order). The first condition is carrying out the precipitation reaction for fluorinated surfactants with NaOH instead of aqueous ammonia. No ordered silica was prepared with the presence of NaOH at room temperature or elevated temperature (above 100 °C). The second condition attempted is a highly acidic environment. Nanocasting (polymerization of an alkoxysilane in a highly concentrated surfactant solution) and the recipe for the acid-catalyzed sample SBA-1 were tested with HFDePC as the template. No ordered silica was obtained at any of the Si: surfactant ratios attempted. The failure of these conditions to yield ordered pore structure further confirms that fluorinated surfactants are different than the corresponding hydrogenated surfactants. It is possible that the fluorinated surfactant mesophases form defects more easily, so that strong interactions with silica are required to induce any ordering. However, ordered silica may still be prepared under these conditions by optimizing the reaction conditions further.

Another direction that we pursued but which did not reach completion was the formation of new types of mesophases. In the presence of aqueous ammonia, we synthesized silica with pore structures of wormhole-like, hexagonal, random mesh phase, and vesicles. However, there are other phases that exist in the phase diagrams of fluorinated surfactants that have not yet been replicated in silica. These phases include cubic, rectangular, trigonal mesh phase, and other novel phases formed by a fluorinated surfactant. Opportunities are still available to form a variety of unusual pore structures.

Besides cationic fluorinated surfactants, we also tried to use anionic surfactants as pore templates. The main motivation for this is that anionic fluorinated surfactants are commercially available (the cationic fluorinated surfactants used in the body of the thesis had to be synthesized). The work on using anionic surfactants was not reported in the dissertation since no ordered silica was synthesized. Most materials prepared had a lamellar pore structure, which was collapsed upon the removal of the surfactant. There are ways to attempt to improve the order of the materials prepared by this process. The
best approaches are to add compounds either to change the phase structure of the anionic surfactant, or to increase the interactions between the surfactant micelles and the silica species.

An unmet challenge was to synthesize ordered organic-inorganic hybrid from silanes with long bridging chain. We did not obtain any ordered structure from pure BTMSPA. Different conditions were tried, and lamellar structures actually were observed for some of as-synthesized samples. However, the structure collapsed after the remove of the surfactant. Ordered structures were obtained in some samples by co-condensation of BTMSPA with TEOS. However, this procedure is not unusual. Basically, a small amount of any silane could be incorporated into an ordered structure through a co-condensation process. The organic and inorganic distributions may not be uniform in these co-condensed materials. With BTMSPA as the precursor, one material with wormhole-like structure was synthesized. This material has uniform pore size and high surface area. This is the first time as we know that a material with wormhole-like structure was prepared with BTMSPA as the precursor. Under similar conditions, no uniform pore was obtained for BTMSH. The difference in these two materials indicated the effect of amine on the interactions between the silica and surfactant micelles. These results are somewhat promising, but still need more exploration.

Finally, in the course of this research, we have investigated the possibility to synthesize ordered materials through the non-hydrolytic sol-gel process. This work is not reported in this dissertation because the goal of forming an ordered structure has not yet been achieved. In this process, different templates have been used. Materials with high surface areas and narrow pore size distributions were obtained without any template. The addition of cationic hydrogenated surfactants did not change the pore structure. The addition of polymeric surfactants expanded the pore size. The presence of fluorinated surfactants accelerated the condensation so much that it could not be controlled. This shows that a fluorinated surfactant (or perhaps the pyridinium head group) can accelerate the reactions. An explanation for this observation could be the subject of a future investigation.
Appendix A. Investigation on the Factors Affecting the Gel Time of Bis(trimethoxysilylpropyl)amine

A.1. Introduction

The kinetics of the sol-gel reaction of 3-aminopropyltrimethoxysilane has been discussed in the second chapter, and compared to the kinetics of bis(trimethoxysilylpropyl)amine (BTMSPA). One of the findings is that the gel time of a solution can not necessarily be predicted based on the reaction kinetics measured early in the process. This is because the sol-gel reaction is a polymerization process and, as such, involves a distribution of species that have not been explicitly considered when we established the model to estimate the reaction rate. These neglected effects of molecular structure on reaction kinetics might be critical to being able to predict the gel times. Gel is due to the formation of a three dimensional network structure. A more reactive precursor will not necessarily form a gel more easily, especially if it forms intermediates which are unreactive toward further polymerization. For example, it has shown in Chapter 3 that bis(trimethoxysilyl)ethane (BTMSE) is much more reactive than bis(trimethoxysilyl)hexane (BTMSH) under the same reaction conditions. However, it has shown in Chapter 4 that it takes a much longer time for BTMSE to gel than BTMSH. The explanation for these discrepancies should be related to structural differences. For instance, cyclization (the formation of rings during polymerization) has been shown to have a profound effect on delaying gelation in ordinary sol-gel silica.1-4

In this chapter, we investigate the factors affecting the gelation kinetics of bis(trimethoxysilylpropyl)amine (BTMSPA). Bridged silanes are organic molecules with two or more covalently attached trialkoxysilyl ligands.5-7 The organic molecule forms a preexisting “bridge” between the silicon sites that will connect the siloxanes together during polymerization. The result is a highly functionalized organic-inorganic hybrid (a “bridged silsesquioxane”) with the organic functionality integral to the network of the material.8 These types of materials have been used to create bulk aerogels or xerogels,5-7,9 and surfactant-templated mesoporous materials.10-12

BTMSPA is a bridged precursor that has not been studied in detail as a sol-gel precursor before. It is commercially available as a coupling agent for improving adhesion
between polymers and fillers. This precursor has not been explored as a bulk material precursor until just recently, when it was incorporated into materials prepared by surfactant templating.\textsuperscript{13,14} It is an interesting precursor not only because it has bridged structure but also it contains amine. The attractions of amine functionality are (1) Amines interact strongly with solutes – a property useful for specific adsorption\textsuperscript{15} and basic catalysis\textsuperscript{16}, (2) amines can be protonated, which makes them useful ingredients for stimulus-responsive materials similar to hydrogels,\textsuperscript{17} and (3) amines are suitable sites for further chemistry and structure building. For example, epoxy functionality can be used to covalently attach field-responsive molecules to create “nanovalves”\textsuperscript{18} in porous materials. In spite of the useful applications of these and other bridged silanes, there have only been a few systematic studies of the gelation kinetics of them.\textsuperscript{19,20} The study of the influence reaction conditions on the gel time of BTMSPA is a first step toward understanding how the structure develops in these systems, and how to engineer the synthesis to obtain desired properties.

A typical sol-gel reaction consists of four ingredients: the precursor, water, catalyst, and solvent. In this chapter, we investigate the effects of each component on the gel time. The results can be compared to the behavior of conventional tetrafunctional sol-gel precursors, as detailed in the book by Brinker and Scherer.\textsuperscript{21} The gel time of BTMSPA shows about what would be expected for the sensitivity to the water content, and exceptionally strong sensitivity to the concentration of the precursor. Solvent effects are explored in detail, and can only be understood in terms of the combined effects of transesterification reactions (for alcohols), polarity, and the specific structure of the solvent.

A.2. Experiments

A.2.1. Materials. Bis(trimethoxysilyl)propyl)amine (BTMSPA, 95\%) was purchased from Gelest, Inc. and used as without further purification. Deionized ultrafiltered water was (Fisher Scientific), normalized 1N HCl (Alfa Aesar) and ethanol (absolute, Aaper Alcohol and Chemical) were used for the preparation of samples. All other solvents were of ACS grade and were purchased from Aldrich.
A.2.2. Synthesis. The sol-gel reaction was carried out at room temperature (21±2 °C). To prepare gels, a solution of precursor in the solvent of interest was first prepared in a polypropylene vessel. Then aqueous catalyst (1N HCl), H₂O and solvent were mixed in a separate vessel. The specific compositions of the samples will be provided below along with the gel time results. At the start of the reaction, these solutions were mixed quickly by hand and the vessel was sealed. The resulting solution was initially colorless and clear. The vials were aged at room temperature until the gel point was determined as the point at which no movement of the meniscus of the sample could be observed upon tilting the vial at 45 ° relative to vertical. More specifically, the gel point was defined as the time at which the meniscus did not move within one minute of being tilted.

A.2.3. Characterization. pH values of the samples were measured with a handheld pH meter and a sure-flow refillable glass pH electrode. The meter was calibrated with pH 4, pH 7 and pH 10 buffers (Fisher Scientific), and the electrode was rinsed thoroughly with DIUF water after each measurement.

A.3. Results and discussion

Different conditions that affect the gel time of a sol-gel reaction are discussed in this section. Because of the amine contained in BTMSPA, solution containing BTMSPA are basic even when a small of amount of acid is added. In basic solution, hydrolysis and condensation reactions proceed through nucleophilic displacements. The hydrolysis has been proposed to be the rate-limiting step in the sol-gel mechanism, as discussed in Chapter 2. Therefore, condensation happens at basically the same rate as the hydrolysis step. The gel time indicates the overall reaction rate of the later stages of the process to obtain a network product. A few of the samples have enough added HCl that they are acidic. In acid solution, the hydrolysis reaction is fast enough that it is able to reach equilibrium, and condensation is the rate-limiting step. The gel time is controlled by the condensation rate at the late stages of the reaction. For TEOS, the reaction having the strongest influence on gel time is between tripoly-condensed silicon sites.
A.3.1. Effect of water on the gel time

To investigate the effects of different conditions on the sol-gel reaction, several series of experiments were performed. In the first, the effect of water on the gel time is investigated. For each sample, 1.716 mmol BTMSPA, 0.1970 g HCl (1N), 5 ml ethanol and a variable amount of water was used. The amount of water and the calculated concentration of water (assuming ideal mixing) are reported in Table A.1, along with the measured gel time. Gel times are compared in Figure A.1.

The solutions were basic with the above compositions. From Table A.1 and Figure A.1, we can observe that with the increase of water, the gel time was shortened initially and then became longer. There are three factors contributing to the change of gel time when water is added. First, the reaction rate will be slowed down by diluting the precursor. Second, the rate of the sol-gel reaction can be slowed down by accelerating the reverse of the water-producing condensation reaction (Equation (2) of Chapter 2). Third, the rate can be accelerated by increasing the rate of the hydrolysis reaction (Equation (1) of Chapter 2).

Comparing the expected water effects to the results observed for the first three samples, we can see that, although the monomer concentration is being reduced by adding water, the gel time is decreased. This indicates that at these compositions, additional water increases the hydrolysis rate to a greater extent than the other two effects reduce the rate of gelation. Thus the total reaction rate increases and the gel time decreases. If more water is added, the dilution and condensation reversibility effects of water dominate, and the net result is to retard the overall sol-gel reaction. In this situation, more water will lead to longer gel time. This trend continues as more water is added, and with 6 ml of added water, no gelation was observed even for one year.

It is possible that the dilution effect alone is responsible for no gelation occurring in the sample with the most water added. To test this, we prepared another sample when the water was replaced with 6 ml of extra ethanol. The concentration of each component except H$_2$O and ethanol is the same between the two samples. The resulting sample gelled in just 30 days. Therefore, it is the effect of H$_2$O as a reactant, and not just dilution, that makes the sample with 6 ml water not gel. The reason may be that the reverse water-producing condensation reaction plays an important role under this condition.
The conclusion for this part of the investigation is that both too little and too much water are not good to the overall rate of the sol-gel reaction of BTMSPA. There is an optimal amount of water, somewhat above the stoichiometric amount required for full hydrolysis, which gives the fastest gelation rate. This is similar to the effect of water on conventional sol-gel materials prepared from tetraalkoxysilanes.\textsuperscript{21} Also, it appears that the reverse water-producing condensation is more important than the reverse alcohol-producing condensation. This investigation also illustrates the complicated role of solvents and reactants in a sol-gel reaction.

\textit{A.3.2. Effect of methanol on the gel time}

To investigate the effect of methanol on the gel time, another solvent is needed to keep the concentrations of the precursor, catalyst, and water to be constant. This solvent should be chosen such that it is not expected to react with the precursors, and to have little effect on the reaction rate. Non-polar solvents are the best choice, as they do not participate in the reaction directly and they have no ability to stabilize the anion reactants or activated transition states.

Chloroform was selected as the non-polar solvent. The change of the concentration of this solvent can be assumed to have little effect on the sol-gel reaction (the concentrations of the reactants are kept the same otherwise). With this assumption, we can conduct a series of experiments isolate the effect of methanol on the gel time.

In this series of experiments, we kept the amount of precursor, acid, water and total volume of solution to be the same. Each sample was made with 0.6215 g BTMSPA, 0.1966 g HCl (1N), and 6 ml solvent. The results are reported in Table A.2.

Figure A.2 shows the dependence of gel time on the fraction of methanol in the solvent. We observe that as the concentration of methanol in the solvent increases, the gel time increases, i.e., the reaction rate decreases. The reason may lie in that the higher concentration of methanol will increase the rates of reverse hydrolysis and alcohol producing condensation, thus retard the gelation. On the other hand, a higher concentration of methanol would be expected to stabilize the anion reactants that participate in the sol-gel reactions (hydroxide and deprotonated silanols) and the reaction will also be slowed down. Both factors contribute together to the change of the gel time.
A.3.3. Effect of the precursor concentration on the gel time

It is known that the hydrolysis rate is first order with respect to the concentration of the precursor.\textsuperscript{21} The condensation rate in a sol-gel solution should be second-order with respect to the precursor concentration. How the concentration of BTMSPA affects the gel time is still unknown. To examine the role of BTMSPA concentration, a series of experiments were performed. 0.1936 g (0.1902 mmol) HCl (1N) and 1.004 g (55.59 mmol) water were used in each sample. The other components as well as the gel times are listed as Table A.3.

The main difference among these samples is the concentrations of BTMSPA. The amount of water is large enough for the hydrolysis to be completed for all samples. The data (Figure A.3) show that the effect of the precursor on the gel time is extremely large. The dependence is far greater than we should have for either a first-order or second-order reaction if gelation occurs at the same extent of reaction for all samples. There may be several factors that contribute to this high sensitivity. First, the precursor also contains an amine, so additional catalyst is added along with the precursor. Second, the structure of the gelling sols may not all be the same. If cyclization reactions play a role in the development of structure, then cyclization should become less important as the concentration of BTMSPA increases. This will help to accelerate gelation. The combined effect of a mass-action kinetic effect with these two additional factors may explain the high sensitivity of the gel time to the precursor concentration.

A.3.4. Effect of pH on the gel time

It is well known that sol-gel chemistry is very sensitive to the pH of the solution.\textsuperscript{21} A series of samples was prepared to investigate this effect for BTMSPA. For these experiments, 5.5 M HCl was prepared by diluting concentrated HCl (36.5 wt \%) with deionized water beforehand. The concentration of HCl was measured with a pH meter. To each sample, 0.4180 g BTMSPA and 2.375 g methanol were added. The other components, the measured pH values and the gel time are reported in Table A.4. The amount of water was kept the same among the samples.
In acidic conditions, the gel time becomes longer with the increase of pH. This is consistent with what we would expect for an acid-catalyzed reaction, although the sensitivity is quite large. The trend is different in basic conditions. The gel time becomes shorter with the increase of pH (Figure A.4). These trends are consistent with the trends reported for other silanes, although the sensitivity is quite high.\(^\text{19,21}\)

**A.3.5. Effect of the type of solvent on the gel time**

Solvents usually are classified as protic, polar aprotic, and non-polar solvents. They may play several roles in a chemical reaction. They may participate in the reaction directly, dissolve the reactants, and provide a favorable environment for the transition state, thus providing some catalytic effect medium. The interactions between the solute/ion and the solvent are very important to a reaction. The large difference of reaction rates in different solvents is caused by these interactions.

In basic solution, the reaction mechanisms are similar for both hydrolysis and condensation. Both of them are nucleophilic substitutions with transition states. The transition states have greater polarizability, charge dispersion\(^\text{25}\) and are more sterically crowded\(^\text{26}\) compared with the reactant anions. In protic solvents, anions are solvated by hydrogen-bonding, and small anions are more stable than larger ones.\(^\text{25}\) These characteristics would be expected to retard the reaction. In polar aprotic solvents, anions are solvated by nonspecific ion-dipolar and dispersion forces.\(^\text{25}\) There is less difference between the transition states and reactant anions. In non-polar solvents, there is little difference between the transition states and reactant anions. The reaction rate in non-polar solvents is therefore expected to be the fastest.

In our research, we found for the sol-gel reaction that the polarity of a solvent is very important to the reaction, as expected. We also find indications that the specific functional group of the solvent might be also important, while the steric effects of the solvent can be neglected if the solvents do not participate in the reaction directly. As electrostatic and steric interactions are the most important interactions between the solute/ion and solvent, we will discuss the effect of the solvent according to its polarity, category and steric effects in separate subsections.
A.3.5.1. Effect of solvents with the same polarity and in same category

We purposely selected three solvents with similar polarity and steric effect to begin our investigation. The compositions of each sample consisted 0.6144 g BTMSPA, 0.1935 g HCl (1N), 5 ml methanol, and 1 ml of the specified solvent were added. The gel times of these samples were measured, and are reported in Table A.5. These three hydrocarbon solvents usually considered as non-polar solvents, and they don’t participate in the reaction directly. As shown in Table A.5, we find that the gel time is almost the same among these solvents. This illustrates that, as expected, the reaction rate is same in different solvents with same polarity and within the same category.

These solvents are non-polar. They don’t tend to stabilize the anionic reactants with respect to the activated transition states. Therefore, these solvents should enhance the reaction significant compared with other solvents.

A.3.5.2. Effect of solvents with different polarities but in the same category
(a) Solvents that don’t participate in sol-gel reaction

In each sample in this series, the composition is 0.6156 g (1.802 mmol) BTMSPA, 0.1936 g HCl (0.1902 mmol), 3 ml methanol, and 3 ml solvent. The gel times of these samples are reported in Table A.6.

The above three solutions have the same functional group, but their polarities are different. Furan and tetrahydrofuran have similar steric bulk. Ethyl ether is less crowded than the other two. We find that the gel time increases with an increase of the polarity of the solvent among these three samples. This effect can be attribute this to the polarity effect, and indicates the solvents with higher polarity are unfavorable toward the sol-gel reaction in basic solution. This is consistent with the solvent effect on a nucleophilic substitution reaction in basic condition. Anionic reactants are more stabilized with respect to the activated transition states in the solvent with higher polarity. The gel time therefore should be longer.

(b) Solvents that participate in sol-gel reaction

All alcohols affect the sol-gel reaction not only by electrostatic and steric interaction, but also by participating in the reaction directly. A series of experiments have been
carried out to investigate this effect. Each of the samples consists of 0.6106g (1.788 mmol) BTMSPA, 0.1905g (0.1871 mmol) HCl, and 5 ml alcohol.

From Table A.7 and Figure A.5, we can see that the gel time decreases as the molecular weight of the alcohol increases. The only exception to this trend is methanol. We propose that this trend may be explained by the participation of alcohols.

When the alcohol is not methanol, transesterification reaction may be involved in the overall scheme. This reaction is shown in equation (A.1).

\[
\text{Si-OCH}_3 + \text{ROH} \rightleftharpoons \text{Si-OR} + \text{CH}_3\text{OH}
\]  

(A.1)

where R stands for CH$_3$CH$_2$-, CH$_3$CH$_2$CH$_2$-, (CH$_3$)$_2$CH-, CH$_3$CH$_2$CH$_2$CH$_2$-, etc.

The transesterification reaction rate is slower if R is bulkier. Thus, the transesterification reaction rate follows the order ethanol>n-propanol>1-butanol>2-propanol.

Si-OR groups produced by transesterification will also be hydrolyze and can participate in condensation reactions. In a sol-gel reaction in basic solution, the reaction is slower if R is bulkier. The more alcohol participates in the transesterification reaction, the slower the sol-gel reaction rate will be compared to the rate with pure methanol without the consideration of other reactions. Thus the reaction rates should follow the sequence ethanol<n-propanol<1-butanol<n-propanol based on the rate and extent to which transesterification would be expected to occur. This trend is consistent with the difference in the gel times.

On the other hand, anions are also solvated by the alcohols through hydrogen-bonding. The order of the ease of forming hydrogen bonds should be ethanol>n-propanol>1-butanol>2-propanol, according to the order of their polarities. The reaction rate in 1-butanol is expected to be slower than that is 2-propanol. What we observe from our experiment is not consistent with this expectation. This indicates that the steric effect of the alcohol on the rate of the transesterification reaction is the more important effect here.
If the solvent is methanol, there will be no transesterification reaction. However, rates of reverse hydrolysis and reverse alcohol producing condensation reactions should increase. This may retard the process to form gels. However, faster gelation is observed for methanol, which shows that transesterification is the dominant effect in this series.

If the concentration of methanol is high enough, the effect of reverse reactions may be greater than the transesterification effect of another alcohol. In this situation, the gel time in methanol will be longer than the gel time in some other alcohol. Otherwise, the gel time in methanol is shorter. The experiments in series (c) were carried out to prove this hypothesis.

(c) Methanol vs. ethanol

In the above series, we find a consistent trend, but it is hard to directly compare the sol-gel reaction rate between methanol and some other alcohol because of the possible influences from several effects. 5 pairs of samples were prepared in an effort to separate transesterification and reaction reversibility effects of alcohols. To each pair of samples, same amount of alcohol was added. The difference between them is that the alcohol is either methanol or ethanol. The difference in the gel time should be due to the different effects of reverse reactions and transesterification for each pair of samples. Amounts of the reactants except alcohol were the same. The composition is 0.6107 g (1.788 mmol) BTMSPA, and 0.1908 g (0.1874 mmol) HCl. The amounts of alcohols and gel times are shown in Table A.8.

From Table A.8, we can see when the concentration of alcohol is lower (samples 1, 1', 2, 2', 3, 3'), the gel time in methanol is shorter than that in ethanol. When the concentration is higher (sample 4, 4', 5, 5'), the gel time is longer in methanol. The difference in the gel times can not be simply explained according to the different polarities of methanol and ethanol. This must be explained based on the possible reactions that participate.

For the samples 1, 1', 2, 2', 3, and 3', the effect of reverse hydrolysis and condensation reactions is less than the effect of transesterification, as the concentration of the alcohol is very large. However, if the concentration of methanol is high enough, reversibility of hydrolysis and condensation reactions become significant. This makes
the gel time increase quickly as the amount of methanol increases in this series. One the other hand, as more ethanol is added, transesterification increases more quickly, but ethanol does not have as strong of an effect in promoting the reverse of the hydrolysis and condensation reactions. Therefore, the gel time of the series with methanol increases more quickly than the gel time of the series with ethanol, and for samples 4/4’ and 5/5’ there is a crossover so that the methanol-containing samples gel more slowly.

A.3.5.3. Effect of solvents with similar polarities but in different categories

As a final investigation of the influence of reaction conditions on gel time, we demonstrate the importance of the specific type of functional group on the solvent. To illustrate the importance of this effect, several samples were prepared. Solvents in the same and different categories were used to illustrate the importance of the functional group. For each sample, 0.6865 g BTMSPA, 0.2033 g HCl (1N), 3 ml methanol, and 4 ml of the specific solvent were added.

The results for this series are reported in Table A.9. In this table, ethyl ether and ethyl acetate fall in the same category. Chloroform and dichloromethane are also in the same category. We can observe from the table that the larger the polarity is, the slower the gelation is. It is the same trend as we observed in A.3.5.2 (a).

However, we see additional effects. In samples 1 and sample 2, the polarity of the ethyl ether is slightly greater than that of toluene, but the gel time is obviously shorter with ethyl ether. This contradicts the general trend expected that less polar solvents permit faster gelation, and indicates the functional group of a solvent is also important to the reaction.

As another example, for sample 5 and sample 6, the polarity of acetone is larger than that of dichloromethane, which means the gel time should be longer. However, the gel time in acetone is actually shorter. This again indicates that polarity alone is not enough to describe the electrostatic interactions between the solute and solvent. Some other factors need to be considered such as the specific electrostatic interactions between the solvent and the solute. As far as we know, functional group is the best choice. It should be combined with polarity to describe the solvation effects on the anionic reactants and activated transition states.
A.4. Conclusions

In this chapter, a comprehensive investigation was carried out to study the effect of reaction conditions on gel times of BTMSPA. The investigation showed that the gel time is affected not only by the concentration of each component, but also by the type of the solvent. The effect of water is similar to the effect observed in other sol-gel systems, and represents a tradeoff between accelerating hydrolysis and diluting the reactants. The gel time decreases as the concentration of the precursor, but much faster than would have been predicted based on mass action kinetics. The role of solvent was discussed in detail. Polarity is a useful index to understand the effects of the solvent, but there are additional effects that must be considered. For alcohols, transesterification may occur, which has retards gelation. For nonreactive solvents, the specific functional group is also important in completely explaining the role of the solvent. All effects were successfully explained based on the anticipated effects of the process parameters on the base-catalyzed hydrolysis and the condensation of the precursor. The investigation may give practical instruction on how to use BTMSPA as a coupling reagent and as a reagent for the synthesis of advanced functional materials.

A.5. References

Table A.1. Effect of water on the gel time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added H₂O (ml)</th>
<th>[H₂O] (mol/l)</th>
<th>Gel Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1.478</td>
<td>160 min</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>2.950</td>
<td>58 min</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>4.343</td>
<td>42 min</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>13.29</td>
<td>10 hr</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>26.20</td>
<td>No gel for 1 year</td>
</tr>
</tbody>
</table>

Table A.2. Effect of methanol on the gel time.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Chloroform (ml)</th>
<th>Methanol (ml)</th>
<th>Gel Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>6</td>
<td>333</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>5</td>
<td>241</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3</td>
<td>187</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>2</td>
<td>170</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>1</td>
<td>109</td>
</tr>
</tbody>
</table>

Table A.3. Effect of precursor on gel time.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>BTMSPA (mol/l)</th>
<th>Methanol (ml)</th>
<th>Gel Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02037</td>
<td>5.20</td>
<td>1584</td>
</tr>
<tr>
<td>2</td>
<td>0.02275</td>
<td>5.15</td>
<td>109</td>
</tr>
<tr>
<td>3</td>
<td>0.02448</td>
<td>5.10</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>0.02693</td>
<td>5.05</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>0.02905</td>
<td>5.00</td>
<td>1</td>
</tr>
</tbody>
</table>
### Table A.4. Effect of pH on gel time.

<table>
<thead>
<tr>
<th>Number</th>
<th>HCl (5.5 M), g</th>
<th>Water, g</th>
<th>pH (measured)</th>
<th>Gel Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2180</td>
<td>0</td>
<td>0.32</td>
<td>8640</td>
</tr>
<tr>
<td>2</td>
<td>0.2086</td>
<td>0.0085</td>
<td>0.46</td>
<td>11520</td>
</tr>
<tr>
<td>3</td>
<td>0.1968</td>
<td>0.0162</td>
<td>1.39</td>
<td>No gel</td>
</tr>
<tr>
<td>4</td>
<td>0.1884</td>
<td>0.0244</td>
<td>7.60</td>
<td>270</td>
</tr>
<tr>
<td>5</td>
<td>0.1782</td>
<td>0.0325</td>
<td>8.00</td>
<td>132</td>
</tr>
<tr>
<td>6</td>
<td>0.1686</td>
<td>0.0410</td>
<td>8.20</td>
<td>94</td>
</tr>
<tr>
<td>7</td>
<td>0.1600</td>
<td>0.0478</td>
<td>8.45</td>
<td>71</td>
</tr>
<tr>
<td>8</td>
<td>0.1485</td>
<td>0.0576</td>
<td>8.62</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>0.0000</td>
<td>0.1796</td>
<td>10.85</td>
<td>23</td>
</tr>
</tbody>
</table>

### Table A.5. Effect of solvents with the same polarity and functional group on gel time.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Solvent</th>
<th>Category</th>
<th>Polarity</th>
<th>Gel Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pentane</td>
<td>Aliphatic Hydrocarbon</td>
<td>0.009</td>
<td>2 hr 53 min</td>
</tr>
<tr>
<td>2</td>
<td>Hexane</td>
<td>Aliphatic Hydrocarbon</td>
<td>0.009</td>
<td>2 hr 51 min</td>
</tr>
<tr>
<td>3</td>
<td>Heptane</td>
<td>Aliphatic Hydrocarbon</td>
<td>0.012</td>
<td>2 hr 49 min</td>
</tr>
</tbody>
</table>

### Table A.6. Effect of solvents with different polarities but in the same category on the gel time.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Solvent</th>
<th>Category</th>
<th>Polarity</th>
<th>Gel Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethyl Ether</td>
<td>Ether</td>
<td>0.117</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>Furan</td>
<td>Ether</td>
<td>0.164</td>
<td>145</td>
</tr>
<tr>
<td>3</td>
<td>Tetrahydrofuran</td>
<td>Ether</td>
<td>0.207</td>
<td>185</td>
</tr>
</tbody>
</table>
### Table A.7. Effect of alcohol on the gel time.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Solvent</th>
<th>Polarity $^{27}$</th>
<th>Gel Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
<td>0.762</td>
<td>109</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol</td>
<td>0.654</td>
<td>235</td>
</tr>
<tr>
<td>3</td>
<td>n-Propanol</td>
<td>0.617</td>
<td>194</td>
</tr>
<tr>
<td>4</td>
<td>2-Propanol</td>
<td>0.546</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>1-Butanol</td>
<td>0.602</td>
<td>74</td>
</tr>
</tbody>
</table>

### Table A.8. Effect of methanol and ethanol on the gel time.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Solvent</th>
<th>Amount of Alcohol (ml)</th>
<th>Gel Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>1'</td>
<td>Ethanol</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>Methanol</td>
<td>4</td>
<td>37</td>
</tr>
<tr>
<td>2'</td>
<td>Ethanol</td>
<td>4</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>Methanol</td>
<td>5</td>
<td>109</td>
</tr>
<tr>
<td>3'</td>
<td>Ethanol</td>
<td>5</td>
<td>235</td>
</tr>
<tr>
<td>4</td>
<td>Methanol</td>
<td>6</td>
<td>360</td>
</tr>
<tr>
<td>4'</td>
<td>Ethanol</td>
<td>6</td>
<td>292</td>
</tr>
<tr>
<td>5</td>
<td>Methanol</td>
<td>7</td>
<td>2220</td>
</tr>
<tr>
<td>5'</td>
<td>Ethanol</td>
<td>7</td>
<td>780</td>
</tr>
</tbody>
</table>

### Table A.9. Effect of solvents with different polarity and different group.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Solvent</th>
<th>Category</th>
<th>Polarity $^{27}$</th>
<th>Gel Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>Aromatic Hydrocarbon</td>
<td>0.099</td>
<td>126 min</td>
</tr>
<tr>
<td>2</td>
<td>Ethyl Ether</td>
<td>Ether</td>
<td>0.117</td>
<td>82 min</td>
</tr>
<tr>
<td>3</td>
<td>Ethyl Acetate</td>
<td>Ether</td>
<td>0.228</td>
<td>103 min</td>
</tr>
<tr>
<td>4</td>
<td>Chloroform</td>
<td>CHC</td>
<td>0.259</td>
<td>254 min</td>
</tr>
<tr>
<td>5</td>
<td>Dichloromethane</td>
<td>CHC</td>
<td>0.309</td>
<td>278 min</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>Ketone</td>
<td>0.355</td>
<td>248 min</td>
</tr>
</tbody>
</table>
Figure A.1. Effect of water on the gel time of BTMSPA sols.

Figure A.2. Effect of methanol on the gel time of BTMSPA sols.
Figure A.3. Effect of precursor concentration on the gel time of BTMSPA sols.

Figure A.4. Effect of pH value on the gel time of BTMSPA sols.
Figure A.5. Effect of alcohol type on the gel time of BTMSPA sols. See Table A.7 to see which alcohol corresponds to the sample number.
Appendix B. The Modified BJH Method for Slit-Shaped Pores

BJH method was first reported by Barrett et al in 1951. Since then, this method has been the one of the standard methods to evaluate the pore size distribution. However, the original BJH method was proposed for pores with cylindrical shapes. This method has to be modified for pores with slit shapes.

In this appendix, we will discuss how to modify the BJH method for slit-shaped pores. The BJH method is basically to solve the Wheeler’s equation, which has the format of

\[ V_s - V = \pi \int_{r_p}^{r_{pn}} (r - t)^2 L(r)dr \]  

(B.1)

where \( V_s \) is the volume of gas adsorbed at saturation pressure, \( V \) is the volume of gas adsorbed at pressure \( p \), \( L(r)dr \) is the total length of pores whose radii fall between \( r \) and \( r + dr \). \( r_{pn} \) is the critical radius. It is the radius of the largest pore still completely filled with liquid adsorbate at any particular pressure, and \( t \) is the multilayer thickness which is normally built up at pressure \( p \).

To solve the equation (B.1), all pores are assumed to be open-ended slit-shaped (Figure B.1) with unlimited lengths and heights. All pores have the same width and respond the same way to a change of pressure. For simplicity, we illustrate the process in one pore. In this pore (Figure B.1), the length \( L_1 \) and the height \( L_2 \) are unlimited long, which will not be considered. The relatively pressure \( (P/P_0)_{r_p} \) is assumed to differ infinitesimally from unity. At this pressure, this pore is filled with liquid. The pore has a half width of \( r_{p1} \). This pore consists of a physically adsorbed layer which is the statistical thickness \( t_1 \) and the inner capillary with a half width \( r_k \), from which evaporation occurs as \( P/P_0 \) is lowered.

The relationship between \( V_{p1} \) and the inner capillary volume, \( V_{k1} \), is

\[ V_{p1} = V_{k1}r_{p1}/r_{k1} \]  

(B.2)

Since \( V_{k1} \) is unknown, another equation has been proposed as

\[ V_{p1} = R_1\Delta V_1 \]  

(B.3)
where \( R_1 = r_p/(r_k + \Delta t_1) \), \( \Delta V_1 \) is the volume of adsorbed gas when the pressure is lowered to a smaller value \((P/P_0)_2\) from \((P/P_0)_1\), \( \Delta t_1 \) is the reduction of the thickness of the physically adsorbed layer during the process.

When the relative pressure continues to be lowered to \((P/P_0)_3\) from \((P/P_0)_2\), we will obtain

\[
V_{p2} = R_2 (\Delta V_2 - V_{\Delta t2})
\]

where \( R_2 = r_p/(r_k + \Delta t_2) \).

To be consistent with the calculations for a cylindrical pore, we can obtain equation (B.5) from Figure B.1.

\[
V_{\Delta t2} = \Delta t_2 A_{c1}
\]

where \( A_{c1} \) is the average area from which the physically adsorbed gas is desorbed.

Equation (B.5) may be generated so as to represent any one of the steps of a stepwise desorption by writing it in the form

\[
V_{\Delta t n} = \Delta t_n \sum_{j=1}^{n-1} A_{c j}
\]

Generalizing equation (B.4) and substituting equation (B.6) for \( V_{\Delta t n} \) yields

\[
V_{p n} = R_n \Delta V_n - R_n \Delta t_n \sum_{j=1}^{n-1} c_j A_{c j}
\]

Equation (B.7) is the exact expression for the porous model under consideration.

The relationship between the pore volume and the pore surface area of a slit-shaped pore is \( A_p = V_p/r_p \) with \( r_p \) is the half width. Following the same strategy as Barret et al.\(^1\) equation (B.7) can be rewritten as

\[
V_{p n} = R_n \Delta V_n - R_n \Delta t_n \sum_{j=1}^{n-1} c_j A_{c j}
\]

where \( R = \bar{r}_p/(r_k + \Delta t) \), \( c = (\bar{r}_p - t_j)/\bar{r}_p \), \( \bar{r}_p \) is the thickness of the physically adsorbed layer at the corresponding value of \( P/P_0 \), \( \bar{r}_p \) is the average radius between the radii corresponding to the upper and lower values of \( P/P_0 \).

To make equation (B.8) work, it is necessary to obtain a relationship between \( P/P_0 \) and \( r_k \) and between \( P/P_0 \) and \( \Delta t \). \( r_k \) is calculated by the Kelvin equation for slit pores.
\[ r_k = \frac{\gamma V_L}{RT \ln[(p/p_0)]} \]  
(B.9)

where

\[
t \text{ is estimated from an experimental relationship proposed by Kruk et al.}^3
\]
\[
t(p/p_0) = 0.1 \left[ \frac{60.65}{0.03071 - \log(p/p_0)} \right]^{0.3968} \]  
(B.10)

where \( t \) is expressed in nanometers.

With these relationships, \( r_p \) can be obtained as

\[
r_p(p/p_0) = r_k(p/p_0) + t(p/p_0) \]  
(B.11)

Equation (B.11) is different to the experimental equation proposed by Kruk et al.\(^3\) in that the correct number 0.3 nm is not used in the current equation, which is found to be more consistent with the pore size calculated by other methods for slit-shaped pores. Since it is almost impossible to choose an average value for \( c \) at each \( P/P_0 \), \( c \) is treated as a constant.\(^1\) Since most of mesoporous materials templated by cationic surfactants have pore sizes or half widths smaller than 5.0 nm, \( c \) is selected as 0.75 according to Barrett et al.\(^1\) Equation (B.8) thus can be rewritten as

\[
V_{pm} = R_n \Delta V_n - R_o c \Delta l_o \sum_{j=1}^{n-1} A_{\rho,j} \]  
(B.12)

which is the working equation. To obtain the pore size distribution for slit-shaped pores, the pore width has to be calculated as twice of the pore size (2\( r_p \) and 2\( r_k \)) discussed in this appendix.

References:

(2) A. Wheeler Presentations at Catalysis Symposia, Gibson Island A. A. A. S. Conferences, June 1945 and June 1946.
Figure B.1. Schematic representation of assumed desorption mechanism showing three different pores and demonstrating the thinning of the physically adsorbed layer over the first three pressure decrements. ¹
Appendix C. Effects of process parameters on pore structures

C.1. Introduction

Fluorinated surfactants are unusual because their tails are both hydrophobic and lipophobic. Fluorocarbon chains not only repel water but also may repel hydrocarbon compounds such as partially hydrolyzed alkoxy silane species. In a cationic fluorinated surfactant templated sol-gel process, the silica species will be attracted to and will aggregate with surfactant headgroups through electrostatic interactions. Meanwhile, these species will be repelled from the surfactant tails because they are both hydrophobic and lipophobic. As a result, the local density of the silica species will be less than that in the presence of a cationic hydrogenated surfactant. In a cationic surfactant templated sol-gel process, the surfactant hydrophobic chains help to attract the partially hydrolyzed silica species to aggregate with the micelles. The low silica density will lead to low condensation rate in a fluorinated surfactant templated process. However, the condensation rate is this process is still much faster than that without any template. This leads to the formation of colloid-like particles instead of gels or precipitates. With the same system, dense particles are obtained with a hydrogenated surfactant as the template. Gels are normally obtained for a sol-gel process without any surfactant template. The colloid-like structure is very sticky when the surfactant concentration is low. This leads to the extremely slow filtering process for this solution. With an increase of the surfactant concentration, more dense particles are formed resulting easier filtering. The formation of the colloid-like particles is not likely due to the formation of small particles. In the latter case, the colloid solution is expected to be very easy to filter and no particles are supposed to be collected. In a stöber process, colloids are formed due to the formation of negative charged small particles. However, these particles can not be collected by filtering since the particles are too small to the holes in a filtering paper.

Because the precursor is not readily dissolved and hydrolyzed, the system might be sensitive to process conditions controlling mixing such as stirring rate, TEOS adding speed, reactor size, and scale of the reaction.

All samples to be discussed in this series are prepared with the same initial molar composition. For the solution with this composition, colloid-like particles are obtained. It
normally takes more than one hour to filter the solution. The reason is that these particles were very sticky. They tend to block holes in the filtering paper very quickly. This makes the filtering process very time-consuming. After filtering, all as-synthesized samples are dried in air for 48 hours before removing the surfactant.

C.2. Experimental Section

C.2.1 Materials

All materials used are the same as being described in Chapter 7.

C.2.2 Synthesis

The synthetic procedure is the same as the procedure to produce HFOPC (see Chapter 7). The initial molar composition was 0.056 HFOPC (F₆H₂)/ 155 water/ 2.45 NH₃/ 1 TEOS. The reaction conditions used are shown in Table C.1. To limit the effects from other factors, all samples were prepared in the same type of reactor with the same scale size.

C.2.3 Characterization

Nitrogen sorption measurements were performed on a Micromeritics Tristar 3000 system. All samples were degassed at 150 °C for 4 hours under flowing nitrogen prior to measurement. The KJS modified BJH method¹ was used to calculate the pore size distribution (PSD) from the adsorption branch of the isotherms. Total surface area and pore volumes are estimated by the αₛ-plot (see Chapter 1).

C.3. Results and Discussion

C.3.1. Effect of the stirring speed

Five samples SS-0 to SS-4 are prepared to investigate the effect of stirring speed on the pore properties. The only difference among these samples is the stirring speed (Table C.1). The stirring speed increases from static in SS-0 to very high speed in SS-4. TEOS is added over 1 minute for all samples. Phase separation is observed for SS-0 after aging for 24 hours. Oil phase from unhydrolyzed precursor is observed on top of the solution.
Isotherm plots and pore size distributions of these samples are compared in Figure C.1. Pore properties of these samples are compared in Table C.1. The adsorption isotherm for sample SS-0 is the lowest among all isotherms. This sample has much broader pore size distribution than the others. It indicates that the mesopore structure in SS-0 is not well formed. The total pore volume for sample SS-0 is 0.31 cm$^3$/g at the relative pressure ($P/P_0$) 0.8. At this pressure, pore volumes of other samples are larger than 0.41 cm$^3$/g. However, the mesopore volume of SS-0 is similar to those for samples SS-2, SS-3, and SS-4. This indicates that mesopores are present in sample SS-0 without any uniform distribution. The surface area for sample SS-0 is smallest among all samples (Table C.1). With an increase of the stirring speed, the surface area increases with then decreases. Both the surface area and mesopore volume are the largest for sample SS-1. This indicates that mild stirring speed is good to main the pore structure. The small pore volume and surface area for sample SS-0 are reasonable since only part of TEOS has participated in the condensation process.

The investigation in this series of samples shows that a mild stirring speed is good to produce materials with high surface areas and large pore volumes. However, some systems may not be homogenous if the stirring speed is too slow (see Chapter 7). Therefore, high stirring speed is necessary for these systems.

C.3.2. Effect of TEOS adding speed

The effect of the stirring speed on the pore structure is obvious. It might be possible that the TEOS adding speed will also affect the pore structure. TEOS adding speed may change the interactions between the silica species and surfactant micelles.

Three samples AS-0, AS-1, and AS-2 are prepared with the adding speed 1 second, 1 minutes, and 5 minutes respectively. Stirring speed is 450 rpm to ensure that all solutions are well mixed.

Isotherm plots of all samples are compared in Figure C.2. Pore properties are shown in Table C.1. All isotherm plots are close to each other. The difference, however, can be noticed from the pore size distribution. With an increase of the adding time, the pore size distribution becomes sharper. This indicates that the mesopore volume increases. This is consistent with the change in the mesopore volume. The mesopore volume increases
from 0.06 cm$^3$/g to 0.19 cm$^3$/g with an increase of the adding time. This shows that slow TEOS adding speed is good to improve the product quality.

C.4. Conclusions

In summary, effects of different process conditions on the pore properties are investigated. We find that pore properties are sensitive to the stirring speed and the TEOS adding time. This may be because of the sensitivity of the colloid-like reaction system. This is the first time as we know that this study is discussed in detail.

C.5. References

Table C.1. Process conditions and Pore Properties for All Samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stirring Speed (rpm)</th>
<th>TEOS Adding Speed (minutes)</th>
<th>Reactor Size (ml)</th>
<th>S (m²/g)</th>
<th>V_p (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-0</td>
<td>0</td>
<td>1</td>
<td>400</td>
<td>491</td>
<td>0.15</td>
</tr>
<tr>
<td>SS-1</td>
<td>150</td>
<td>1</td>
<td>400</td>
<td>799</td>
<td>0.30</td>
</tr>
<tr>
<td>SS-2</td>
<td>300</td>
<td>1</td>
<td>400</td>
<td>661</td>
<td>0.13</td>
</tr>
<tr>
<td>SS-3</td>
<td>450</td>
<td>1</td>
<td>400</td>
<td>617</td>
<td>0.16</td>
</tr>
<tr>
<td>SS-4</td>
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<td>1</td>
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<td>569</td>
<td>0.13</td>
</tr>
<tr>
<td>AS-0</td>
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<td>0</td>
<td>400</td>
<td>647</td>
<td>0.06</td>
</tr>
<tr>
<td>AS-1</td>
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<td>400</td>
<td>661</td>
<td>0.13</td>
</tr>
<tr>
<td>AS-2</td>
<td>300</td>
<td>5</td>
<td>400</td>
<td>696</td>
<td>0.19</td>
</tr>
</tbody>
</table>

S_BET: BET surface area (m²/g); V_p: Primary mesopore volume (cm³/g).
Figure C.1. Isotherm plots and pore size distributions for samples SS-0 to SS-4.
Figure C.2. Isotherm plots and pore size distributions for samples AS-0 to AS-2.
Appendix D. Effects of solvents on pore structures.

Solvents have been used to control pore sizes and pore structures in surfactant templated sol-gel materials. These solvents either act as co-surfactants or co-solvents in this process (see Chapter 5).\textsuperscript{1−3} In this Appendix, we observe the influence of four solvents: ethanol, 1-butanol, Vertrel (C\textsubscript{5}H\textsubscript{2}F\textsubscript{10}), and HFE-7100 (C\textsubscript{4}F\textsubscript{9}OCH\textsubscript{3}). Each sample has the initial composition of 0.4 g HFOPC: 13.92 g water: 0.1 ml solvent: 0.75 g aqueous ammonia: 1.08 g TEOS. FSS is prepared with the same composition but without any solvent for the comparison. The other samples are named as FSS-Ethanol, FSS-Butnaol, FSS-Vertrel, and FSS-HFE based on the solvent added. Before adding TEOS, the mixture is stirred for 2 hours. All samples are aged at room temperature for 24 hours.

Isotherm plots and PSDs of all samples are compared in Figure D.1. Isotherms for FSS-Ethanol and FSS-Butanol are almost the same as those for FSS. PSDs of these samples are also almost the same. This means that the addition of 0.1 ml ethanol or 1-butanol does not affect the pore structure. This indicates that these solvents are probably not incorporated into the cores of the surfactant micelles. Another possibility is that the solvent added is not large enough to affect the micelle sizes. With the addition of HFE-7100 (C\textsubscript{4}F\textsubscript{9}OCH\textsubscript{3}), the total surface and pore volume increase noticeably as shown in Figure D.1. The pore size of FSS-HFE is slightly larger than that of FSS. With the addition of Vertrel (C\textsubscript{5}H\textsubscript{2}F\textsubscript{10}), the pore volume has reached the largest value among all samples. The pore size of FSS-Vertrel is also the largest. The increase of the pore volume and pore size in FSS-HFE and FSS-Vertrel is reasonable considering the possible role of fluorocarbon solvents in this process. The surfactant employed was a cationic fluorinated surfactant. Micelles are presumed to form with fluorinated chains inside and hydrophilic heads outside. Because fluorocarbon solvents are hydrophobic and lipophobic, they will penetrate inside the micelles to stay with the fluorinated chains of the surfactant. This will expand the micelle size, which leads to an increase of the pore size. HFE-7100 has four fluorinated carbons and Vertrel has five. The comparison in the pore size shows that Vertrel swells the micelles more than HFE-7100. The pore size for sample FSS-Vertrel is larger than that for sample FSS-HFE.
XRD patterns of all samples are shown in Figure D.2. The XRD pattern for FSS is typical for 2D hexagonal pattern (see Chapter 7). With the addition of ethanol, 1-butanol, or HFE, the peaks (1 1 0) and (2 0 0) become more obvious, indicating the pore ordering has been improved. The position of the first peak (1 0 0) becomes smaller with the addition of 1-butanol, HFE, or Vertrel, indicating that the d-spacing of the hexagonal structure has increased. This is consistent with an increase in the pore size for samples FSS-HFE and FSS-Vertrel. The pore size for sample FSS-Butanol is similar to that for sample FSS. The increase in the d-spacing indicates an increase in the pore wall thickness. The XRD pattern for sample FSS-Vertrel does not have resolved (1 1 0) and (2 0 0) peaks. The two peaks might be overlapped because of weak orderings. The surfactant micelles may be over-expanded by Vertrel to form highly ordered hexagonal pattern.

The addition of ethanol and 1-butanol does not change the pore size obviously in previous study. The reason might be that not enough solvent is added. Two extra samples are prepared with the addition of 1 ml of either alcohol instead of 0.1 ml alcohol in samples FSS-Ethanol and FSS-Butanol. The prepared samples are called FSS-E2 and FSS-B2. The isotherm plots and pore size distributions are compared in Figure D.3. For the sample prepared with ethanol FSS-E2, the pore size decreases slightly. This indicates that ethanol acts as a cosolvent. By decreasing the hydrophobic driving force for micellization, ethanol decreases the aggregation numbers, therefore decreases the pore size. For FSS-B2, no sharp pore size distribution is observed. This indicates that all mesopores collapsed upon the removal of surfactant. It is interesting to see that there is a large hysteresis loop in FSS-B2. It is the Type H4 hysteresis loop. The hysteresis loop indicates that large pores (much larger than the surfactant micelle size) were present in the sample surrounded by smaller pores (most likely micropores). For both FSS-E2 and FSS-B2, the pore volume and the pore surface area decrease. With an increase in the alcoholic chain, the pore volume and the surface area decrease.

In the materials synthesis literature, the role of ethanol is controversial. Roles as both cosolvent and cosurfactant for CTAB have been suggested by researchers making mesoporous silica (Chapter 5). If ethanol works as cosurfactant, it has been suggested that it will swell the palisade layer and increase the diameter of the micelles (and
If it acts as cosolvent, it will reduce the micelle (pore) sizes by decreasing the aggregation number. In a fluorinated surfactant templated system, the role of ethanol is expected to be the same. If the pore size increase, it indicates that ethanol acts as a cosurfactant. If an opposite trend is observed, it indicates that ethanol may act as a cosolvent. 1-Butanol is generally believed to act as a cosurfactant when used with hydrophobic surfactants. It is prone to mixing with the hydrophobic tails of surfactants in the micelles. The situation is different in with the presence of fluorinated surfactant. The fluorinated chain is lipophobic. It would be expected to repel 1-butanol. 1-butanol may therefore be incorporated into the micelles. With an increase of 1-butanol, the micelle size is expected to increase. However, the pore size distribution of FSS-B2 does not meet this expectation. Most mesopores in this material collapsed. There is a possibility that the lack of mesopores is due to the over-swollen micelles. However, this mechanism would require needs further investigation. For both ethanol and 1-butanol, however, the pore texture results are consistent with the solvent not mixing with the fluorocarbon tails of the micelles.

References.

Figure D.1. Nitrogen sorption for samples FSS series: (a) Isotherm plots and (b) Pore size distributions (same legend as in (a)).
Figure D.2. XRD patterns for samples FSS series.
Figure D.3. Nitrogen sorption for samples FSS-E2 and FSS-B2: (a) Isotherm plots and (b) Pore size distributions.
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