Formation of block-copolymer-templated mesoporous silica

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Abstract

In situ attenuated total reflectance Fourier transform infrared spectroscopy is used to monitor the chemical evolution of the mesoporous silica SBA-15 from hydrolysis of the silica precursor to final silica condensation after the particle formation. Two silica precursors, tetraethyl orthosilicate (TEOS) or sodium metasilicate (SMS) were used, and the effects of additive (heptane and NH_4F) concentrations were studied. Five formation stages are identified when TEOS is used as the precursor. The fourth stage correlates with the appearance and evolution of diffraction peaks recorded using *in situ* small angle x-ray diffraction. Details of the formed silica matrix are observed, e.g. the ratio between six-fold cyclic silica rings and linear bonding increases with the NH_4F concentration. The TEOS hydrolysis time is independent of the NH_4F concentration for small amounts of heptane, but is affected by the size of the emulsion droplets when the heptane amount increases. Polymerization and condensation rates of both silica precursors are affected by the salt concentration. Materials synthesized using SMS form significantly faster compared to TEOS-materials due to the pre-hydrolysis of the precursor. The study provides detailed insights into how the composition of the synthesis solution affects the chemical evolution and micellar aggregation during formation of mesoporous silica.

Keywords

Mesoporous silica, SBA-15, formation, silica precursor, *in situ* ATR, *in situ* SAXRD.

Introduction

Mesoporous materials are today used in several applications, e.g. drug delivery,¹ sensing,² and catalysis.³ To optimize the materials performance, it is necessary to tune the materials characteristics. Mesoporous silica of SBA-15 type,⁴ has with its flexible pore size and controllable morphology been a popular choice for these purposes. However, information regarding the material formation is crucial for controlling the material characteristics, e.g. intrawall porosity,⁵ surface silanol content,⁶ and for growth of mesoporous films on substrates.⁷

The SBA-15 is synthesized through a sol-gel process, where a silica precursor is added to an acidic micellar solution. The silica walls are formed around the micelles followed by hydrothermal treatment at elevated temperatures, and finally, the surfactants are removed by calcination or chemical extraction to yield the mesoporous material.⁴ The formation can be described by three, sometimes overlapping, periods: the micellar period, the micellar-to-structured material period, and the particle development period.⁸ Even though several different analysis techniques have been applied, such as x-ray and neutron scattering,⁹⁻¹¹ nuclear magnetic resonance (NMR),¹²⁻¹³ electron paramagnetic resonance spectroscopy (EPR),¹⁴ and cryo transmission electron microscopy,^{13, 15} there is no consensus on how SBA-15 is formed. The discrepancy is mainly in the second period, regarding how the micelles interact with each other to form the ordered material. One proposed mechanism is where spherical micelles are elongated to non-interacting, cylindrical, silicated micelles, followed by aggregation to larger domains with hexagonal packing.¹⁵⁻¹⁷ Another study suggests that the spherical micelles aggregate into flocs of spherical micelles and that these form cylindrical micelles that rearrange into the hexagonal structure.¹⁸ However, the synthesis conditions have varied for the different studies, for example which surfactant and silica precursor that were used, reaction temperature etc. A correlation between the synthesis conditions and micellar evolution is also lacking. Attenuated total reflectance Fourier transform infrared (ATR-FTIR, from here on simply recalled as ATR) spectroscopy has previously been overlooked, as an *in situ* technique to study the formation of mesoporous silica, due to large water representation,¹⁹ and instead Raman spectroscopy has been favored. However, using ATR enables observation of the silica evolution also after the formation of particle aggregates, which is something not possible with Raman spectroscopy.^{19,11} Tejedor-Tejedor *et al.*²⁰ showed that ATR is suitable for monitoring the hydrolysis of TEOS, and it has also been used to study the formation of mesoporous films in dip coating.²¹⁻²³ To our knowledge, the presented study is the first to follow the formation of mesoporous particles using *in situ* ATR.

Low temperature syntheses have been shown to favor large pore SBA-15, and fluoride ions to control the particle morphology, where the particles become more narrow when the F⁻ concentration increases.²⁴⁻²⁷ To enable the formation of ordered materials, swelling agents such as alkanes^{24, 28} or TIPB²⁶ have been used. Furthermore, it has been shown that F⁻ ions affect the formation rate of mesoporous

silica, even though the formation path is unclear.²⁴ Manet *et al.*²⁹ showed by small angle x-ray scattering (SAXS) that P123 micelles at 20 °C are spherical, also in the presence of TMB as a swelling agent, but how the structure evolves to form SBA-15 remains to be illuminated.

An alternative to use orthosilicates as silica precursor is the cheaper sodium metasilicate (SMS).³⁰⁻³¹ Materials synthesized with SMS exhibit a smaller mesopore size and thicker silica walls compared to when TEOS is used as the precursor.³⁰ This indicates a different (unknown) interaction with the micelles. However, the formation of mesoporous silica synthesized with SMS has not been studied *in situ* previously.

In the presented study, the formation of mesoporous silica at 20 °C and the effect of additives, NH₄F and heptane, as well as silica precursor, TEOS and SMS, are investigated using *in situ* ATR and *in situ* small angle x-ray diffraction (SAXRD). The ATR provides chemical data during the entire formation process, from addition of the silica precursor to the final condensation in the formed particles. The detailed information about the species present has not been provided by other characterization methods previously and resolves the effect of each reagent. Information regarding the formation kinetics is also obtained. By using the same set up, just exchanging the analysis cell, studies using different techniques during the exact same synthetic conditions are enabled. Hence, it is possible to combine the structural information from SAXRD with chemical information from ATR to understand the formation path of mesoporous silica.

Materials and methods

Synthesis

Hydrochloric acid (purity $\geq 37\%$, Fluka), triblock copolymer EO₂₀PO₇₀EO₂₀ (P123) (Aldrich), tetraethyl orthosilicate (TEOS) (reagent grade 98%, Aldrich), heptane (99%, Sigma-Aldrich), ammonium fluoride ($\geq 98.0\%$, Fluka), and sodium metasilicate (SMS) (Aldrich) were used as received.

In a typical synthesis, 2.4 g of P123 and a given amount of NH₄F was dissolved in 80 mL 1.84 M HCl solution. The mixture was kept at 20 °C and stirred until the polymer was dissolved. A specified volume of heptane was premixed with 5.5 mL TEOS and added to the micellar solution. This time point is defined as $t = 0$. The synthesis was stirred for 4 minutes and then kept under static conditions at 20 °C until the end of the measurement. The resulting material was filtered and dried at room temperature. For the materials synthesized with SMS, 10 mL of the total 80 mL 1.84 M HCl was used to dissolve 3.01 g SMS. The SMS solution and the heptane were not premixed but added simultaneously to the micellar solution. The molar ratios for all reagents were: P123:HCl:H₂O:heptane:NH₄F:silica precursor 1:353:10325: X : Y :60 where $16 \leq X \leq 280$, and $0 \leq Y \leq 1.8$. The obtained materials are labeled:

Silica precursor_XH_YF, e.g. TEOS_16H_0.9F, where H and F stands for heptane/P123 and NH_4F /P123 molar ratios, respectively.

Characterization

In situ SAXRD experiments were performed at beamline P07 at PETRA III using a 50.0 keV ($\lambda = 0.248 \text{ \AA}$) x-ray beam. The experimental setup is illustrated in Figure 1. The sample solution was peristaltically pumped through a quartz capillary with an inner diameter of 5.0 mm, and a wall thickness of 1 mm, with a pumping speed of 170 mL/min. The solution was transported through a Fluran tube with an inner diameter of 4.8 mm. The x-rays were transmitted through the capillary and detected on a 2-dimensional Perkin Elmer detector ($200^2 \mu\text{m}^2$ pixel size; 2048×2048 pixels). The sample-to-detector distance was 12213 mm, as determined from measurements of a NIST LaB_6 reference sample. A 2 mm beam-stop was used in front of the detector to avoid damage. The time $t = 0$ is defined as the time when the silica precursor is added to the micellar solution. The 2D data was integrated to get one-dimensional lineouts. The peak position and the integrated intensity was extracted from the 1D data by fitting pseudo-Voigt functions to the data. Distilled water was used as background.

Figure 1. Illustration of the setup used for *in situ* SAXRD and ATR measurements.

In situ ATR-FTIR was also performed with the setup illustrated in Figure 1, similar to SAXRD but with an ATR cell (Pike Technology). ATR was conducted in a flow-through liquid cell, using a Ge crystal providing 20 internal reflections at 45° angle of incidence. Distilled water was used as background and each spectrum was an average of 32 scans at 4 cm^{-1} resolution. The FTIR spectrometer was a Bruker Vertex 70 equipped with a LN_2 cooled broad-band mercury cadmium telluride detector and a water cooled glowbar mid-infrared source.

Results

Kinetics of the TEOS hydrolysis

The evolution of the silica species and the aggregation of micelles were studied using *in situ* ATR. For the materials synthesized with TEOS, the initial minutes after the addition of the silica precursor ($t = 0$) are used to hydrolyze TEOS to form silicic acid and ethanol, c.f. Eq. 1.

The assignments of bands corresponding to TEOS and ethanol are presented in Table 1, and the ATR spectra of pure references are available in Supporting information S1. Hydrolyses of TEOS in synthesis solutions containing various NH_4F and heptane concentrations are presented in Figure 2. Figure 2 (a) shows spectra from a synthesis solution at $t = 0 - 5$ min, representative for the initial evolution of all TEOS samples. To follow the hydrolysis of TEOS, the evolution of unique ethanol bands at 880 cm^{-1} , 1048 cm^{-1} and 1088 cm^{-1} , were monitored by plotting the integrated peak areas. It is apparent that all peaks attributed to ethanol increase, while the water peak at 1630 cm^{-1} decreases because of water consumption in the hydrolysis process. No TEOS-peaks can be detected in the spectrum. This is probably due to a delay when pumping the synthesis solution to the ATR cell, causing TEOS to hydrolyze in the pumping tube prior to reaching the cell, combined with overlaps of the characteristic TEOS peaks at 1168 cm^{-1} and 960 cm^{-1} with the bands related to new silica species.

Figure 2. ATR spectra of the synthesis solution at (a) $t = 0 - 5$ min, and the evolution of bands related to the hydrolysis of TEOS for (b) TEOS_16H_0.0F, (c) TEOS_16H_0.9F, (d) TEOS_16H_1.8F, (e) TEOS_280H_0.4F, and (f) TEOS_280H_1.8F.

As can be seen in Figure 2 (b)-(d), all samples synthesized with a heptane to P123 molar ratio of 16 have the same hydrolysis rate, where the band evolution is terminated at 2.5 min, followed by static water and ethanol peaks, indicating that the hydrolysis of TEOS is completed, which corresponds well with the results from Manet *et al.*¹¹. The time to complete the hydrolysis is independent of the NH_4F concentration when low heptane amounts are used. When a heptane to P123 molar ratio of 280 is used, the hydrolysis is completed after 4.5 min for TEOS_280H_0.4F, and 2.8 min for TEOS_280H_1.8F. The broad peak at 1130 cm^{-1} (silica) continues to increase even after hydrolysis completion due to the formation of a silica network.

The peak at $\sim 950\text{ cm}^{-1}$ (Figure 2 (a)) shifts, in the first 5 min, from 940 cm^{-1} to 958 cm^{-1} . The peak is initially attributed to monomeric silicic acid as the product of TEOS hydrolysis, but as the condensation of the silica network is initiated, these monomers will bond and form three-dimensional SiO_2 with silanol vibrations at 970 cm^{-1} .²⁰

Formation of the silica network

After the first 2.5 min, the hydrolysis of TEOS is completed and free silicic acid is available to form the silica network. This evolution was monitored with ATR, and the peak evolution for TEOS_16H_0.0F is presented in Figure 3. This material was chosen for representation since it forms slowly, which allow for fine details to be observed.

Figure 3. Differential ATR spectra for TEOS_16H_0.0F showing the band evolution during the time periods: (a) 2.5-50 min, (b) 30-70 min, (c) 50-120 min, and (d) 105-150 min.

Figure 3 (a) shows that the silicic acid band (940 cm^{-1}) decreases to a constant value during the first 15 min. Simultaneously, growth is seen for the bands at 980 cm^{-1} , 1044 cm^{-1} , and $\sim 1180\text{ cm}^{-1}$, corresponding to silanols, chain/sheet silica, and Si-O-Si asymmetric stretching, respectively (Table 2). This shows that during the first 20 minutes after the TEOS hydrolysis, the only activity in the synthesis solution is the formation of silica clusters. After 20 min, a broad shoulder appears at $\sim 1080\text{ cm}^{-1}$,

revealing the formation a three-dimensional, cyclic silica network. To resolve the following step in the reaction, the spectrum of the $t = 30$ min is used as background and subtracted in the spectra shown in Fig. 3 (b). After 30 min, a broad band at $1025 - 1265 \text{ cm}^{-1}$, corresponding to formation of various silica species, increases. After 55 min, the growth rate of the silica bands strongly increases, accompanied by an evolution of smaller bands at $\sim 930 \text{ cm}^{-1}$, 1348 cm^{-1} , 1374 cm^{-1} , and 1458 cm^{-1} . These peaks are all related to CH_2 vibrations in the PPO part of the micelle, see Table 1.³² To observe the rapid band growth in more detail, the $t = 50$ min spectrum was subtracted to the spectra shown in Figure 3 (c). This figure shows that rapid silica growth occurs for all silica related bands, with a preferential growth of linear structures (1147 cm^{-1}). The growth of PPO related bands follows the evolution of silica. The final stage of the material formation, i.e. the final condensation, is presented in Figure 3 (d). When the growth rate of the silica band decreases, only three bands around 1065 cm^{-1} , 1140 cm^{-1} , and 1190 cm^{-1} continue to grow. These can be attributed to the six-fold and linear asymmetric Si-O-Si stretches, see Table 2. The growth of these bands is the last change seen by ATR.

Figure 4. Differential ATR spectra for SMS_16H_0.4F showing the band evolution during the time periods: (a) 0 – 4.7 min, (b) 1 – 6.1 min, (c) 3 – 11 min, and (d) 10 – 28 min.

The analysis of the formation evolution of materials synthesized with SMS was performed on SMS_16H_0.4F, since SMS_16H_0.0F showed instabilities in the formation, both during the ATR and SAXRD analysis. Figure 4 (a) shows a broad band between $1000 - 1200 \text{ cm}^{-1}$ corresponding to various silica vibrations, indicating the presence of silica clusters, alongside with the Si-OH vibration at 960 cm^{-1} , and the water band at 1630 cm^{-1} directly after the SMS addition. The increased intensity of the water band is a result of using an aqueous solution for the pre-hydrolysis of the silica precursor. Figure 4 (b) shows the material evolution starting at 1 min after the addition of the SMS. It is observed that the growth of the broad silica band starts as soon as the SMS has been added to the micellar solution. After 3 min, the silica band growth increases rapidly and, similar as for the TEOS materials, the PPO related bands evolve in the same manner. The final stage of the material formation, after the rapid silica band growth, again consists of an increase of three silica bands. The bands are the same as in the

final stage for TEOS_16H_0.0F (Figure 3 (d)), but the fraction of six-fold cyclic species (1070 cm^{-1} and 1190 cm^{-1}) compared to linear structures (1140 cm^{-1}) is larger.

All produced materials show the same ATR patterns as those presented in Figure 3 and Figure 4 for TEOS and SMS respectively, but with different formation kinetics. Figure 5 presents a summary of the formation stages determined from *in situ* ATR measurements for materials synthesized with a heptane to P123 molar ratio of 16. The materials synthesized with TEOS (Figure 5 (a)) have five formation stages: (i) TEOS hydrolysis, (ii) silica polymerization, (iii) siliceous network formation, (iv) silica densification, and (v) continued condensation. It is clearly visible that the times for stage (ii) – (v) depend on the NH_4F concentration, while the time for the TEOS hydrolysis is constant. For the material synthesized with SMS, there are three stages, identical to stage (iii) – (v) for the TEOS materials (Figure 5 (b)). Naturally, there is no hydrolysis step for the SMS, since the precursor is already added in a hydrolyzed state. Polymerization has also occurred to a large extent prior to the addition to the micellar solution, see Figure 4, which explains why this stage is not observed for the SMS materials. The squares in Figure 5 correspond to the appearance of the first Bragg peak from the SAXRD measurements. From this it is clear that stage (iv) is correlated to the formation of an ordered hexagonal phase of the material. We noted, similar to Baccile *et al.*¹⁹, that the synthesis solution turned milky white at the same time as the appearance of the first Bragg peak. Therefore, we have assigned the formation of hexagonal structure for SMS_16H_1.8F to 1 min, even though the first available data point is recorded later.

Figure 5. The different stages during the silica formation as a function of NH_4F concentration for (a) TEOS and (b) SMS as silica precursors.

Formation of the hexagonal phase

Figure 6 shows the correlation between the formation stages determined by ATR and the evolution of the 100 Bragg peak from the hexagonally ordered micelles using *in situ* SAXRD. The 100 peak appears a few minutes into the silica densification stage (iv). The 100 peak shifts rapidly towards larger

angles (smaller d-spacing), indicating shrinkage of the hexagonal structure upon silica condensation. Simultaneously, the peak intensity increases, verifying that the amount of the hexagonal phase increases. For the materials synthesized with TEOS as the silica precursor (Figure 6 (a), (c), and (e)), the formation of the hexagonal structure mainly occurs during the silica densification stage, where the 100 peak reaches ~80 % of its final intensity. Also, the most distinct shrinkage of the unit cell occurs during stage (iv). This is followed by a slower unit cell shrinkage during stage (v), even after that the peak has reached its maximum intensity. Materials synthesized with SMS (Figure 6 (b) and (d)) show a similar behavior, where the 100 peak appears a few minutes into the silica densification stage. However, this stage is very short for SMS materials, and the structural progression continues well into the final stage of the materials formation.

Figure 6. The correlation between the silica formation and evolution of the 100 Bragg peak in (a) TEOS_16H_0.4F, (b) SMS_16H_0.4F, (c) TEOS_16H_0.9F, (d) SMS_16H_0.9F, and (e) TEOS_16H_1.8F.

The silica structure as function of NH_4F concentration

The final ATR spectrum of each material is presented in Figure 7. It is apparent that when TEOS is used as silica precursor, the maximum peak intensity is shifted from 1134 cm^{-1} to 1083 cm^{-1} as the NH_4F concentration is increased (Figure 7 (a) and (c)). This shift occurs independently of the heptane amount. Considering the different silica species possible, this indicates that the materials synthesized with a higher NH_4F concentration contain more of the cyclic silica species compared to the materials synthesized with no or low salt amounts, see Table 2, which is also confirmed in Figure 8. The trend is not as visible for materials synthesized with SMS as silica precursor (Figure 7 (b)). A slight broaden-

ing can be observed when NH_4F is introduced, but the maximum band intensity is located at a constant wavenumber (1113 cm^{-1}). The wavenumber shifts for all materials are presented in Figure 7 (d).

Figure 7. The final ATR spectrum of (a) TEOS_16H_YF, (b) SMS_16H_YF, and (c) TEOS_280H_YF. (d) shows the shift of the wavelength with the highest absorbance as a function of NH_4F concentration.

The effect of NH_4F on the silica structure during the silica formation is shown in Figure 8. Figure 8 (a) and (b) show the stage (ii) evolution for $\text{NH}_4\text{F}/\text{P123} = 0.9$ and 1.8 respectively. We note that for the higher NH_4F concentrations, cyclic silica species are formed directly after the TEOS hydrolysis, while for lower concentrations, linear structures are formed initially. The band evolution in stage (v) (Figure 8 (c) and (d)) show that the growth of linear silica species (1140 cm^{-1}) is significantly less compared to the six-fold cyclic structure (1070 cm^{-1} and 1190 cm^{-1}) when the NH_4F concentration is increased. When no NH_4F is used (Figure 3 (d)), the strongest band is related to linear structures, while for $\text{NH}_4\text{F}/\text{P123} = 0.9$ (Figure 8 (c)) the six-fold cyclic structure is stronger, and finally it is the dominating phase for $\text{NH}_4\text{F}/\text{P123} = 1.8$. It can also be noted that the band at 960 cm^{-1} decreases with increasing salt content. This indicates that the number of silanols is very much less after the particle formation for the materials with high NH_4F concentration.

Figure 8. The material evolution in TEOS_16H_0.9F in (a) stage (ii) and (c) stage (v), and TEOS_16H_1.8F in (b) stage (ii) and (d) stage (v).

Discussion

The formation stages

From the results presented in Figure 3, there are five stages in the material synthesis when TEOS is used as the silica precursor. During the first two stages, there is no apparent interaction between the silica species and the micelles. Silica oligomers enter the corona and polymerize to small silica clusters without indications of affecting the micelle structure. Sundblom *et al.*³³ showed that the micelle-silica interaction mainly is enthalpy driven, and that a certain size of the silica species is required for the interaction to occur. This is the reason for the much faster material evolution when SMS is used as the silica precursor. As can be seen in Figure 4 (a), silica clusters are already formed before the precursor is added to the micellar solution. These species are large enough to interact with the micelles, which initiates the micelle elongation and formation of the hexagonal network.

In stage (iii), the silica clusters start to interact with each other and form a network in the micellar corona. At this stage a large variety of silica species are formed. In the end of stage (iii) PPO related bands start to grow. This is due to changes in the hydration of the PPO core of the micelles. Su *et al.*³² showed that the bands at 1374 cm^{-1} and 1344 cm^{-1} are very weak for low concentrations of pluronic P104 in aqueous solution, but increase for higher surfactant concentrations. They concluded therefore that the PPO is not hydrated at high surfactant concentrations. This indicates that the water in the corona is expelled when the silica network is formed, which enables methyl group vibrations in the PPO core. These findings correlate well with the EPR study from Ruthstein *et al.*¹⁴ who observed a depletion of water in the corona region upon the condensation of the silica network. Flodström *et al.*¹³ followed the material formation using NMR and observed a broadening in the PO signal upon the micellar elongation from spheres to cylinders. This indicates that it is possible to monitor the micelle shape evolution by observing the PPO related bands in the ATR spectra.

In stage (iv), the rapid growth of silica related bands in combination with the PPO related bands display condensation of silica in the micelle corona. The appearance of Bragg peaks at this stage also shows that elongated micelles aggregate and form the hexagonal structure at this stage. A material with long-range order is needed for diffraction to occur. To achieve long range order, several micelles need to aggregate to form the hexagonal structure. This takes time and causes a delay before Bragg peaks are observed. Stage (iv) proceeds faster for SMS synthesized materials. It is completed in less than 10 min compared to 15-35 min for TEOS materials. This time difference indicates that for TEOS materials, formation of the hexagonal framework is more successive and occurs alongside with micelle elongation due to the continued growth of silica species in the corona, i.e. micelle aggregation is ac-

accompanied by condensation of silica walls around each micelle. In the case of SMS, the silica clusters in the corona are initially large, and therefore the main silica condensation is between these large clusters to form the silica walls. The aggregation of micelles needs further time and therefore the intensity of the Bragg peak is growing also in stage (v). The evidence of large silica clusters in the corona already at the beginning of the condensation can explain the thicker silica walls in materials synthesized with SMS.

The final stage is the last silica condensation, where additional silica bonds are formed as the walls between the aggregated micelles densify. At this stage the silica walls surrounding the micelles are mainly formed, and the silicated micelles bind stronger together.

Effect of NH_4F on the formation kinetics and silica structure

From Figure 8, it is clear that NH_4F affects which silica species that are formed, especially for TEOS materials. When a higher concentration of NH_4F is added, more six-fold cyclic silica species are formed, and the amount of linear structure decreases. This is especially obvious comparing the band intensities in Figure 3 (d), Figure 8 (c) and (d). The fluoride ion increases the coordination number of silicone. Silicone with a higher coordination number is also more reactive and will polymerize faster compared to four-fold silica species.³⁴ The rate change in polymerization is clearly observed in Figure 5, where all stages, except stage (i), become faster in the presence of high NH_4F concentrations. The time needed for the formation of the hexagonal framework is in good agreement with previous results where SBA-15 rods were formed within 7 min after the addition of TEOS at a $\text{NH}_4\text{F}/\text{P123}$ molar ratio of 1.83,⁷ and that only minor changes at the mesoscopic range occurred after 30 min.³⁵ The fast polymerization can also be the reason for the difference in particle morphology, where a high NH_4F concentration yields more narrow particles.^{24-25, 35} The micelles attach through condensation of silanol groups, and as can be seen in Figure 7 and Figure 8, the number of uncondensed silica species, silanols and Si-O^- at $\sim 960\text{ cm}^{-1}$ decreases with increasing salt concentration.

Figure 7 also shows that NH_4F affects the final structure less for SMS materials. The reason for this is again the pre-hydrolysis of the silica precursor, which is made in a HCl solution without NH_4F additions. Therefore, the added silica clusters will have the same structure, and only the surface of these can be affected by the fluoride ions. The NH_4F still affects the coordination number on the surface silica, which affects the formation rate of the materials (Figure 5 (b)).

The TEOS hydrolysis rate

When the TEOS/heptane mixture is added to the micellar solution, an oil-in-water emulsion is formed. The TEOS hydrolysis occurs at the TEOS/water interface,¹¹ and therefore the amount of heptane and NH_4F affect the hydrolysis rate. When heptane/P123 = 16, the heptane is solvated in the TEOS, and the droplet size is equal independent of NH_4F , due to the low oil concentration. When larger amounts

of heptane are used, the TEOS is solvated in the heptane and hydrolyses when it reaches the emulsion droplet surface. When the NH_4F concentration increases, the ionic strength of the solution increases, leading to smaller oil droplets. The emulsion with smaller droplets has a higher surface area causing a higher hydrolysis rate.

Conclusions

We have studied the formation of mesoporous silica at various synthesis compositions using *in situ* ATR and SAXRD. Five stages in the material formation were identified: TEOS hydrolysis, silica polymerization, siliceous network formation, silica densification, and continued condensation. The fourth stage could be correlated with hexagonal ordering of the micelles. When SMS was used as the silica precursor, the two first stages were not observed due to the pre-hydrolysis of the SMS resulting in that small silica clusters were formed prior to the addition into the micellar solution. A specific size of the silica clusters in the micelle corona is required for the micelle elongation, and hence, materials synthesized from SMS form faster compared to TEOS materials. In the end of stage three, bands related to PPO vibrations in the micellar core start to grow, indicating elongation of the micelles from spheres to cylinders. NH_4F affects both the formation kinetics and silica structure due to its ability to change the coordination number of silicone, yielding more six-fold, more reactive, cyclic silica species. The TEOS hydrolysis rate is affected by the amount of heptane and NH_4F due to alterations in the oil droplet size.

The study demonstrates that *in situ* ATR is a powerful tool for monitoring the formation of mesoporous silica, both in terms of formation kinetics and elucidating details in the silica network. Previously, this technique has been neglected due to the strong water contribution.^{8, 19} This is the first time that details of the chemical structure of the silica species during the material formation can be observed. The study provides detailed insights into the formation of mesoporous silica and can be used for future fine tuning of the materials characteristics. We envision that the presented method can be used to study doping mechanisms in the silica framework, as well as the formation of other sol-gel synthesized materials.

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Supporting Material

Reference ATR spectra of P123, ethanol and TEOS, as well as SEM micrographs and physisorption data for selected mesoporous materials are provided.

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Figure captions

Figure 1. Illustration of the setup used for *in situ* SAXRD and ATR measurements.

Figure 2. ATR spectra of the synthesis solution at (a) $t = 0 - 5$ min, and the evolution of bands related to the hydrolysis of TEOS for (b) TEOS_16H_0.0F, (c) TEOS_16H_0.9F, (d) TEOS_16H_1.8F, (e) TEOS_280H_0.4F, and (f) TEOS_280H_1.8F.

Figure 3. Differential ATR spectra for TEOS_16H_0.0F showing the band evolution during the time periods: (a) 2.5-50 min, (b) 30-70 min, (c) 50-120 min, and (d) 105-150 min.

Figure 4. Differential ATR spectra for SMS_16H_0.4F showing the band evolution during the time periods: (a) 0 – 4.7 min, (b) 1 – 6.1 min, (c) 3 – 11 min, and (d) 10 – 28 min.

Figure 5. The different stages during the silica formation as a function of NH_4F concentration for (a) TEOS and (b) SMS as silica precursors.

Figure 6. The correlation between the silica formation and evolution of the 100 Bragg peak in (a) TEOS_16H_0.4F, (b) SMS_16H_0.4F, (c) TEOS_16H_0.9F, (d) SMS_16H_0.9F, and (e) TEOS_16H_1.8F.

Figure 7. The final ATR spectrum of (a) TEOS_16H_YF, (b) SMS_16H_YF, and (c) TEOS_280H_YF. (d) shows the shift of the wavelength with the highest absorbance as a function of NH_4F concentration.

Figure 8. The material evolution in TEOS_16H_0.9F in (a) stage (ii) and (c) stage (v), and TEOS_16H_1.8F in (b) stage (ii) and (d) stage (v).

Table 1. Assignments of FTIR bands of TEOS, ethanol, and P123

TEOS ^a	Ethanol ^b	P123 ^c	Assignment
	3320		O-H stretch
2976	2973	2971	C-H asym. stretch
2929	2929	2928	C-H asym. stretch
2890	2882	2890	C-H asym. stretch
		1458	CH ₂ scissor
1390	1380	1374	CH ₃ symmetric deformation
		1344	CH ₂ wag
1295			CH ₂ twist
		1281	CH ₂ twist
		1242	CH ₂ twist
1168			C-H rock
		1142	C-O-C stretch, C-C stretch
		1108	C-O-C stretch
1103			CH ₃ rock
1077	1088		C-C stretch
		1063	C-O asym. stretch, CH ₂ rock
	1048		C-O sym. stretch
		1015	CH ₃ vibration
961		962	C-O stretch, CH ₂ rock
		931	C-H vibration
	880		CH ₃ or CH ₂ deformation
		843	CH ₂ rock

^a Assignment based on Ref ^{20, 32, 36}

^b Assignment based on Ref ^{20, 37}

^c Assignment based on Ref ^{32, 36, 38}

Table 2. Assignment of silica related bands

Wavenumber (cm ⁻¹)	Assignment ³⁹⁻⁴¹
1250	LO ₃ asym. stretching
1200	Si-O-Si asym. stretch 6-ring
1147	Si-O-Si asym. stretch linear structure
1100	Si-O-Si sym. stretch linear structure
1086	Si-O-Si sym. stretch cyclic structure
1070	TO ₃ asym. stretch 6-ring
1035	Si-O-Si chain
960	Si-OH
920	Si-O ⁻ open rings

Supporting Material

Figure S1. Reference ATR spectra of ethanol, TEOS and P123.

Figure S2. SEM micrographs of (a) TEOS_16H_0.4F, (b) SMS_16H_0.4F, (c) TEOS_16H_1.8F, and (d) SMS_16H_1.8F, showing that the particle morphology is similar independent of silica precursor. Physisorption isotherms and pore size distributions of materials synthesized with (e) TEOS and (f) SMS, showing the cylindrical pore structure of the materials.

The SEM micrographs were taken using a Leo 1550 Gemini Scanning Electron Microscope operated at 3 kV and a working distance of 3–5 mm. N₂ physisorption isotherms were recorded on a Micromeritics ASAP2020 at 77 K. The pore size distributions were calculated using the KJS-method on the adsorption isotherms.