

Directing the Formation of Vinyl-Functionalized Silica to the Hexagonal SBA-15 or Large-Pore *Ia3d* Structure

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Vinyl-functionalized ordered mesoporous silica can be prepared by co-condensation of tetraethoxysilane (TEOS) and triethoxyvinylsilane (TEVS) in the presence of the triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀) and inorganic salts such as NaCl. At low molar percentage of 10% TEVS, the hexagonal structure analogous to SBA-15 is obtained. With 15% TEVS, a less defined material, but probably closer to the cubic *Ia3d* structure, is formed. 20% TEVS leads to the formation of well-ordered *Ia3d* materials over a relatively wide range of temperatures and acid concentrations. The concentration of the added inorganic salts has an influence on the formation of a specific structure. The pore system can be made accessible by treatment with sulfuric acid at elevated temperatures, which selectively removes the copolymer template and does not lead to the cleavage of the Si–C bond. With use of the triblock copolymer Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) as a template, a vinyl-functionalized structure analogous to SBA-16 can be synthesized.

Introduction

Shortly after the discovery of ordered mesoporous silica,^{1,2} scientists started to explore possibilities to modify the surface properties of such materials by modifying them with organic groups. Already in one of the first publications from the Mobil group trimethylsilylation, known for the surface modification of conventional silica for a long time, was used also for the modification of MCM-41.³ A reduction of pore size due to the additional space occupied by the trimethylsilyl groups was already demonstrated in this early work. In subsequent years, many other methods for surface modification of MCM-41 type materials by postsynthesis reactions were described, for instance hydrophobize the material⁴ or use it for selected applications.⁵ Many different reagents have been used for this purpose, such as different organoalkoxysilanes, organochlorosilanes, or hexymethyldisilazane.

Alternatively, the framework can be functionalized by direct co-condensation of a tetraalkoxysilane and a trialkoxyorganosilane.⁶ This can either be used to create

a material with pendant Si–R groups or, if silanes with bridging organic groups are used, also with organic groups fully connected within the framework.⁷ The latter approach can be extended to the point that every silicon atom in the framework is connected via one organic bridge to another silicon atom. Moreover, crystalline packing of the organic groups within the walls has been shown to occur in such materials.⁸

A particularly useful pendant organic group is the vinyl group since the double bond is fairly stable under the reaction conditions for the synthesis of the mesostructured material, but sufficiently reactive to allow further postsynthesis functionalization.⁹ Several types of vinyl-functionalized ordered mesoporous materials have been synthesized.¹⁰ However, most of the publications were focused on the small pore MCM-41^{11,12} and little work has been devoted to the triblock copolymer-templated silicas, such as SBA-15.¹³ It seems to be especially difficult to synthesize cubic materials (*Ia3d*) via the triblock copolymer route. Only recently, some reports on the synthesis of large pore *Ia3d* materials

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Table 1. Structural Properties of Vinyl-Functionalized Mesoporous Silica, Synthesized under Different Conditions

TEVS/%	[HCl]/M	$T_{\text{aging}}/^{\circ}\text{C}$	[NaCl]/M	phase	a_0^a/nm		$S_{\text{BET}}/\text{m}^2\text{g}^{-1}$	pore size/nm	$V_t/\text{cm}^3\text{g}^{-1}$
					as-prepared	acid-treated			
10	1.0	80	0	$P6mm$	11.4	11.4	573	7.3	1.14
10	1.0	80	1.5	$P6mm^b$	11.3	11.3	510	7.4	1.11
15	1.0	80	0	$Ia3d^c$	22.8	22.2	641	6.6	1.25
15	1.0	80	1.5	$Ia3d$	22.8	22.2	601	6.8	1.10
20	1.0	80	0	$Ia3d^d$			605	6.0	0.67
20 ^e	1.0	80	1.5	$Ia3d$	21.8	21.5	580	6.2	1.04
20	1.5	80	1.5	$Ia3d$	21.5	21.2	552	6.2	1.00
20	2.0	80	1.5	$Ia3d$	21.3	19.7	522	6.0	0.90
20	1.0	60	1.5	$Ia3d$	20.3	19.5	501	5.0	0.66
20	1.0	80	1.5	$Ia3d$	22.2	21.5	580	6.2	1.04
20	1.0	100	1.5	$Ia3d$	22.8	22.1	620	6.8	1.27

^a a_0 : cell dimension. ^b With a small amount of cubic structure from XRD. ^c Mixture of cubic and hexagonal structures from TEM. ^d Disordered structure with a small amount of cubic structure from TEM. ^e The major part of the description in the text refers to this sample.

have appeared, which used small amounts of mercaptopropyltrimethoxysilane in addition to the silicon source TEOS,¹⁴ high concentrations of NaI,¹⁵ a special polymer,¹⁶ or the addition of butanol in the synthesis mixture.¹⁷ The results obtained with the mercaptopropyltrimethoxysilane and the butanol suggested that the hydrophilic/hydrophobic balance under synthesis conditions determines the phase that is eventually formed.

The goals of the present work were (i) to synthesize vinyl-functionalized $Ia3d$ silica, which provides the 3-D pore system for easy mass transfer, as an interesting material for the immobilization of different species and (ii) to investigate whether the fraction of organosilanes in the synthesis mixture could be used to control the nature of the phase formed.

Experimental Section

Synthesis. In a typical synthesis, first 5.68 g of Pluronic P123 (P123, obtained from BASF) and 14.4 g of NaCl (from Merck) were dissolved in 160 mL of 1.0 M HCl aqueous solution (the final concentration of NaCl is 1.5 M). Some experiments were also performed with copolymer F127. A homogeneous solution was obtained after stirring at 35 °C for several hours. Then a mixture of TEVS and TEOS (53.2 mmol in total, the molar percentage of TEVS was varied between 0% and 20%, 20% TEVS for most of the experiments) was added slowly under stirring. The mixture was further stirred at 35 °C for 4 h and then aged at 80 °C for 24 h. The product was filtered, washed with deionized water, ethanol, and acetone, and dried at 80 °C overnight. The polymer was removed by 60 wt % H_2SO_4 treatment.¹⁸ For the investigation of the effects of salt concentration and aging temperature on the structure formed, concentrations of NaCl between 0 and 2.0 M and temperatures between 60 and 100 °C were applied.

Characterization. Small-angle X-ray diffraction patterns (XRD) were recorded with a Stoe STADI P diffractometer in reflection mode operating with Cu K α radiation (scanning step: 0.01°/s). Transmission electron microscope (TEM) images were obtained with a HF2000 electron microscope from Hitachi. The samples for TEM measurements were prepared by dispersing the powdery silica in ethanol. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2010 sorption analyzer. Before the measurements, the solvent-

extracted samples were evacuated for 10 h at room temperature. The BET surface areas were obtained from the adsorption branches in the relative pressure range of 0.05–0.20. The total pore volume was evaluated at a relative pressure of 0.98. The pore size distributions were calculated from the desorption branches using the Barrett–Joyner–Halenda (BJH) method. The weight loss curves in air were measured on a TG/DTA instrument (Netzsch STA 449 C) with a heating rate of 5 K min^{-1} . The MAS NMR spectra were measured on a Bruker Avance 500WB instrument using a 4-mm MAS probe at a spinning rate of 10 kHz. The experimental conditions for ^{13}C CP/MAS NMR were 2-s recycle delay, 32 000 scans, 1-ms contact time, and 4.4- μs ^1H $\pi/2$ pulse and those for ^{29}Si MAS NMR were 30-s recycle delay, 2400 scans, and 2.2- μs $\pi/4$ pulse.

Results and Discussion

Under all conditions investigated, mesostructured materials, albeit with different degree of order, were obtained. Table 1 summarizes the properties of the materials synthesized under different conditions. Syntheses were repeated several times for most of the conditions to check the reproducibility. In general, the nature of the structure formed was reproducible in all cases, and the unit cell sizes only showed small variance within 0.1 nm. Textural parameters as analyzed by nitrogen sorption scattered within wider margins, but were still found to be reproducible within 10%. The template removal process by H_2SO_4 is very sensitive with respect to the conditions (concentration, time, temperature), and the reason for the scatter in the texture data can be attributed to this effect.

As can be seen from the table, at a TEVS molar percentage of 10% in the mixture of the silica sources, a mesoporous silica with hexagonal structure was obtained, as indicated by the XRD shown in Figure 1. An increase of the TEVS percentage to 15% leads to a pronounced change in the diffraction pattern with a shift of the first intense reflection to smaller angles and a shoulder on the right-hand side of the reflection. This is indicative of the change of the hexagonal SBA-15 structure to a material with $Ia3d$ symmetry. Upon further increase in the TEVS percentage to 20%, this structural change is more obvious, and the pattern of a cubic $Ia3d$ material can be clearly distinguished. In Figure 1b, the patterns of the H_2SO_4 -treated samples are shown, and their XRD patterns are better resolved and more intense as compared to the as-synthesized samples (Figure 1a). This finding is due to the enhanced contrast of the electron density after the removal of the

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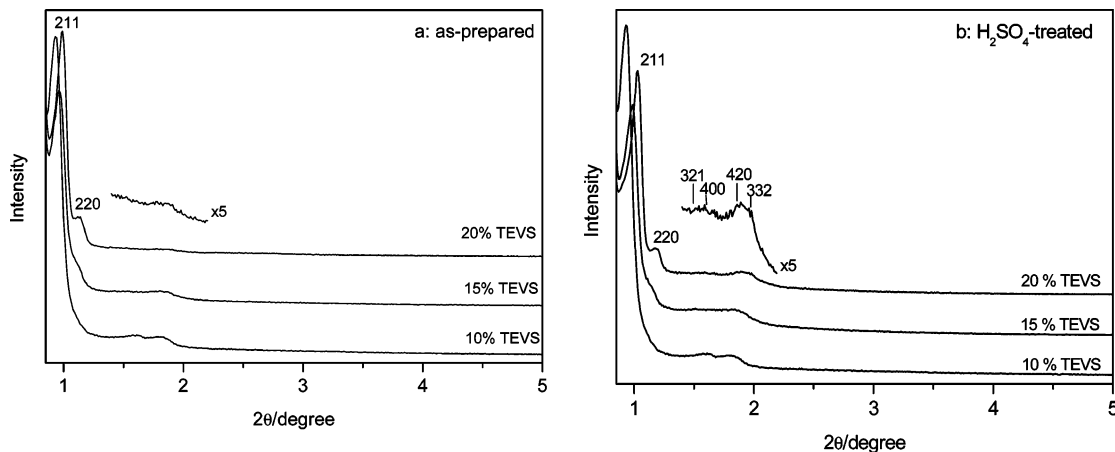


Figure 1. XRD patterns of as-prepared (a, left) and H_2SO_4 -treated (b, right) samples synthesized from starting mixtures containing 1.5 M NaCl and different amount of TEVS (expected higher index reflections are indicated).

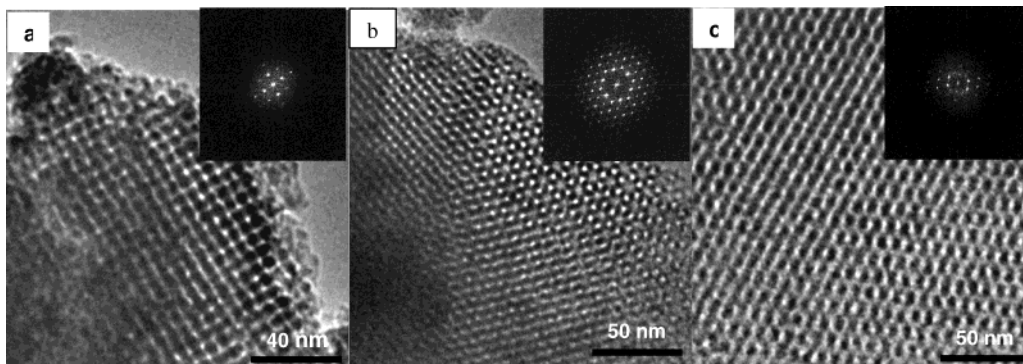


Figure 2. TEM images and Fourier diffractograms of the $Ia3d$ cubic structure synthesized with 1.5 M NaCl and 20% TEVS in the starting mixture along (a) [100], (b) [111], and (c) [110] directions.

copolymer surfactant from parent materials.¹⁹ Taking the sample synthesized with 20% TEVS as an example, the as-made material has two sharp reflections at 8.7 and 7.9 nm and one broad feature centered at 4.8 nm. This pattern fits well the structure with $Ia3d$ symmetry,^{1,3} with the first two peaks corresponding to (211) and (220) reflections and the broad feature resulting from a superposition of the (321), (400), (420), and (332) reflections. A unit cell parameter of 21.8 nm has been calculated from the position of the (211) reflection, which is much bigger than the unit cell parameter of MCM-48 (ca. 10 nm) synthesized with tetraalkylammonium surfactant templates.³ After treatment with H_2SO_4 , the cell dimension becomes slightly smaller, which is indicated by a slight shift of the reflection positions to larger angles. The shrinkage of the cell dimension is on average about 2%, which is much smaller than the shrinkage of 19% for a sample calcined at 540 °C. In addition, the broad feature is now better resolved.

The structural assignment based on the XRD patterns is corroborated by the TEM analysis of the sample prepared with 1.5 M NaCl and 20% TEVS in the starting mixture. Figure 2 shows TEM images with the Fourier diffractograms along the [100], [110], and [111] directions of the sample synthesized with 20% TEVS. The images, which were found throughout the sample, correspond to those expected for the ordered bicontinuous $Ia3d$ structure. The sample with 10% TEVS pre-

pared in the absence of NaCl exhibited TEM images corresponding to the hexagonal SBA-15 material. On the other hand, images of the samples with 15% TEVS could not be as clearly assigned. While in most regions the images were compatible with the $Ia3d$ structure, other regions were present, which could not be assigned either to the $Ia3d$ or the hexagonal structure. In addition, disordered regions in the sample with 15% TEVS were observed. However, the addition of 1.5 M NaCl to this synthesis facilitated the formation of a well-developed $Ia3d$ phase.

At a TEVS molar percentage of 10%, a pure hexagonal structure was obtained in the absence of salt (Figure 3). Adding NaCl, additional intensity at the right-hand side of the (100) reflection of the hexagonal structure is observed, which could indicate the coexistence of the cubic phase, which is fully developed at 2 M NaCl. If KCl is added, the pure hexagonal phase is formed to 1.5 M. At 15% TEVS, both with and without NaCl addition the cubic structure was obtained. However, the XRD patterns (Figure 4) reveal that the addition of NaCl induces the formation of a more well-ordered structure, showing overall higher intensity reflections. TEM analysis showed that the structure was more regular in samples prepared in the presence of salt, while disordered regions and regions which could not clearly be assigned to the $Ia3d$ structure were present in samples synthesized without salt.

Similar results were obtained for the samples with 20% TEVS in the starting mixture. The XRD patterns

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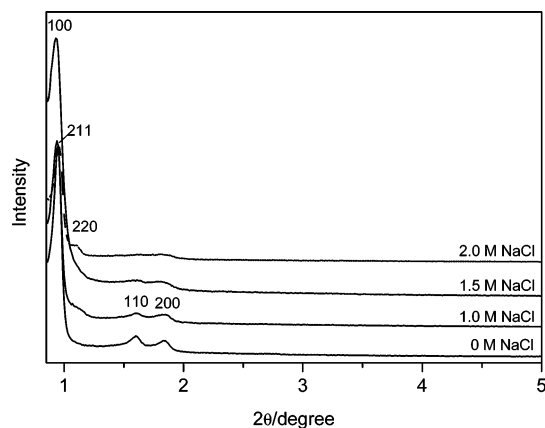


Figure 3. XRD patterns of as-prepared samples synthesized from starting mixtures containing 10% TEVS and different concentrations of NaCl.

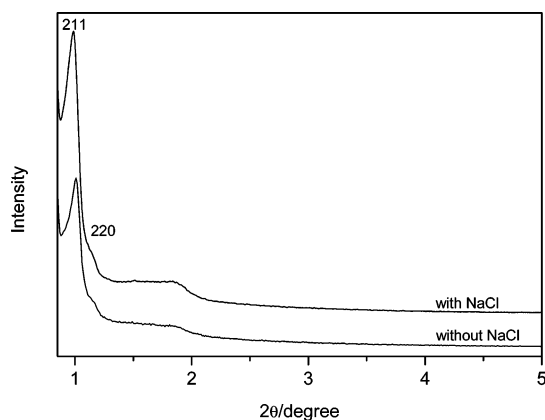


Figure 4. XRD patterns of H_2SO_4 -treated samples synthesized from a starting mixture containing 15% TEVS with or without inorganic salts.

indicated a better quality of these samples synthesized in the presence of NaCl. Structures could not clearly be assigned from the XRD for samples prepared without salt, and in addition, the pore volume for such samples was substantially lower. This suggests that the primary influence on the phase formed is exerted by the ratio between hydrophobic and hydrophilic silica source, but that the salt has an additional effect on the ordering of the material, possibly in the sense of a salting-out, in that it dehydrates the polyethylene units and thus renders them more hydrophobic. The effect of inorganic salt was further confirmed by the synthesis of mesoporous materials with 20% TEVS at 2.0 M HCl. Well-ordered cubic $Ia3d$ structure was obtained in the presence of NaCl, while no precipitate was formed without the addition of salt.

Aging temperature is also known to influence the formation of surfactant templated silica. Since at higher temperature the effective volumes of the different parts of the surfactant increase, increasing temperature normally leads to increases of lattice parameters and pore volumes after template removal.²⁰ This effect was also observed for the cubic vinyl silica described here. In Table 1, the results of aging temperatures of 60, 80, and 100 °C are compared. The unit cell parameter increases by 2.5 nm, and the pore volume of the material

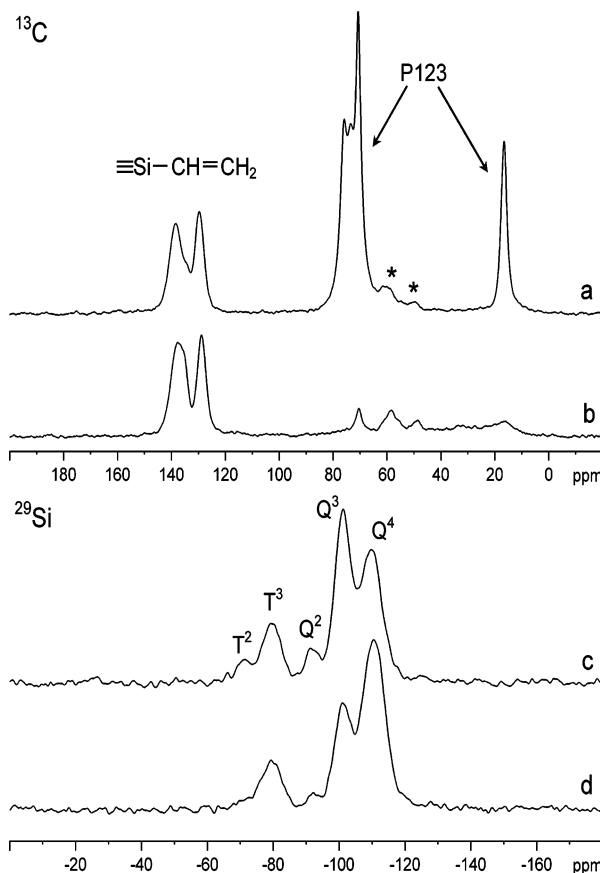


Figure 5. ^{13}C CP/MAS NMR (a, b) and ^{29}Si MAS NMR (c, d) of as-synthesized (a, c) and H_2SO_4 -treated (b, d) samples synthesized with 1.5 M NaCl and 20% TEVS in the starting mixture. Asterisks denote spinning sidebands.

is almost doubled when going from 60 to 100 °C aging temperature. This demonstrates that the structural properties can be influenced within certain limits by small variations of the processing conditions. It is in line with the observations of Kleitz et al.,¹⁷ although here the effect of the aging temperature was even more pronounced for a pure silica $Ia3d$ mesostructure.

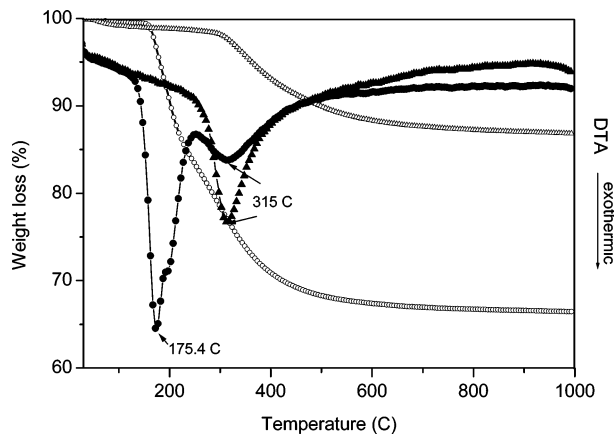
Since the sample contains organic groups linked to the silica framework, the template cannot be removed by calcination. We have recently developed a gentle and very efficient pathway for removal of the polyether template by H_2SO_4 treatment at elevated temperatures to result in ether cleavage with subsequent easy removal of the fragments.¹⁸ This process was also used in this case. The success of the procedure used for the template removal has been assessed by NMR spectroscopy. Figure 5 shows the ^{13}C CP/MAS NMR and ^{29}Si MAS NMR spectra of a sample before and after treatment with sulfuric acid. In the ^{13}C NMR spectra, the lines at about 129 and 138 ppm are attributed to the vinyl carbons, and the line at 17 ppm and those between 70 and 76 ppm are attributed to the carbon species of P123. Although slight changes in the line shape in the vinyl region and an ill-defined broad line at about 30 ppm indicate a reaction of some of the vinyl groups, possibly a coupling as described before,²¹ the majority of vinyl groups is still present in the acid-treated

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Table 2. Integral Intensities of Tⁿ and Qⁿ Lines of the ²⁹Si NMR Spectra in Figure 5c,d

	T ²	T ³	Q ²	Q ³	Q ⁴
as-prepared	5	15	7	38	35
acid-treated	3	13	4	25	55

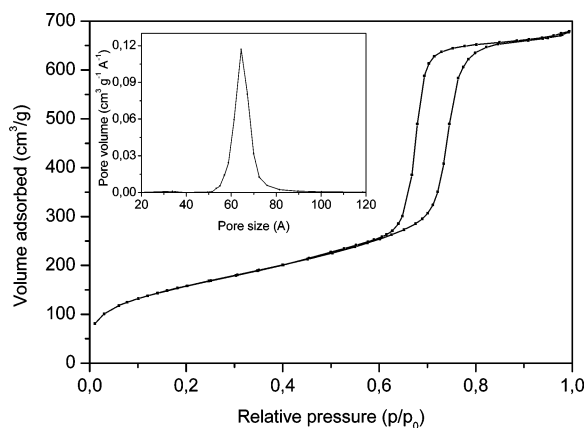
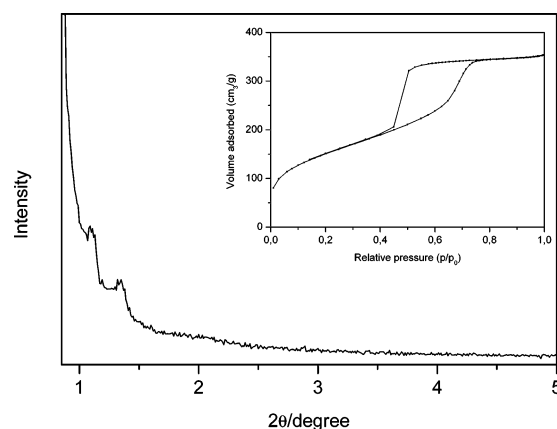
**Figure 6.** TGA (open) and DTA (close) curves of the as-prepared and H₂SO₄-treated samples with 20% TEVS in the starting mixture. (Circles: as-prepared; triangles: H₂SO₄-treated).

material. The lines corresponding to the P123 template, however, are strongly reduced in intensity, demonstrating that nearly all the template has been removed by ether cleavage. In the ²⁹Si NMR spectra, the lines corresponding to the various Tⁿ and Qⁿ groups can clearly be identified. Their relative intensities obtained by deconvolution of the spectra are summarized in Table 2. From these data it follows that the fraction of silicon atoms bound to carbon agrees well with the fraction of functional silane used as silica source. The strong increase of Q⁴/Q³ ratio after the acid treatment indicates further condensation brought about by the strongly acidic conditions.^{13,18}

The conclusions drawn from the NMR spectra are supported by the results of the TG/DTA-analysis (Figure 6). The as-synthesized sample lost weight in two steps: one at 175 °C (approximately 15–20%), which is due to the copolymer decomposition,²² and the other at 315 °C (approximately 15–20%), which is attributed to both the loss of vinyl groups and the copolymer left in the sample. In contrast, the acid-treated sample only shows a weight loss around 315 °C, corresponding to about 12%. This indicates almost complete removal of template by the H₂SO₄ treatment.

Assuming a complete condensation of all the silanols, that is, both the silanol groups present after the acid treatment and those generated by the removal of vinyl groups in the course of the TG measurement, ²⁹Si NMR spectroscopy allows an upper limit for the weight loss to be predicted. From the data given in Table 2, the expected weight loss is 10%. The small difference between the expected and experimental value can be explained by the removal of the remainder of P123 detected by ¹³C NMR spectroscopy after the acid treatment.

Success of the template removal can also be seen in the sorption analysis. Table 1 contains the textural data

**Figure 7.** Nitrogen sorption isotherm of the sample synthesized with 1.5 M NaCl and 20% TEVS in the starting mixture. The inset shows the pore size distribution from the desorption branch.**Figure 8.** XRD patterns of the as-prepared sample containing 10% TEVS in the starting mixture prepared with F127. The inset shows the sorption isotherm.

determined for the different materials; Figure 7 gives a sorption isotherm of vinyl-functionalized mesoporous silica with 20% TEVS in the starting mixture. The steep step in the isotherm indicates the narrow pore size distribution, which is expected for samples corresponding to the *Ia3d* structure. In general, the textural data correspond to those reported in the literature for silica *Ia3d* materials synthesized in the presence of block copolymers. The slightly smaller pore sizes compared to literature data are probably due to the pendant vinyl groups, which on average make the pore narrower. However, also other synthesis parameters were different in the cited references. As shown above for the temperature, small variations in conditions can lead to significant effects on textural parameters, such as increasing the temperature from 60 to 100 °C, which leads to an increase in pore size from 5.0 to 6.8 nm.

Finally, some experiments were also carried out with the more hydrophilic F127 as the structure-directing agent. Cubic structures analogous to SBA-16 were also obtained at a TEVS molar percentage of 10%. Figure 8 shows the small-angle XRD pattern and the nitrogen sorption isotherm. It can be seen from the XRD pattern that only two shoulders are observed. TEM confirms the formation of the cubic mesostructure, but there are also parts of the sample which were disordered. From the sorption isotherm, high surface area and large pore size are obtained, which are 547 m² g⁻¹ and 6.6 nm,

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respectively. A similar structure without any functional groups was also prepared in the presence of KCl by Zhao's group.²³

The pronounced influence of the TEVS/TEOS ratio on the phase behavior of the studied systems is understandable since the vinyl group is hydrophobic enough for TEVS to exhibit cosurfactant properties; that is, it will be preferentially adsorbed close to the hydrophobic PPO portion of the micelles and therefore cause a decrease in the preferential interfacial curvature, eventually favoring the formation of the *Ia3d* phase over the 2D hexagonal phase. Such an effect has also been observed when a mercapto-functionalized organosilane was used as the silica precursor in the synthesis of *Ia3d*-type silica.¹⁴ Furthermore, the addition of aliphatic alcohols has also been shown to induce a similar change in the preferential interfacial curvature of P123-TEOS¹⁷ and CTAB-TEOS²⁴ hybrid materials.

The addition of chloride salts has a similar effect in decreasing the preferential interfacial curvature of the inorganic-organic assembly. Inorganic salts are known to facilitate the formation of ordered mesostructures²⁵ and affect the phase behavior of block copolymers. The addition of 1.0 M NaI has been shown to induce the formation of the *Ia3d* structure of block copolymer templated silica in a synthesis that leads to a coexistence of multilamellar vesicular structures and a 2D hexagonal phase in the absence of added NaI.¹⁵ Anions can be either preferentially depleted (lyotropic ions) or adsorbed (hydrotropic ions) to the palisade layer of the surfactant micelles, while cations are generally all depleted.²⁶ For example, chloride and bromide ions have been shown to be lyotropic while iodide ions are hydrophobic. Nonadsorbing species dehydrate the hydrophilic portion of the surfactants ("salting out"), rendering the surfactants more hydrophobic and the preferential interfacial curvature of the micelles decreases, while adsorbing anions could increase the preferential interfacial curvature ("salting in"). We also observe that the addition of NaCl decreases the preferential interfacial curvature in our case. If the synthesis was carried out at TEVS/TEOS ratios close to the 2D hexagonal-bicontinuous cubic transition, addition of salt stabilized the cubic phase, in agreement with an expected decrease in interfacial curvature due to the salting-out effect. However, the fact that no precipitation was observed at 2.0 M HCl without addition of salt is difficult to rationalize solely based on the salting-out effect of the electrolyte since the chloride ion concentration in solution is already 2 M without added salt. Therefore, we suggest that another important effect of the added electrolyte is to influence the hydrolysis and condensation and aggregation kinetics of the silica precursors.

Furthermore, the presence of salt will most probably also decrease the aqueous solubility of the hydrophobic TEVS precursor. Indeed, it is well-known that electrolytes have a pronounced influence on silica solubility under alkaline conditions where the silicate species are negatively charged, due to screening of the repulsive electrostatic forces. Under the strongly acidic conditions employed here (2.0 M HCl), the silica species carry a net positive charge and a similar reasoning could be applied, although it should be noted that the ionic strength is already high under these highly acidic conditions even in the absence of added electrolyte, which effectively screen electrostatic interactions. Furthermore, the concentration of unbound water will decrease when salt is added as a consequence of ion hydration.

The increase in pore diameter with increasing temperature upon aging is well-documented in the literature¹⁷ and is probably a combined effect of dehydration of the ethoxylate chains of the surfactant, causing an increase in the effective diameter of the hydrophobic portion of the micelles and an increase in the degree of silica condensation. It is clear that the decrease in interfacial curvature favoring the bicontinuous cubic phase over the 2D hexagonal phase can therefore be induced by an increase in TEVS/TEOS ratio, temperature, or salt concentration. However, opposite to the effect of temperature, the addition of salt seems to have a limited influence on the observed pore size of the material in our case. Therefore, the optimization of aging temperature and salt concentration can be used for independent control of both the mesoscopic order and the pore size.

Conclusions

Co-condensation of TEVS and TEOS in the presence of a triblock copolymer surfactant allows the synthesis of hexagonal and *Ia3d* cubic silica with vinyl group bearing silicon atoms incorporated in the material. The TEVS molar percentage governs the nature of the phase formed: At low TEVS percentage the hexagonal phase analogous to SBA-15 is obtained; TEVS percentage equal to or higher than 15% induce the formation of the cubic *Ia3d* phase, which is related to MCM-48 as is SBA-15 to MCM-41. The addition of inorganic salts improves the quality of the materials. With 10% TEVS in the starting mixture, a predominated hexagonal structure was obtained up to a NaCl concentration of 1.5 M, increasing the concentration to 2.0 M, cubic *Ia3d* structure formed. In addition, often ill-defined diffraction patterns are obtained for samples prepared without salts and much better patterns resulted, if the syntheses were carried out in the presence of NaCl. Using the F127 surfactant, a structure probably close to SBA-16, but functionalized with organic groups, is accessible.

The ordered mesoporous vinyl silicas have surface areas on the order of 600 m² g⁻¹ and pore volumes around 1 cm³ g⁻¹. Pore sizes are appreciably larger than those for the MCM-48 *Ia3d* structure and can be adjusted by the synthesis temperature between about 5 and 7 nm. It is expected that the vinyl groups in the samples can be modified in a manner similar to that described by Asefa et al.,⁹ that is, hydroboration, bromination, and epoxidation, and thus allow the introduc-

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tion of additional functionality in an ordered *Ia3d* silica with large pore sizes.

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