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# Metamorphosis of Ordered Mesopores to Micropores: Periodic Silica with Unprecedented Loading of Pendant Reactive Organic Groups Transforms to Periodic Microporous Silica with Tailorable Pore Size

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***Abstract:*** Ordered porous silicas with unprecedented loadings of pendant vinyl groups have been synthesized via co-condensation of tetraethyl orthosilicate (TEOS) and triethoxyvinylsilane (TEVS) under basic conditions in the presence of cetyltrimethylammonium surfactant. The resulting organosilicate-surfactant composites exhibited at least one low-angle X-ray diffraction (XRD) peak up to the TEVS:TEOS molar ratio of 7:3 (70% TEVS loading) in the synthesis gel. The surfactant was removed from these composites without any structural collapse. Nitrogen adsorption provided strong evidence of the presence of uniformly sized pores and the lack of phase separation up to TEVS:TEOS ratios as high as 13:7 (65% TEVS loading), whereas $^{29}$Si MAS NMR and high-resolution thermogravimetry showed essentially quantitative incorporation of the organosilane. Thus, a hitherto unachieved loading level for pendant groups, considered by many to be impossible to achieve for stable organosilicas because of the expected framework connectivity constraints, has been obtained. The resulting vinyl-functionalized silicas exhibited gradually decreasing pore diameter (from 2.8 to 1.7 nm for TEVS loadings of 25−65%) and pore volume as the loading of pendant groups increased, but the specific surface area was relatively constant. Because of the reactivity of vinyl groups, ordered silicas with very high loadings of these groups are expected to be robust starting materials for the synthesis of other organic-functionalized ordered microporous materials. Herein, we demonstrate that these starting materials can also be transformed via calcination into ordered microporous silicas with pore diameters tailorable from 2.5 to as little as 1.4 nm simply by using an appropriate loading of the vinyl-functionalized precursor. This ease of the micropore size adjustment and the attained degree of structural ordering (as judged from XRD) have not been reported before. The novel ordered microporous materials reported herein are promising as adsorbents and catalyst supports.

## Introduction

Over the last several years, there has been a quest for ordered mesoporous organic−inorganic composites with a high content of organic groups uniformly distributed over the ordered structure.[1−7] These materials are desirable from the point of view of specific adsorption, ion-exchange, and catalytic applications. The content of organic groups is a major factor that determines many important properties of composites, such as adsorption capacity for metal ions (including highly toxic ones, such as mercury),[8] ion-exchange capacity,[9] and surface hydrophobicity.[10] Moreover, organic groups incorporated in the framework influence dielectric constant, hardness, and modulus,[11] whereas surface-bonded (pendant) organics may improve hydrothermal stability[10] and mechanical properties.[12] The uniformity in organic group distribution may affect the surface properties, the organic functional group reactivity, and accessibility of the porous organic−inorganic composite. A common way to synthesize ordered mesoporous organic−inorganic composites is the postsynthesis functionalization via surface reaction of surfactant-free ordered mesoporous silica with a suitable organic coupling

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agent (usually organosilanes).[1,2,13] If the organic moiety introduced is reactive, its structural and chemical properties can further be tailored.[1,2,14] However, the postsynthesis modification has some drawbacks, including its multistep nature, some degree of nonuniformity of organic group distribution,[10] and a limited loading of organic group, although the latter can be made high using a method based on the formation of self-assembled monolayers.[8,15] Some of the aforementioned limitations can be largely overcome[16,17] when as-synthesized rather than surfactant-free ordered mesoporous silica is modified,[18,19] which involves a surfactant-displacement reaction.[16] Another approach to the synthesis of ordered silicas with high loadings of pendant organic groups is based on the surfactant-templated co-condensation of organotrialkoxysilane and tetraalkyl orthosilicate.[20,21] This methodology has become widely used because of its many beneficial features, including its simplicity, versatility, and high efficiency.[1,2,22] Another attractive feature of this method is the ability to attain high loadings of organic groups, as silicas with up to 40% of their silicon atoms carrying pendant organic groups can readily be synthesized.[23] However, further increase in the loading was envisioned to be hindered by the fact that the introduction of pendant groups may decrease the degree of cross-linking to a level at which a stable ordered silica-based framework cannot form.[20] This view has been expressed in recent review articles.[1−3] The validity of this framework connectivity rule has been supported by unsuccessful attempts of the synthesis of ordered silicas with higher loadings of pendant groups, which resulted in the formation of nontemplated disordered materials.[22,24] However, the preparation of ordered materials with potentially higher loadings (based on the synthesis mixture composition) has also been described in the literature.[25−28] Yet, in most of these cases, no evidence of structural ordering[25] and quantitative incorporation of organic groups was reported,[25,26] while in another case, a strong evidence of separation into an amorphous organosilica-rich phase and ordered silica-rich phase was found.[27] To the best of our knowledge, the only well-documented exception from the putative framework connectivity rule was the successful synthesis of mercaptopropyl-functionalized silicas using a neutral amine template, in which case a 50% functionalization level was attained, and even a sample with 60% functionalization level exhibited some residual ordering based on XRD data.[28] However, the degree of framework cross-linking in these materials was not particularly low, because the silanol group content was very small.

It was recently demonstrated that high loadings of organic groups can readily be incorporated into frameworks of ordered mesoporous silica-based materials via the condensation of bis(trialkoxysilyl)organic precursors or the co-condensation of the latter with tetraalkyl orthosilicate in the presence of surfactant template.[4−7] This approach gave rise to a new group of ordered organosilicas with hybrid inorganic−organic frameworks,[4−7,11,29] referred to as periodic mesoporous organosilicas (PMOs). PMOs exhibit up to 100% of silicon atoms bonded to organic groups, but in contrast to silicas with pendant organic groups, each of these organic bridging groups is connected with at least two silicon atoms, thus promoting framework cross-linking. Beneficial features of organosilicate frameworks and pendant organic functionality have recently been realized in a novel class of materials called bifunctional PMOs (BPMOs) that are formed via co-condensation of bis(trialkoxysilyl)organic and organotrialkoxysilane precursors.[30,31] BPMOs can be synthesized with as much as about 50% of silicon atoms functionalized with pendant organic groups, whereas attempted higher loading of pendant groups results in the formation of disordered materials.[30] BPMOs with a high loading of pendant groups have a rather low silanol content, which allows them to attain an appreciable degree of framework cross-linking. It was also recently demonstrated that methylene groups in PMO can transform to pendant methyl groups upon heating.[29] This potentially allows one to obtain an ordered silica with up to 50% of silicon atoms that carry pendant methyl groups. However, the actual achievable loading and the suitability of this procedure for other organic groups are yet to be explored.

Herein, we report a successful synthesis of ordered silicas with extremely high loading of pendant organic groups via templating with a cationic surfactant. More than three out of five silicon atoms (up to 62%) in these ordered materials can be functionalized with vinyl groups without inducing phase separation. Pendant vinyl groups are known to undergo various reactions, such as bromination,[32] hydroboration,[33,34] that can be followed by alcoholysis,[34] as well as epoxidation, that can be an intermediate step to the formation of diol functional groups.[34] Therefore, one can envision that a host of highly functionalized ordered mesoporous and microporous materials can be derived from the vinyl-functionalized silicas. Because of the presence of an ordered silica backbone of tailorable dimensions in the vinyl-functionalized silicas, they can also be readily transformed to ordered microporous silicas with high specific surface area, appreciable pore volume, and tailorable pore diameter. Such materials were a subject of a very active research during the last several years,[35−45] but the success in achieving ordered

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microporous materials other than those with crystalline frameworks and pore sizes below 1.3 nm[46] was limited.[42] The simple strategy proposed herein allows one to readily synthesize exclusively microporous silica that exhibits a narrow X-ray diffraction (XRD) peak, whose position corresponds to a (100) interplanar spacing as low as 2.28 nm.

## Experimental Section

**Reagents and Materials.** Organic-functionalized silicas were synthesized using the following synthesis gel composition: $x$/100 TEVS (or $x$/100 TEMS), $(100 - x)$/100 TEOS, 0.24 CTAB, 16.10 $NH_4OH$, 128.70 $H_2O$, where CTAB, TEVS, TEMS, and TEOS stand for cetyltrimethylammonium bromide, triethoxyvinylsilane, triethoxymethylsilane, and tetraethyl orthosilicate, respectively. CTAB and all the silanes were obtained from Aldrich and were used as received. The amount of organosilane was varied from $x = 25$ to 100 in the case of TEVS and from $x = 20$ to 100 in the case of TEMS. The following synthesis procedure was typically used. In a tightly closed plastic bottle, a solution of CTAB (0.54 g, 1.48 mmol), ammonium hydroxide (5.7 g, 30 wt %, 0.10 mol), and water (10.6 g, 0.59 mol) was prepared at room temperature. To this solution was added 6.23 mmol of silica source prepared from a mixture of TEOS and TEVS (for instance, for 43% TEVS, $x = 43$, 0.51 g (2.70 mmol) TEVS and 0.74 g (3.53 mmol) TEOS). The mixture was stirred for 30 min at room temperature and then aged at 353 K for 4 days. The product was then filtered and washed thoroughly with a copious amount of water and dried under ambient conditions resulting in a fine white powder. The surfactant was extracted from the samples by mildly stirring ca. 0.2 g of the as-synthesized materials in HCl (5 g, 35 wt %)/methanol (100 g) solution at 313 K for 6 h. The product was then isolated by filtration on a Büchner funnel, washed with methanol, and dried in air. The materials prepared from 100% TEVS and 100% TEMS remained as a gel after aging for 4 days, and the bottle was left open at 353 K to let the solvent evaporate and to obtain solid products. The resulting vinyl-functionalized samples are denoted VIN*x*A and VIN*x*E, where $x$ reflects the synthesis gel composition (see above), and A and E denote the as-synthesized and solvent-extracted form, respectively. The synthesis, structure, and reactivity of the sample with the lowest loading of vinyl groups (VIN25A and -E) have been reported elsewhere.[34] Porous silicas were synthesized from either as-synthesized VIN*x*A or surfactant-extracted VIN*x*E precursors ($x = 25-65$) via calcination under air at 823 K for 16 h and are denoted VIN*x*AC or VIN*x*EC, respectively.

**Measurements.** Powder XRD patterns were acquired on a Siemens D5000 diffractometer operating at 35 mA/50 kV using Ni-filtered Cu K$\alpha$ radiation ($\lambda = 0.154178$ nm). Solid-state $^{13}C$ (100.6 MHz) and $^{29}Si$ (79.5 MHz) NMR spectra were obtained on a Bruker DSX 400 spectrometer with the following experimental parameters: for $^{13}C$ CP-MAS NMR experiments, 6.5 kHz spin rate, 3 s recycle delay, 2 ms contact time, $\pi/2$ pulse width of 6.5 $\mu$s, 5000−10000 scans; for $^{29}Si$ CP-MAS NMR experiments, 6.5 kHz spin rate, 3 s recycle delay, 10 ms contact time, $\pi/2$ pulse width of 6.0−7.5 $\mu$s, 200−1000 scans; and for $^{29}Si$ MAS NMR experiments, 6.5 kHz spin rate, 100 s recycle delay, $\pi/6$ pulse width of 2.2 $\mu$s, 500−1000 scans were used. Adamantane (major peak, 38.4 ppm vs TMS) and $Si[Si(CH_3)_3]_4$ (major peak, −9.98 ppm vs TMS) were used as external references for $^{13}C$ and $^{29}Si$ spectra, respectively. Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before the measurements, the samples were outgassed under vacuum in a port of the adsorption analyzer for 2 h or until the residual pressure was equal to or below 6 $\mu$m Hg. The outgassing temperature was 373 K for VIN*x*E, and 473 K for VIN*x*AC and VIN*x*EC samples. Weight change curves under nitrogen and air atmospheres were measured on a TA Instruments TGA 2950 thermogravimetric analyzer in a high-resolution mode with a maximum heating rate of 5 K min$^{-1}$.

**Calculations.** The BET specific surface area[47] was calculated in a relative pressure range from 0.01 to 0.02. It was shown elsewhere that the use of this range allows one to obtain a good estimate of the specific surface area for small-pore silicas.[42] The total pore volume[47] was evaluated from the amount adsorbed at a relative pressure of 0.99. The primary pore volume (primary pores are defined herein as uniform interparticle pores, whose arrangement may give rise to XRD reflections) and the external surface area was evaluated using the $\alpha_s$ plot method[47,48] in the $\alpha_s$ range from 1.5 to 2.0 ($\alpha_s$ is defined as the amount adsorbed at a given relative pressure divided by the amount adsorbed at a relative pressure of 0.4). Reference adsorption data for macroporous silica[48] were used in the $\alpha_s$ plot analysis. The pore size distributions (PSDs) were evaluated using the Barrett−Joyner−Halenda (BJH) calculation method with the pore diameter−capillary condensation pressure relation and the statistical film thickness curve (reported in ref 48) determined using a series of MCM-41 silicas.[49] The BJH pore diameter is defined as the position of a maximum on the BJH PSD. In the case of ordered porous silicas, their pore diameter, $w_d$, was estimated using a geometrical equation derived under the assumption of a 2-D hexagonal (honeycomb) porous structure:[50]

$$w_d = cd_{100}\left(\frac{\rho V_p}{1 + \rho V_p}\right)^{0.5} \tag{1}$$

where $c$ is a constant equal to 1.213 for cylindrical pore geometry, $\rho$ is the pore wall density assumed to be 2.2 g cm$^{-3}$ for silicas, $V_p$ is the primary pore volume, and $d_{100}$ is the (100) XRD interplanar spacing.

## Results

**Vinyl-Functionalized Silicas. XRD.** Shown in Figure 1 and Supporting Information Figure 1S are XRD patterns for vinyl-functionalized silicas synthesized with different TEVS:TEOS ratios in the synthesis gel. At least one peak was observed for both as-synthesized and surfactant-extracted products when up to 70% of silicon atoms in the precursors came from the organosilica precursor, while materials obtained using a larger proportion of organosilica in the synthesis gel had featureless XRD patterns. The XRD intensity decreased as the proportion of organosilica precursor increased, whereas the position of the main XRD reflection shifted to higher angles for loadings up to 60%. This shift corresponds to the interplanar spacing reduction from about 3.3 to 2.6 nm for 25−60% loadings (see Table 1 and Figure 1B). The decrease in the interplanar spacing as the loading of pendant groups increases is a known phenomenon for organic-functionalized silicas synthesized via co-condensation.[1] The products with the intended organosilica loadings of 25, 33, and 43% exhibited XRD patterns with up

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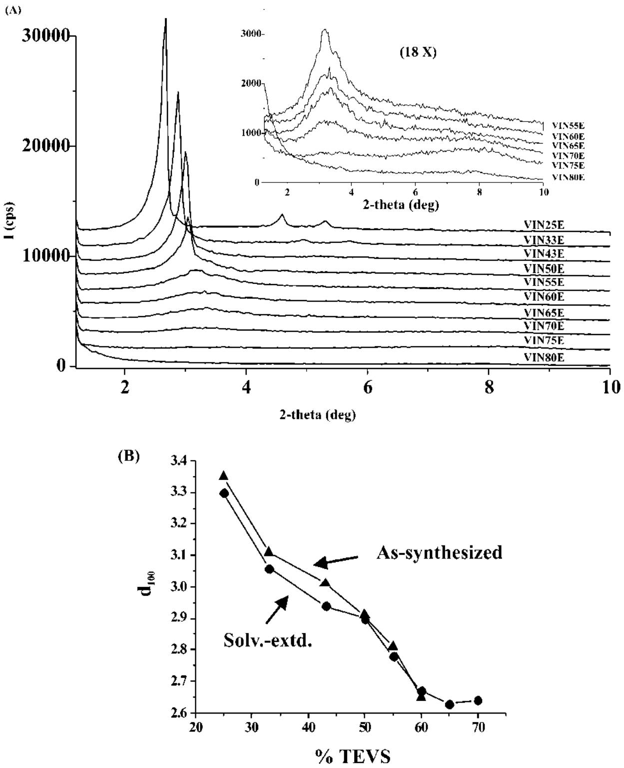

***Figure 1.*** (A) XRD patterns for solvent-extracted vinyl-functionalized silicas and (B) $d_{100}$ values as a function of the percentage of the organosilica in the synthesis mixture.

***Table 1.*** Structural Properties of Vinyl-Functionalized Silicas[a]

| sample | $d_{100}$ (nm) | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_t$ (cm$^3$ g$^{-1}$) | $V_p$ (cm$^3$ g$^{-1}$) | $S_{ex}$ (m$^2$ g$^{-1}$) | $w$ (nm) |
|---|---|---|---|---|---|---|
| VIN25E | 3.30 | 830 | 0.68 | 0.64 | 30 | 2.7 |
| VIN33E | 3.06 | 840 | 0.57 | 0.53 | 20 | 2.3 |
| VIN43E | 2.94 | 850 | 0.49 | 0.44 | 30 | 2.1 |
| VIN50E | 2.90 | 870 | 0.48 | 0.44 | 20 | 2.0 |
| VIN55E | 2.78 | 790 | 0.41 | 0.36 | 30 | 1.8 |
| VIN60E | 2.67 | 710 | 0.36 | 0.32 | 20 | 1.7 |
| VIN65E | 2.63 | 680 | 0.36 | 0.31 | 30 | 1.8 |
| VIN70E | 2.64 | 530 | 0.43 | 0.21[c] | 90[c] | 1.7 |
| VIN75E | [b] | 360 | 0.83 | 0.11[c] | 170[c] | 1.6 |
| VIN80E | [b] | 300 | 1.41 | 0.06[c] | 260[c] | [e] |
| VIN100E | [b] | 250 | 1.13 | 0.00 | [d] | [e] |

[a] Notation: $d_{100}$, XRD (100) interplanar spacing; $S_{BET}$, BET specific surface area; $V_t$, total pore volume; $V_p$, primary pore volume; $S_{ex}$, external surface area; $w$, primary pore diameter calculated as in ref 49. [b] No XRD peaks observed. [c] These results may be significantly inaccurate. [d] $S_{BET}$ can be considered as $S_{ex}$. [e] No observable peak for primary pores on pore size distribution.

to three (or even more for 25% loading) peaks characteristic of a 2-D hexagonal structure. The surfactant extraction enhanced the XRD intensity but usually led to some decrease in the (100) interplanar spacing (see Figure 1B).

**NMR.** The $^{13}$C CP MAS NMR spectra (Figure 2) exhibited resonances corresponding to the vinyl functional groups (130, 137 ppm)[34] which remain in the materials both after synthesis and solvent-extraction. To assess the extent of the organosilane incorporation in the products, selected solvent-extracted samples were studied using $^{29}$Si MAS NMR (spectra shown in Figure 2B). Using a standard methodology for the assessment of the relative population of Q$^n$ and T$^n$ silicons (Q$^n$ silicon atom is connected with $n$ other silicon atoms via oxygen bridges and with 4-$n$ silanol groups (−OH), whereas T$^n$ silicon atom is bonded with one carbon atom, with $n$ silicon atoms via oxygen bridges and with 3-$n$ silanols), it was possible to determine approximate formulas of the products. For intended 25, 50, and 65% functionalization levels, the obtained formulas were $SiO_{1.634}(OH)_{0.480}(CH{=}CH_2)_{0.252}$, $SiO_{1.548}(OH)_{0.386}(CH{=}CH_2)_{0.518}$, and $SiO_{1.545}(OH)_{0.287}(CH{=}CH_2)_{0.619}$. These formulas show that the loadings of 25, 52, and 62% were actually achieved, which are very close to those in the synthesis gel. This corresponds to 3.64, 7.06, and 8.32 mmol, respectively, of vinyl groups per gram of the product. The latter two loadings are higher than the highest loading of reactive pendant groups ever reported for ordered materials with silica and organosilica frameworks. Previous successfully achieved loadings were below 5.5−6.0 mmol g$^{-1}$ for silicas with pendant mercaptopropyl groups,[28] and below 7 mmol g$^{-1}$ for BPMOs with pendant vinyl groups,[30] as estimated under the assumption of stoichiometric incorporation of silica and organosilica precursors.

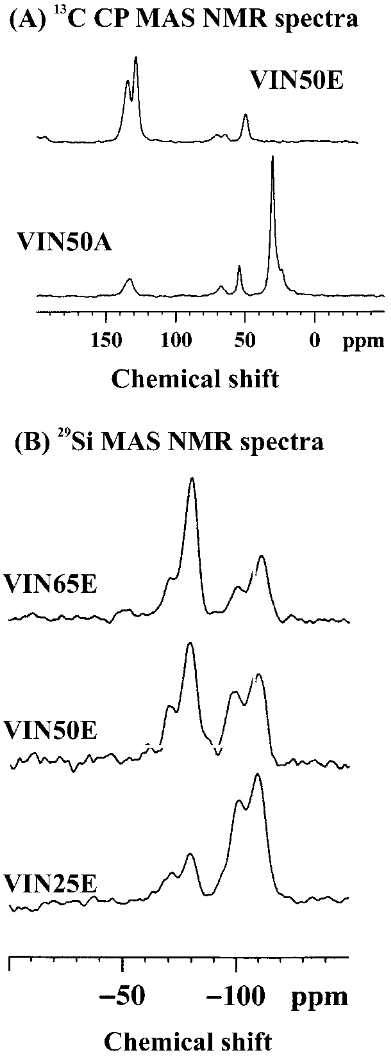

***Figure 2.*** $^{13}$C CP MAS and $^{29}$Si MAS NMR spectra for selected solvent-extracted vinyl-functionalized silicas.

**Thermogravimetry.** Upon heating under air, the surfactant-extracted samples exhibited complicated weight change patterns that featured weight loss at temperatures below about 500 K, weight gain at temperatures around 550 K, followed by weight loss at higher temperatures (see Figure 2S). The initial weight loss below 373 K is primarily related to the removal of

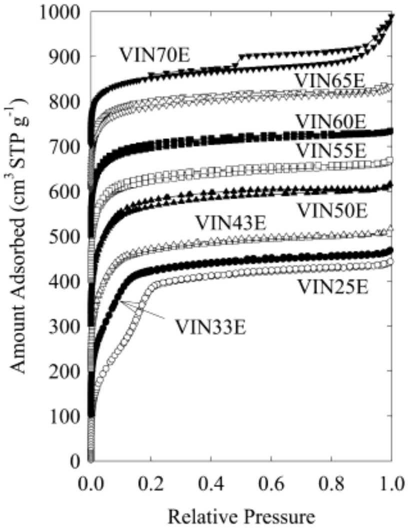

***Figure 3.*** Nitrogen adsorption isotherms for vinyl-functionalized silicas, which exhibit at least one XRD reflection. The isotherms are offset vertically by 100, 200, 300, 400, 500, 600, and 700 cm$^3$ STP g$^{-1}$ for VIN33E, -43E, -50E, -55E, -60E, -65E, and -70E, respectively.

physisorbed water and solvents left after the surfactant extraction (if any), whereas the weight gain, which is not observed at this temperature under a nitrogen atmosphere, appears to be related to the reaction of vinyl groups with oxygen. The subsequent weight loss at higher temperatures is related to the oxidation and removal of the vinyl groups. The weight loss measured from about 500 K (from the minimum before the onset of the weight gain region) to 1270 K tended to gradually increase as the content of the organosilicate precursor in the synthesis gel increased. This weight loss was, in fact, correlated with the formulas for vinyl-functionalized materials established from NMR data. These weight losses were 10.4, 16.4, and 18.2% for VIN25E, VIN50E, and VIN65E samples, respectively, being close to 12.5, 18.0, and 19.0% expected for these samples on the basis of their formulas under the assumption that the composition of a given sample at about 500 K corresponds to the formulas derived from NMR and the product of heating under air to 1270 K is pure $SiO_2$.

The overall weight losses recorded for surfactant-extracted samples under a nitrogen atmosphere were generally smaller than those under air, especially for higher vinyl group loadings (see Figure 4S). Weight gain was usually observed at about 1100 K under nitrogen, which is reminiscent of the behavior of ethanesilica PMO[51] and indicative of reaction with nitrogen. Weight change patterns were also recorded under nitrogen for the as-synthesized (surfactant-containing) samples (Figure 3S), and prominent weight losses centered at a temperature of about 500 K were observed, which are attributable mainly to the surfactant decomposition. These weight losses tended to decrease as the content of the organosilicate precursor in the synthesis gel increased.

**Nitrogen Adsorption.** Nitrogen adsorption isotherms for vinyl-functionalized samples with the organosilica loading levels of 25−70% in the synthesis gel are shown in Figure 3. As the loading increased, adsorption isotherms gradually changed from type IV to type I.[47] Type IV isotherms feature capillary condensation steps and are characteristic of mesoporous materials (pore diameter from 2 to 50 nm), whereas type I isotherms level off already at quite low relative pressures and are characteristic of microporous materials (and often also for materials with pore sizes on the borderline between the micropore and mesopore ranges).[52] The gradual change in the shape of the nitrogen adsorption isotherms suggests the decrease in the pore diameter as the loading of organic groups increased. The pore size distribution (PSD) calculations provided a more detailed picture of this trend (see Figure 4). The pore diameter gradually decreased from about 2.7 to 1.7 nm (see Table 1) as the organosilica precursor loading in the synthesis gel increased from 25 to 60%, whereas further increase in the loading level essentially did not produce further pore size lowering, although the height of the PSD peak was appreciably diminished as the loading exceeded 65%. The BET specific surface area appeared to be relatively constant for loadings up to 50%, somewhat decreased for loadings up to 65%, and more rapidly declined for yet higher loadings. The primary pore volume decreased as the loading of organic groups increased up to 65% and subsequently considerably decreased for higher loadings. The primary pore volume tended to decrease as the surfactant content in the as-synthesized samples decreased, as expected for supramolecular-templated materials that are stable upon surfactant removal.[42,51] The external surface area was low for loadings up to 65%, but dramatically increased for higher loadings. This was related to the development of secondary porosity (most likely interparticle mesopores and small macropores) which was clear from the occurrence of pronounced hysteresis loops at pressures close to the saturation vapor pressure (Figure 5S). Secondary pore volume, which can be estimated as a difference between the total pore volume and the primary pore volume, did not exceed 0.05 cm$^3$ g$^{-1}$ for loading levels up to 65%, but sharply increased for higher loadings, being as much as 1.35 cm$^3$ g$^{-1}$ for VIN80E. The occurrence of secondary porosity may be due to the decrease in particle size of the materials. This may be accompanied by some extent of phase separation with organosilicate-rich and silica-rich phase, especially in the case of the sample with 70% organic group loading in the synthesis gel, for which there was still some evidence of structural ordering and the pore diameter was similar to that for the samples with somewhat lower loadings, but the primary pore volume was considerably lower, and secondary porosity developed. The adsorption isotherm for

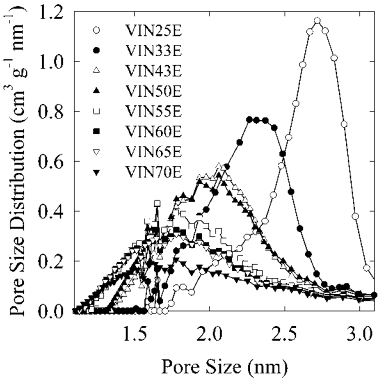

***Figure 4.*** Pore size distributions for vinyl-functionalized silicas that exhibit at least one XRD reflection.

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(51) Kruk, M.; Jaroniec, M.; Guan, S.; Inagaki, S. *J. Phys. Chem. B* **2001**, *105*, 681−689.

(52) Kruk, M.; Jaroniec, M. *Chem. Mater.* **2001**, *13*, 3169−3183.

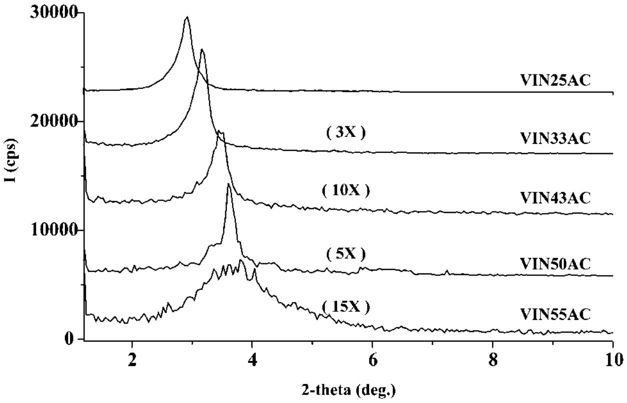

***Figure 5.*** XRD patterns for silicas obtained via calcination of as-synthesized vinyl-functionalized silicas.

a sample with 100% loading of vinyl group was characteristic of a nontemplated material with relatively large mesopores.

Low-pressure nitrogen adsorption of vinyl-functionalized silicas systematically changed as the loading of organosilica precursor increased from 25 to 50%. The increase in loading led to a decreased low-pressure relative adsorption (relative adsorption is defined here as a ratio of the amount adsorbed to the BET monolayer capacity) (see Figure 6S), as expected for materials whose surfaces exhibit gradually decreased interactions with nitrogen as a result of the introduction of higher coverage of organic surface groups.[52] For loadings above 50%, low-pressure relative adsorption started to increase to some extent. This may be related to the fact that for such high loadings, the surface is largely covered by vinyl groups, so the increase in loadings may no longer change to any significant extent the nature of surface groups with which nitrogen interacts,[52] whereas the decrease in pore diameter within the micropore range is likely to result in appreciably enhanced nitrogen−pore wall interactions.[42] This contention is consistent with the fact that the mesoporous vinyl-functionalized material VIN100E prepared from pure organosilica precursor exhibited the lowest low-pressure relative adsorption among the vinyl-functionalized materials studied, as expected for a material with the highest loading of organic groups.[52]

**Methyl-Functionalized Silicas.** Similar results were obtained for materials functionalized with methyl groups, but only lower loadings of organic pendant groups (up to 33%) have been achieved without occurrence of an apparent phase separation.

**Ordered Mesoporous and Microporous Silicas. XRD.** The use of ordered organic-functionalized silicas as precursor materials for ordered silicas has been documented in the literature.[53,54] Because of the fact that vinyl-functionalized silicas reported herein exhibited small and tailorable unit-cell dimensions and a significant degree of structural ordering, it was attempted to use them as starting materials to obtain ordered microporous silicas. XRD patterns for silicas obtained by calcining as-synthesized or solvent-extracted precursors exhibited one XRD peak, which was narrow for samples derived from precursors with loading of 50% or less of vinyl groups, and broad, yet observable, for materials derived from precursors with 55 and 65% loadings (Figures 5 and 7S). These peaks were observed at 2$\theta$ angles from 3° to as high as 4°, which are at very high angles as compared to main XRD peaks of ordered materials synthesized via surfactant templating. The corresponding (100) interplanar spacings were tailorable from 3.04 to as low as 2.15 nm (Table 2) simply by changing the organic group loading in the vinyl-functionalized precursor. These interplanar spacings are among the lowest reported in the literature for surfactant-templated ordered silicas with noncrystalline frameworks.[39,55] Somewhat lower (100) interplanar spacings were usually achieved when the solvent-extracted rather than the as-synthesized materials were calcined. For some of the silicas derived from 25% vinyl-functionalized precursor, (110) and (200) reflections characteristic for 2-D hexagonal ordering were also observed.

***Table 2.*** Structural Properties of Small-Pore Silicas[a]

| sample | $d_{100}$ (nm) | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_t$ (cm$^3$ g$^{-1}$) | $V_p$ (cm$^3$ g$^{-1}$) | $S_{ex}$ (m$^2$ g$^{-1}$) | $w$ (nm) | $w_d$ (nm) |
|---|---|---|---|---|---|---|---|
| VIN25AC | 3.04 | 950 | 0.67 | 0.59 | 30 | 2.6 | 2.8 |
| VIN33AC | 2.79 | 940 | 0.56 | 0.51 | 20 | 2.3 | 2.5 |
| VIN43AC | 2.55 | 880 | 0.44 | 0.39 | 20 | 2.1 | 2.1 |
| VIN50AC | 2.45 | 920 | 0.39 | 0.38 | <10 | 1.7 | 2.0 |
| VIN55AC | 2.31 | 710 | 0.29 | 0.28 | <10 | 1.6 | 1.7 |
| VIN25EC | 2.98 | 900 | 0.57 | 0.50 | 20 | 2.5 | 2.6 |
| VIN33EC | 2.75 | 910 | 0.48 | 0.43 | 20 | 2.1 | 2.3 |
| VIN43EC | 2.47 | 810 | 0.37 | 0.32 | 20 | 1.8 | 1.9 |
| VIN50EC | 2.28 | 690 | 0.28 | 0.27 | <10 | 1.5 | 1.7 |
| VIN55EC | 2.47 | 550 | 0.23 | 0.22 | <10 | 1.3 | 1.7 |
| VIN65EC | 2.15 | 520 | 0.21 | 0.20 | <10 | 1.3 | 1.4 |

[a] Notation: $w_d$, pore diameter estimated using eq 1. Other quantities defined as in Table 1.

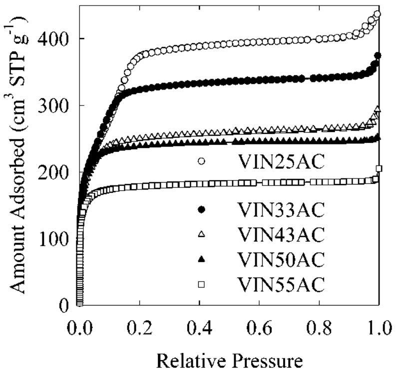

***Figure 6.*** Nitrogen adsorption isotherms for silicas obtained via calcination of as-synthesized vinyl-functionalized silicas.

**Nitrogen Adsorption.** Nitrogen adsorption isotherms of silicas synthesized via calcination of vinyl-functionalized as-synthesized and solvent-extracted materials are shown in Figures 6 and 8S, respectively. The shape of these isotherms gradually changed from type IV characteristic of mesoporous materials to type I typical for microporous materials. The adsorption isotherm for VIN25AC silica was similar to those reported for MCM-41 synthesized using decyltrimethylammonium surfactant as a template.[56] The adsorption isotherms for VIN33AC and VIN25EC silicas were similar to those reported for MCM-41 synthesized using octyltrimethylammonium template, although the latter had a lower adsorption capacity.[56] MCM-41 synthesized using a mixture of gemini and bichain surfactants with octyl tails exhibited a similar adsorption capacity and a similar

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(53) Ogawa, M.; Kikuchi, T. *Adv. Mater.* **1998**, *10*, 1077−1080.
(54) Goletto, V.; Dagry, V.; Babonneau, F. *Mater. Res. Soc. Symp. Proc.* **1999**, *576*, 229−234.
(55) Ogawa, M.; Ishikawa, H.; Kikuchi, T. *J. Mater. Chem.* **1998**, *8*, 1783−1786.
(56) Kruk, M.; Jaroniec, M.; Sayari, A. *J. Phys. Chem. B* **1997**, *101*, 583−589.

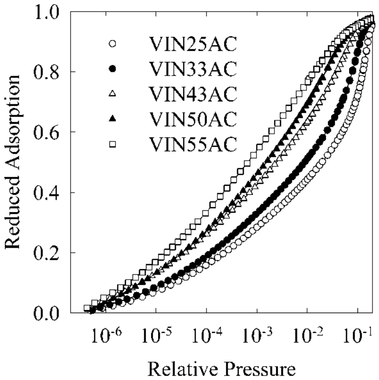

***Figure 7.*** Reduced adsorption curves (amounts adsorbed divided by the amount adsorbed at a relative pressure of 0.40) for silicas obtained via calcination of as-synthesized vinyl-functionalized silicas.

adsorption isotherm,[42] although with a distinct capillary condensation step, which is indicative of its higher degree of structural ordering. However, both of the structure-directing agents required for this synthesis are not commercially available. The primary pore volume of the materials described here systematically decreased as the loading of the organic groups in the precursor increased. For higher loadings, the BET specific surface area also decreased. The external surface area and secondary pore volume were small for all of these silicas. Low-pressure nitrogen adsorption data provided evidence that the observed gradual decrease in the XRD interplanar spacing as the loading of organic groups in the precursor increased was accompanied by the pore diameter decrease. As can be seen in Figures 7 and 9S, reduced adsorption (the amount adsorbed at a given relative pressure divided by the amount adsorbed at 0.4) for the silicas systematically increased in the low-pressure range as the loading of organic groups in the precursor increased, and the step related to capillary condensation or secondary micropore filling became less distinct and was not apparent for higher loadings. Similar changes in the shape of the nitrogen adsorption isotherms were recently shown as evidence of the ability to tailor the pore diameter of silicon imido nitrides in the micropore size range.[57] This identification is consistent with nonlocal density functional theory and computer simulation studies of microporous materials,[58] and with experimental studies of microporous carbons.[59]

PSDs of the silicas were evaluated using a method[49] calibrated for MCM-41 silicas with pore diameters from 2.0 to 6.5 nm (as calculated using eq 1). As can be seen in Figures 8 and 10S, the position of the maximum on the PSD systematically decreased from 2.6 to 1.6 nm and from 2.5 to 1.3 nm (see Table 2), when as-synthesized and solvent-extracted vinyl-functionalized materials were used. In general, for the same vinyl group loading, pore diameters of silicas obtained from calcination of the as-synthesized starting materials were 0.1−0.3 nm larger than those obtained from the solvent-extracted starting materials, but the (100) interplanar spacings were in most cases only slightly larger (see Table 2). This suggests that the differences in pore diameters for these two types of precursor materials are related not only to the interplanar spacing differences, but also to the larger pore wall thickness for silicas derived from solvent-extracted precursor materials. This contention is consistent with the fact that the latter silicas exhibited significantly smaller pore volumes and BET specific surface areas. Because of the fact that the pore diameter changes paralleled the (100) interplanar spacing changes, one can expect that all these silicas have a similar type of porous structure. Vinyl-functionalized precursor materials with lower organic group loadings (up to 33−43%) exhibited XRD patterns characteristic of 2-D hexagonal structure symmetry. Some silicas prepared from the precursor with 25% loading also exhibited XRD patterns that suggested 2-D hexagonal pore structure. Therefore, one can expect that the pore structures of the silicas under study are generally similar to 2-D hexagonal structures characteristic of MCM-41, although the degree of structural ordering decreases with the increased loading of vinyl groups in the precursors. If one neglects the imperfections in ordering of these silicas and assumes that the structure is 2-D hexagonal, it is possible to use eq 1 to determine the pore diameter of these samples. Thus, the values from 2.8 to 1.7 nm and from 2.6 to 1.4 nm were obtained for silicas derived from as-synthesized and solvent-extracted vinyl-functionalized precursors, respectively (Table 2). The pore diameters assessed using eq 1 and the maxima of PSDs calculated using another method[49] (Figures 8 and 10S) coincide quite well, although the former are about 0.2 nm larger. From the results presented above, it is clear that ordered silicas with very small interplanar spacings, relatively large pore volumes and specific surface areas, and tailorable pore sizes on the borderline between micropore and mesopore ranges can readily be prepared from vinyl-functionalized precursors.

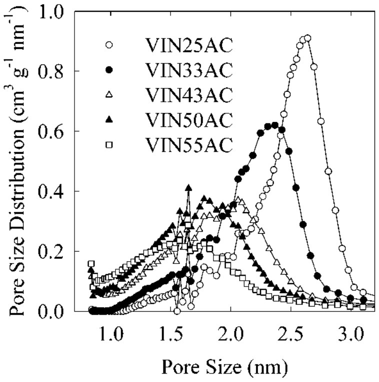

***Figure 8.*** Pore size distributions for silicas obtained via calcination of as-synthesized vinyl-functionalized silicas.

## Discussion

**Synthesis of Silicas with High Loadings of Pendant Groups.** There are many reported attempts to introduce very high loadings of pendant groups in ordered materials with silica and organosilica frameworks. Liu et al. reported that very high loadings of mercaptopropyl groups per gram of MCM-41 can be attained using a methodology based on the synthesis of self-assembled monolayers (SAMs).[8,60] However, because of the fact that this methodology is based on the introduction of organosilane groups on the surface of preformed ordered silica, the attainable organic group loadings per silicon content are moderate despite very high surface coverage of groups. One

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(57) Farrusseng, D.; Schlichte, K.; Spliethoff, B.; Winger, A.; Kaskel, S.; Bradley, J. S.; Schuth, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4204−4207.
(58) Lastoskie, C.; Gubbins, K. E.; Quirke, N. *Langmuir* **1993**, *9*, 2693−2702.
(59) Kruk, M.; Jaroniec, M.; Gadkaree, K. P. *Langmuir* **1999**, *15*, 1442−1448.
(60) Liu, J.; Shin, Y.; Nie, Z.; Chang, J. H.; Wang, L.-Q.; Fryxell, G. E.; Samuels, W. D.; Exarhos, G. J. *J. Phys. Chem. A* **2000**, *104*, 8328−8339.

can estimate that in the case of mercaptopropyl-[8] and aminopropyl-modified[60] materials, only about 25 and 30%, respectively, of silicon atoms in the structure of the functionalized material carry organic groups. It was later demonstrated that the methodology based on the introduction of SAMs may lead to the formation of a nonuniform, monolayer−multilayer structure of bonded ligands for the high surface coverages.[60] Recently, even higher surface coverages of organic groups were successfully obtained using this methodology in supercritical fluid media,[15] but still it appears that only about 37% of silicon atoms in the functionalized material carry organic ligands. Other methods of postsynthesis modification of ordered silica supports with organosilanes, that is, those that do not involve the formation of self-assembled monolayers, usually provide much lower degrees of functionalization. This is because, in these cases, each organosilane needs to be bonded directly to the surface of the support, whereas in the case of SAMs, some organic groups may be bonded to other organic groups in the monolayer rather than to the surface. Nonetheless, one study reported results suggesting that up to about 23−32% of silicon atoms in the functionalized material may carry organic groups.[17] In comparison to the methods based on functionalization of a preformed silica support, methods based on co-condensation of silica and organosilica precursors in the presence of a structure-directing agent are more efficient in the synthesis of ordered materials with silica frameworks and high loadings of organic groups. Mann and co-workers suggested that 40% is likely to be the upper limit of organic group functionalization,[20] because the presence of a sufficient content of $Q^4$ silicon atoms is necessary for structural stability of silica-based frameworks. However, a success in producing ordered silicas and BPMOs with 50−60% of silicon atoms that carry organic groups has recently been reported,[28,30] as discussed in the Introduction. These highly organic-functionalized materials were reported to exhibit high degrees of framework cross-linking and very low contents of silanols, so their successful formation can be considered as a minor violation of the predictions of Mann et al.[20]

Herein, we provide strong evidence that silica frameworks with up to 62% of silicon atoms carrying pendant vinyl groups can be synthesized in such a way that the resultant materials exhibit at least one XRD peak and no evidence of phase separation. Moreover, even several percent higher loadings of vinyl groups can be introduced without complete loss of ordering. Thus, monophasic, ordered silicas with more than three organic groups per five silicon atoms in the framework can be synthesized. In the case of cationic templates under basic conditions used herein, deprotonated silanols are necessary to balance the charge of surfactant templates. Therefore, the presence of silanols appears to be mandatory for the templating effect to take place. This was indeed the case, as the content of silanols was quite high (0.39 per one silicon atom) for a sample with the actual 52% organic functionalization level (VIN50E), and still moderate (0.29 per one silicon atom) for a material with the actual 62% functionalization level (VIN65E). So, the ordered vinyl-functionalized silicas reported herein are unprecedented not only because of very high contents of pendant organics, but also because of very low degrees of framework cross-linking. Thus, their successful formation constitutes a strong violation of the predictions by Mann et al.[20] In fact, each silicon atom in the samples with 52% and 62% vinyl group loadings was connected via oxygen bridges with only 3.09−3.10 other silicon atoms, which is an exceptionally low level of cross-linking for an entirely ordered porous structure from which the template was removed. This provides us with new perspectives on conditions required for the formation of three-dimensional ordered mesoporous frameworks. It is now clear that even relatively low degrees of framework cross-linking can render a stable structure. So, the lack of success in many previous attempts for the synthesis of silicas with high loading of pendant groups via co-condensation may be related with the synthesis conditions used and not with the impossibility to achieve structural stability. It is notable that the success of the incorporation of high loadings of organic groups seems to be highly dependent on the organic groups themselves. In our work, much higher loadings of vinyl groups than methyl groups were attained without the occurrence of apparent phase separation. This suggests that the interactions between the pendant groups and the surfactant template may be very important in the formation of highly functionalized ordered materials, similar to what was concluded elsewhere[61] for materials with low organic group loadings. It should be noted that PMOs can readily be synthesized with 100% of the silicon atoms bonded to organic groups. However, these organic groups are bridging groups and they provide connectivity between silicon atoms in the framework, in addition to the connectivity provided by Si−O−Si linkages. Because of this, PMOs can readily attain high degrees of framework cross-linking, despite their high organic group loadings.

**Synthesis of Ordered Microporous and Mesoporous Silicas.** Because of the presence of spatially separated inorganic and organic moieties in the structure of vinyl-functionalized silicas with pendant groups, these materials can also be useful for the synthesis of nanostructures without organic functionality. This idea is demonstrated here by the successful transformation of these materials into ordered silicas with very small XRD interplanar spacings and pore diameters. The synthesis of ordered small-pore silicas has been an active area of research during the past decade.[35−45] As was discussed elsewhere,[42] there are two main strategies for the synthesis of ordered supramolecular-templated small-pore silicas. One of them is based on the use of short-chain surfactants,[36,40−42] which often need to be purposefully synthesized to achieve a satisfactory structural ordering. In particular, highly ordered small-pore (diameter of 2.4 nm) MCM-41 with three pronounced peaks in the XRD pattern and with a (100) interplanar spacing as low as 2.79 nm was synthesized using a mixture of gemini and bichain octylammonium surfactants, which are not commercially available.[42] A similar synthesis with a mixture of surfactants with heptyl chains afforded a disordered silica with a (100) interplanar spacing of 2.57 nm and a pore diameter of about 2.2 nm.[42] The use of bichain dihexyldimethylammonium surfactant afforded a silica with an even smaller pore diameter of about 2.0 nm, but with a weak XRD peak, whose position corresponds to a surprisingly large interplanar spacing of about 3.0 nm.[42] Highly ordered SBA-1 silica with small unit-cell dimensions was synthesized using dodecyltriethylammonium surfactant.[40] In addition, silica with a sharp XRD peak corresponding to a (100) interplanar spacing of 2.5 nm was successfully synthesized using

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(61) Mercier, L.; Pinnavaia, T. J. *Chem. Mater.* **2000**, *12*, 188−196.

hexylamine as a template,[36] but the material had a very high external surface area and appeared to partially transform upon calcination to some other phase of higher interplanar spacing, as inferred from adsorption and XRD data reported.

The second strategy that proved to be quite successful in producing ordered small-pore silicas is based on the phenomenon of an extensive structural shrinkage upon surfactant removal via calcination in certain surfactant-templated silicas and organosilicas.[37,39] This allowed one to produce silicas with XRD peaks corresponding to very small interplanar spacings[35,53,55] (even below 2 nm),[55] but neither gas adsorption nor other structural parameters were reported for most of these materials, which makes the assessment of the practical usefulness difficult. One of the few calcined samples with very low unit-cell sizes that was described in more detail was obtained via co-condensation of tetramethyl orthosilicate and TEVS (molar ratio of 75:25).[53] Its (100) interplanar spacing was 2.6 nm, and the XRD pattern featured more than one peak, but the pore volume reported was 0.2 $cm^3\ g^{-1}$ (and primary pore volume of about 0.15 $cm^3\ g^{-1}$ can be estimated), which is very low, and the authors noted that they were working on the improvement of this property. It is notable that this very low interplanar spacing was attained using cetyltrimethylammonium surfactant that normally templates materials with much larger unit-cell dimensions, which is mainly because of extremely high shrinkage upon calcination ((100) interplanar spacing decreased by 24%). However, such a prominent shrinkage usually results in the low pore volume and moderate specific surface area of thus obtained samples. The recent successful synthesis of ordered silicas with 2-D hexagonal structure and (100) interplanar spacing as low as 2.35 nm using decyltrimethylammonium surfactant[39] belongs to this shrinkage-driven small-unit-cell formation category. In the case of the latter synthesis approach, it is expected that one can adjust the pore diameter by using surfactants of different chain length to tailor unit-cell sizes of as-synthesized precursors[53] and by adjusting the calcination temperature to vary the extent of shrinkage.[55] Most of the reported data revealed only the interplanar spacing variation, and little insight can be gained into the actual pore tailoring capabilities. The shrinkage and thus the formation of small pores appear to be also facilitated by introduction of an aluminum source to the synthesis mixture.[37] This may be a major factor responsible for the formation of aluminosilicates with tailorable, small-pore dimensions.[37,38] However, the (100) interplanar spacing for these samples was not lower than 2.8 nm, which is much higher than that attainable using other methods discussed above, thus suggesting that the latter are more suitable to produce silicas with smaller pore dimensions. It is also worth mentioning that it is difficult to compare pore diameters reported in the literature for small-pore materials because these estimates are usually derived from calculations based on gas adsorption data, in which case various calculation methods are highly inconsistent and can produce differences up to about 1.0 nm.[52] In fact, most of the researchers adopt calculation procedures that were recently found to underestimate pore diameters by up to 1.0 nm,[52] which explains why many MCM-41 and related silicas were reported to exhibit pore dimensions in the micropore region despite their relatively large unit-cell dimensions. Because of the fact that structural parameters are interrelated in ordered structures,[50] the aforementioned combination is highly unlikely for any silica with reasonably large pore volume, unless the pore wall of such a material is microporous.

Herein, we propose a novel approach for the synthesis of ordered small-pore silicas with tailorable pore dimensions, which is based on the use of organic-functionalized silicas as precursor materials whose unit-cell dimensions can readily be tailored by adjusting the organic-group loading. The selection of precursor materials with sufficiently low unit-cell sizes, in addition to the fact that they undergo some shrinkage upon calcination, allowed us to generate silicas with (100) interplanar spacings that systematically decrease from 3.04 to 2.15 nm using a single structure-directing agent (cetyltrimethylammonium bromide), which is the most commonly used alkylammonium surfactant in the synthesis of supramolecular-templated silicas. Our method can be readily used to routinely synthesize silicas with the (100) interplanar spacing as low as 2.28 nm and a remarkably narrow XRD peak, unlike the XRD peaks reported for most of the other supramolecular-templated silicas with similar or even higher unit-cell dimensions.[37−39] Alternative approaches for unit-cell size tailoring usually require the use of a series of surfactants of gradually decreasing tail length,[42,53] some of which are not even commercially available.[40−42] In other cases, the calcination temperature needs to be varied[55] which is likely to result in silicas with a variable degree of surface dehydroxylation. On the basis of an earlier study,[53] it is expected that the pore diameter range attainable using the approach proposed herein can be further expanded by using surfactants of different chain length. The use of some other surfactants may also lead to the improvement of structural ordering of small-pore silicas.

The approach proposed herein is suitable to provide silicas that exhibit XRD interplanar spacings in the range recently reported for syntheses based on dendrimer templating,[43] collective templating by small rigid molecules,[44] or co-condensation of organosilica and silica precursors under appropriate conditions without template.[45] However, these approaches so far produced silicas that exhibit a single very broad XRD peak, in contrast to a remarkably narrow XRD reflection observed for most of the silicas synthesized using our novel approach.

## Conclusions

The current study demonstrated that ordered silica frameworks are capable of supporting remarkably high loadings of pendant organic groups. In fact, more than three out of five silicon atoms in such ordered frameworks can bear organic functionality, despite the additional requirement of the presence of appreciable amount of silanols to maintain organosilicate−ionic surfactant interactions required for the supramolecular assembly to take place. This leads to a surprisingly low degree of framework cross-linking, as each silicon atom in such a structure forms on average only about 3.1 bonds within the framework, while the remaining are dangling bonds. The tendency to form monophasic ordered silicas with high loadings of pendant groups during surfactant-templated co-condensation of organosilica and silica precursors depends on the nature of the organic groups. Because of the fact that an increase in the loading of pendant organic groups leads to an appreciable reduction of unit-cell dimensions for the same structure-directing surfactant used, vinyl-functionalized silicas have proven in this study to be excellent starting materials for the synthesis of ordered small-pore silicas, including those with (100) interplanar spacings as low as about 2.15 nm. These unit-cell sizes are difficult to achieve otherwise, even when purposefully synthesized structure-directing agents are used.

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**Supporting Information Available:** Graphs with XRD patterns, weight change curves, and nitrogen adsorption data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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