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Chemical removal of organic polymers from highly porous sol-gel-derived silica monoliths

Chia-Min Yang,†[a] Jan-Henrik Smått,[b] Bodo Zibrowius[a] and Mika Lindén*[ab]

[a] *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany.*

[b] *Department of Physical Chemistry, Åbo Akademi University, Porthansgatan 3-5, FI-20500 Turku, Finland. E-mail: mlinden@abo.fi; Fax: +358-2-215 4706; Tel: +358-2-215 2355.*

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A new method for the removal of the organic polymer poly(ethylene glycol) (PEG) from silica monoliths exhibiting a hierarchical, bimodal porosity is described. The method is based on post-synthesis treatment with sulfuric acid and does not necessarily require calcination of the monoliths. This procedure preserves the mechanical integrity of the highly porous monoliths. Furthermore, it can be applied to remove PEG from one-pot-synthesized monoliths bearing organic functional groups that would not withstand high-temperature treatments but could survive in acidic conditions. The sulfuric acid treatment also results in less shrinkage than does calcination, which is related to an increase in the degree of silica condensation during the treatment. This could allow the removal of organic polymers to be carried out in the final monolith carrier, and hence reduce the number of steps needed for the fabrication of silica monoliths as HPLC columns, catalyst supports, *etc*. Furthermore, silica monoliths treated with sulfuric acid have larger amounts of surface silanol groups than calcined monoliths. They also show a higher degree of surface functionalization with functional silanes than calcined samples under the same reaction conditions.

Introduction

Hierarchical materials have attracted a lot of interest during recent years due to the possibility of optimizing several material properties in parallel. In order for a material to be hierarchical, one or several material properties have to be arranged in a "structure-within-structure" fashion. Silica monoliths are good examples of synthetic hierarchical materials exhibiting fully interconnected porosity on both the nanometer and the micrometer scale. An elegant and flexible means for the preparation of such types of materials has been described in a series of papers by Nakanishi *et al*.[1,2] Here, the kinetics of phase separation and gelation are matched so that gelation occurs on a similar time-scale as spinoidal decomposition. Thus, the pore dimensions of the resulting macropores can be adjusted by chemical tuning of the kinetics of the two processes and by applying different post-synthesis treatment conditions.[1–3] A hydrophilic polymer, typically poly(ethylene oxide), PEG, is used in order to induce phase separation. In addition to the macropores, the thus-prepared monoliths also exhibit textural porosity originating from the voids between the primary silica particles forming the silica gel phase. We have shown recently[4] that mixtures of surfactants and polymers can be used to extend the structural flexibility of the synthesis. Monoliths exhibiting three types of pores, macropores, textural mesopores, and supramolecularly templated mesopores, can be prepared and the pore dimensions of all three pore types can be controlled by fine-tuning the surfactant-to-polymer ratio in the synthesis.[4] Furthermore, the successful preparation of macroporous-mesoporous silica monoliths exhibiting an ordered mesopore structure has also been described recently.[5,6] The mesoporosity gives the above mentioned materials a high surface area, while the presence of macropores ensures a low pressure drop over the monolithic silica. The hierarchical nature of the porosity therefore makes these monoliths highly interesting for applications such as column material for chromatography and as catalyst supports. Furthermore, they can be readily used as molds for the synthesis of other hierarchical monolithic materials, such as nanocast carbon monoliths.[7–10]

However, the as-synthesized monoliths are fairly brittle and post-synthesis treatment in ammonia solutions is normally used in order to increase the degree of silica condensation. A dissolution-reprecipitation mechanism leads to a net material transport to the necks between the particles in the gel due to Ostwald ripening. The treatment increases the mechanical stability of the silica monoliths and modifies the mesopore size of the monoliths. The organic additives in the monolith are generally removed by calcination, which increases the degree of silicate condensation further. Although calcination is a widely used means to remove the organic portion from inorganic-organic hybrid materials, such a treatment at high temperatures has some limitations. Firstly, it inevitably leads to a contraction of the inorganic matrix, which requires all parameters of the process to be fully controlled in order to ensure a high reproducibility as regards the macroscopic volume of the final inorganic porous material. High-temperature treatment also decomposes additional organic functional groups introduced during the synthesis. Furthermore, it leads to a decrease in the number of surface silanol groups, which may be a drawback for post-synthesis surface functionalization of the monoliths by reaction with functional silanes, a necessary step for applying the monoliths as columns for reverse phase chromatography. Therefore, there are clear incentives for the development of a low-temperature reaction to remove organic polymers from the silica monoliths.

† Present address: Department of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan.

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In this paper, we present results related to successful template removal, either from as-synthesized monoliths or from monoliths treated in ammonia, by treatment in sulfuric acid solution. The treatment is similar to that for the removal of supramolecular triblock copolymer template in siliceous or functionalized mesoporous silicas.[11–14] However, in the present case, the PEG is dispersed within the gelling silica during the monolith synthesis and is thus not as easily accessible. Despite this, the treatment with H_2SO_4 is found to effectively remove the remaining PEG organic polymer and to facilitate the condensation of the silica matrix, resulting in mechanically stable silica monoliths with a lower degree of shrinkage. Thus, H_2SO_4 treatment is shown to be an efficient means for the removal of organics for a wide range of sol-gel derived materials. In addition, the H_2SO_4-treated silica monoliths are found to have larger amounts of surface silanol groups, which allows a higher degree of post-synthesis surface functionalization as compared to the calcined monoliths.

Experimental

The porous silica monoliths were prepared according to a synthesis procedure described by Nakanishi *et al.*[1] PEG ($M_w \approx$ 35,000 g mol^{-1}) was initially dissolved in HNO_3 aqueous solution. After complete dissolution, tetraethoxysilane (TEOS) was added at room temperature and the mixture was subsequently stirred until a clear, homogeneous solution was obtained. The molar ratio of the starting composition was $1.00 : 0.25 : 14.69 : 8.23 \times 10^{-4}$ TEOS : HNO_3 : H_2O : PEG. The sol was cast into molds of the desired shapes and was allowed to gel and age at 40 °C for a total of 56 h. Monoliths with a cylindrical shape (10 mm in length and 5 mm in diameter) were used for the studies of the effects of further treatments.

Some of the monoliths were first treated with a 1.0 M NH_4OH aqueous solution at 90 °C for 6 h.[15] For the removal of the remaining PEG, monoliths were either calcined at 550 °C with a temperature ramp of 1 K min^{-1}, or were exposed to a 48 wt % H_2SO_4 solution at 95 °C for 24 h. Some other as-synthesized monoliths were either directly calcined at 550 °C, or exposed to H_2SO_4 solutions (60 wt % H_2SO_4 or 48 wt % H_2SO_4/10 wt % H_2O_2) at 95 °C for 24 h. After treatment with H_2SO_4 or H_2SO_4/H_2O_2, the monoliths were washed with diluted NH_4OH solution, followed by washing with water and acetone and then dried at 80 °C. Table 1 summarizes all the silica monoliths, with or without various post-synthesis treatments, used in this study.

Additional batches of silica monoliths firstly treated with NH_4OH, followed by either 48 wt % H_2SO_4 (denoted as sample C′) or calcination (denoted as sample D′), were prepared for surface functionalization. Two functional silanes with different chain lengths, trimethylchlorosilane (TMCS) and octadecyldimethylchlorosilane (ODMCS), were used for comparison. Prior to surface functionalization, both monoliths were dried in vacuum at 250 °C for 12 h. They were then immersed in a toluene solution of the functional silane. The resulting functionalized silica monoliths are referred to as X–Y, where X indicates the sample (C′ or D′) and Y indicates the surface functional group, TM or ODM.

Table 1 Description of the samples discussed in this article

Sample	Description of the monolith
A	As-prepared
B	Treated with NH_4OH
C	Treated with NH_4OH and subsequently with 48 wt % H_2SO_4
D	Calcined after NH_4OH treatment
E	Calcined without NH_4OH treatment
F	Treated with 60 wt % H_2SO_4
G	Treated with 48 wt % H_2SO_4/10 wt % H_2O_2

The physicochemical properties of porous silica monoliths were characterized by various techniques. The thermal analyses were carried out on a TG/DTA instrument (Netzsch STA 449 C) in air with a heating rate of 10 K min^{-1}. Nitrogen sorption isotherms at 77 K were measured on a Micromeritics ASAP 2010 instrument. Each sample was evacuated at 250 °C for 10 h. The BET surface areas were calculated from the adsorption branches in the relative pressure range of 0.05–0.20, and the total pore volumes were evaluated at a relative pressure of 0.98. The pore diameters and the pore size distributions were calculated from the desorption branch using the Barrett–Joyner–Halenda (BJH) method. Mercury porosimetry measurements were performed on a Micromeritics AutoPore III mercury porosimeter, and a contact angle of 130° was assumed in the pore size calculations. The ^{29}Si MAS NMR spectra were measured on a Bruker Avance 500WB spectrometer using a 4 mm MAS probe at a spinning rate of 10 kHz. The experimental conditions were 30 s recycle delay, 2400 scans, and 2.2 μs π/4 pulse. The FT-IR spectra were measured on a Nicolet Magna 750 spectrometer. Each sample was ground and directly mixed with KBr for the measurements. The scanning electron microscope (SEM) images were obtained with a Hitachi S-3500N electron microscope.

Results and discussion

Control of the macroscopic shrinkage of porous silica monoliths is very important with regard to overall synthesis reproducibility, and for a successful fixation of the monoliths in supports. Therefore, the effects of different post-synthesis treatments and the removal of organic polymer on the macroscopic appearance of the monoliths are first discussed. The shrinkage of the cylindrical monoliths after various treatments was evaluated by the normalized diameters of the treated monoliths with respect to the as-prepared monolith at the wet stage. The results are summarized in Fig. 1. After NH_4OH treatment (sample B), the diameter of the monolith decreased by 3.6%. If the NH_4OH-treated monolith was subsequently calcined (sample D), the total decrease in the monolith diameter reached 5.7%. However, if the monolith was treated in 48 wt % H_2SO_4 after the NH_4OH treatment instead of being calcined, no further shrinkage of the monoliths was observed (sample C). Post-synthesis treatment of the as-synthesized monoliths in 60 wt % H_2SO_4 (sample F) or in 48 wt % H_2SO_4/10 wt % H_2O_2 (sample G) without any pre-treatment in NH_4OH solution reduced the diameter by 6.2%. The importance of chemical post-synthesis treatment to enhance the mechanical integrity of the monoliths is highlighted by the

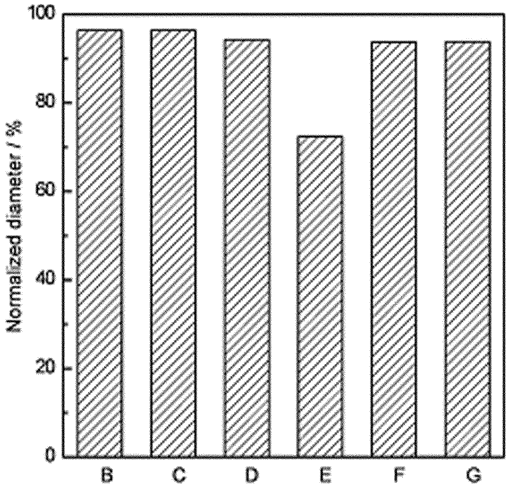

Fig. 1 Comparison of the normalized diameters of selected silica monoliths.

observed decrease of 27.6% in the diameter of the as-synthesized monolith calcined directly after drying (sample E). Thus, in order to achieve minimum shrinkage of the monolith, a combination of NH_4OH and H_2SO_4 treatments appears to be a very straightforward and efficient procedure. Although not quantifying the degree of shrinkage as judged from the macroscopic dimensions of the monoliths, Nakanishi *et al.*[3] also concluded that the as-synthesized monoliths exhibit the largest degree of shrinkage, while direct post-synthesis treatment in either 1 M HNO_3 or 1 M NH_3 leads to an enhanced mechanical stability of the silica gel network, and that the acid treatment results in a gel structure that is closer to that of the original silica network before post-synthesis treatment.

Thermogravimetrical analyses (TG/DTA) were carried out to quantify the amount of PEG present in the silica monoliths at different stages of the process, and the results of selected samples are shown in Fig. 2. The as-prepared monolith (sample A) showed a weight loss of *ca.* 29% in the temperature range between 150 and 350 °C, due to the exothermic decomposition of PEG around 210 °C. For monoliths subjected to NH_4OH treatment (sample B), the weight loss attributed to the remaining PEG in the same temperature range decreased to about 7%. This finding suggests that about 81% of the PEG originally present in the monolith was dissolved and removed from the monolith during the NH_4OH treatment. Further treatment of the ammonia-treated monolith in 48 wt % H_2SO_4 effectively removed the remaining PEG, as the resulting silica monolith (sample C) showed no exothermic peak at 210 °C in the thermal analysis. A weight loss of 2% in the same temperature range may be attributed to desorption of physisorbed water from the monolith. Alternatively, the PEG in the as-synthesized silica monolith can be decomposed and removed by treatment with 48 wt % H_2SO_4/10 wt % H_2O_2 solution, as indicated by the absence of the exothermic peak at 210 °C in the TG/DTA curve. The treatment with 60 wt % H_2SO_4 can also completely remove all the PEG in the as-synthesized monolith (sample F, data not shown). For samples C, F and G, which were subjected to H_2SO_4 treatment without further calcination, the total weight loss in the temperature range of 150 to 600 °C was similar (*ca.* 6%). On the other hand, calcined monoliths (samples D and E, data not shown) showed less weight loss (*ca.* 3%) in the same temperature range. The weight loss in this temperature range may be due to the further condensation of silanol groups in the monolith. Therefore, the results suggest that the PEG-free monoliths may have more silanol groups after treatment with H_2SO_4 or H_2SO_4/H_2O_2 than the calcined monoliths, a finding that is important for further surface functionalization of the silica monoliths with functional silanes.

The degree of silicate condensation of the different monoliths was studied by ^{29}Si MAS NMR spectroscopy. The spectra of selected samples are shown in Fig. 3, and the relative amounts of Q^n species $[Si(OSi)_n(OH)_{4-n}$, $n = 2, 3, 4]$ are summarized in Table 2. The spectrum of the as-prepared silica monolith shows a Q^3 line that is more intense than the Q^4 line, indicating that the as-synthesized monoliths have a fairly low degree of condensation, which is the reason for their mechanical instability and pronounced shrinkage if dried without any post-synthesis treatment. After NH_4OH treatment, the degree of condensation of silica in the monolith is much enhanced, as suggested by the pronounced increase of the Q^4 line and the corresponding reductions of the Q^2 and Q^3 lines in the spectra. As discussed in the introduction section, the silica particles in the as-synthesized silica monolith undergo Ostwald ripening during the ammonia treatment. The dissolution and re-precipitation of the silicate involves material transport from the highly convex surfaces of small silica particles to the concave surfaces forming the necks that bind the particles together in the gel, resulting in an enhanced mechanical stability of the monoliths.[3] Further treatment with H_2SO_4 has a very limited effect on the composition of the silica in the monolith. The effect of H_2SO_4 treatment on the silica was not expected to be as pronounced as in the case of mesoporous silica SBA-15,[11]

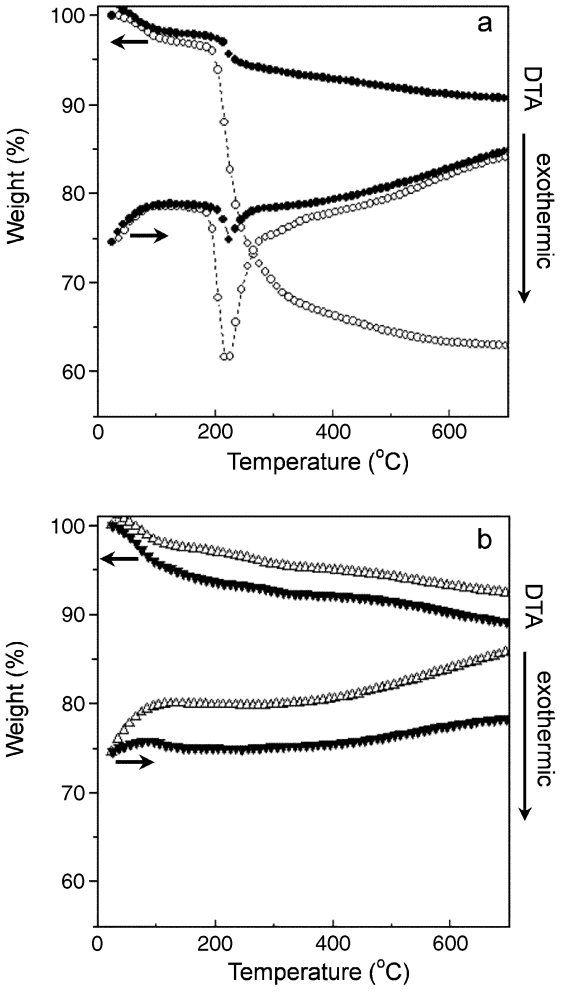

Fig. 2 TG/DTA analysis of monoliths A (○), B (●), C (Δ) and G (▼).

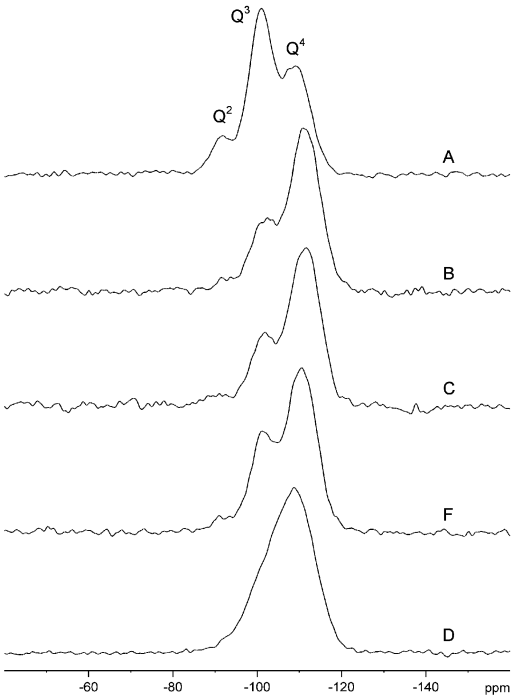

Fig. 3 ^{29}Si MAS NMR spectra of selected silica monoliths.

Table 2 Relative intensities (%) of the ^{29}Si NMR lines assigned in Fig. 3[a]

Sample	Q^2	Q^3	Q^4
A	11	48	41
B	5	24	71
C	5	25	70
F	5	30	65
D	5	33	63

[a] The linewidths used for the deconvolution of the Q^2, Q^3 and Q^4 lines were 600, 650 and 810 Hz, respectively, except for sample D where 880, 890 and 930 Hz, respectively, were used.

since the surface-to-volume ratio of macroporous silica monoliths is much smaller than that of SBA-15, which is highlighted by the differences in the corresponding surface areas, about 300 $m^2\ g^{-1}$ for the silica monoliths *versus* $>600\ m^2\ g^{-1}$ for triblock copolymer templated mesoporous silica. Finally, if the silica monolith was directly treated with 60 wt % H_2SO_4 without NH_4OH treatment, the resulting monoliths also showed a clear increase in the degree of condensation as compared to the as-synthesized monolith, but less than that of monoliths first treated with ammonia. The higher condensation degree of the initially ammonia treated monoliths can be explained by the formation of larger particles with a higher degree of internal condensation as a consequence of the Ostwald ripening processes. For the calcined monolith, for example sample D, the spectrum exhibits a broad asymmetric line mainly due to Q^3 and Q^4 species. It should be emphasized that even though the relative intensity of the Q^3 line for the calcined sample D is higher than for samples B and C, this does not mean that there are more surface silanol groups in the monolith. Furthermore, the deconvolution of this spectrum is less reliable because of the ill-defined line shape. The amounts of accessible surface silanol groups in the calcined and H_2SO_4 treated monoliths were compared by surface functionalization with different functional silanes as discussed below.

Mercury porosimetry and nitrogen sorption measurements were applied to study the pore structure of selected organic-free silica monoliths and the derived textural characteristics are summarized in Table 3. Fig. 4 shows results of the mercury porosimetry measurements and the corresponding pore size distributions. The monoliths firstly treated with NH_4OH followed either by calcination (sample D) or by treatment with 48 wt % H_2SO_4 (sample C) exhibit bimodal pore structures with pore diameters of 1.0 μm and around 10 nm and narrow pore size distributions. In other words, the low-temperature treatment of H_2SO_4 can be used to replace the calcination process to generate the same pore structure. On the other hand, the mercury intrusion/extrusion plot of the monolith directly treated with 48 wt % H_2SO_4/10 wt % H_2O_2 (sample G) suggests only the existence of uniform macropores with diameters of *ca.* 0.75 μm, together with a not-so-well-defined textural porosity. The smaller values of the macropore diameter and macropore volume measured for this monolith are consistent with its diminished macroscopic size, which may be

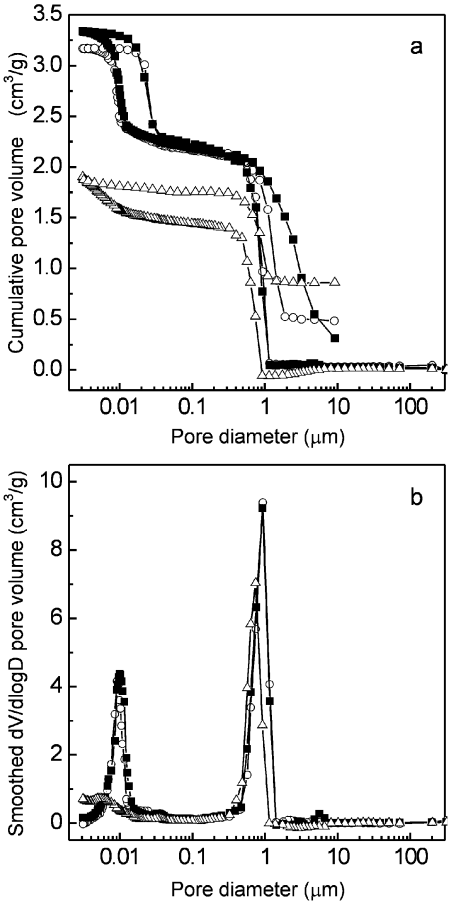

Fig. 4 Mercury porosimetry results of silica monoliths C (○), D (■) and G (Δ). (a) Cumulative mercury intrusion and extrusion plots and (b) dV/dlog$D$ pore size distributions.

related to a more pronounced shrinkage of the monolith not subjected to NH_4OH treatment. Furthermore, a hump in the small diameter region implies the presence of smaller mesopores that are below the limit of detection for mercury porosimetry.

The mesopores in these silica monoliths were investigated by nitrogen sorption measurements. The sorption isotherms and the BJH pore size distributions derived from desorption branches are shown in Fig. 5. The isotherms of monoliths firstly treated with NH_4OH are very similar, and their derived mesopore diameters are nearly the same with a pore size distribution centered around 16 nm. This again supports the conclusion that H_2SO_4 treatment can be used as an alternative to thermal removal of the organic species from monoliths without changing the textural properties of the materials. For monoliths not subjected to NH_4OH treatment (sample G), on the other hand, the mesopore diameter is clearly smaller with a narrow pore diameter distribution centered around 7 nm, in agreement with previous studies where post-treatment in nitric acid solutions was applied.[3] The clearly smaller value of the

Table 3 Physicochemical properties of selected silica monoliths

	Hg porosimetry				N_2 sorption measurements			
Sample	d_{macro}/μm	d_{meso}/nm	V_{macro}/$cm^3\ g^{-1}$	V_{meso}/$cm^3\ g^{-1}$	d_{meso}/nm	V_{micro}[a]/$cm^3\ g^{-1}$	A_{BET}/$m^2\ g^{-1}$	A_{micro}[b]/$m^2\ g^{-1}$
C	0.93	9.31	2.20	0.97	16.1	0.14	226	44
D	0.93	10.1	2.22	1.12	16.1	0.15	249	48
E	0.50	NA[c]	0.70	NA[c]	NA[c]	0.23	485	354
G	0.72	5.4	1.46	0.44	7.3	0.37	503	49

[a] The values are estimated at the relative pressure of 0.6. Therefore, some contribution from smaller mesopores is possible. [b] Micropore surface areas calculated from *t*-plots. [c] Not available.

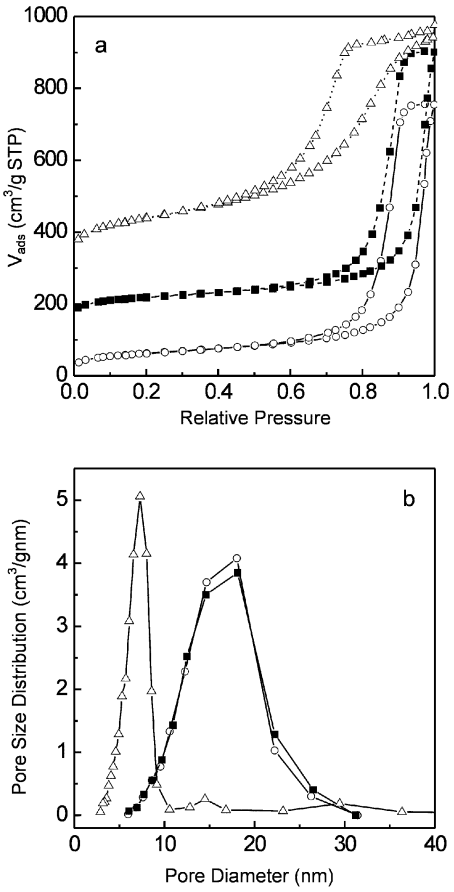

Fig. 5 (a) Nitrogen sorption isotherms and (b) derived pore size distributions of silica monoliths C (○), D (■) and G (Δ). The isotherm for sample D is offset by 150 cm^3 g^{-1} and that of sample G by 300 cm^3 g^{-1}.

mesopore diameter measured for the monolith directly treated with H_2SO_4/H_2O_2 cannot be rationalized solely based on the difference in the degree of shrinkage of the monolith upon the removal of PEG (see Fig. 1). Therefore, the main reason for this observation may be ascribed to a lower degree of Ostwald ripening due to lower silica solubility in H_2SO_4 or H_2SO_4/H_2O_2 than in NH_4OH solution. This conclusion is also supported by the fact that the isotherm is very similar to that observed for monoliths post-treated in more dilute NH_4OH solutions, where Ostwald ripening is less extensive due to the lower solubility of silica.[1] The influence of Ostwald ripening can also be seen in the other characteristics of the monoliths. Post-treatment in NH_4OH leads to high macropore and mesopore volumes and to a fairly low BET surface area, typically around 250 cm^3 g^{-1}, as compared to the dried and calcined as-synthesized monoliths. However, substituting the calcination step by treatment with 48 wt % H_2SO_4 for removal of the organics leads to virtually identical textural characteristics for NH_4OH treated monoliths. Direct treatment of the as-synthesized monoliths in H_2SO_4, however, leads to a high degree of microporosity, a large BET surface area and low macropore and mesopore volumes, all of which are normally unwanted material characteristics for applications such as chromatography, for example. These results again suggest that a NH_4OH treatment followed by treatment in H_2SO_4 is the method of choice in order to ensure an efficient removal of the organics without compromising on the textural properties of the monoliths.

The pore structures of the silica monoliths with different treatments were also imaged by SEM. As shown in Fig. 6, the monoliths firstly treated with NH_4OH share the same features of a uniform and interconnected macropore system. Further-

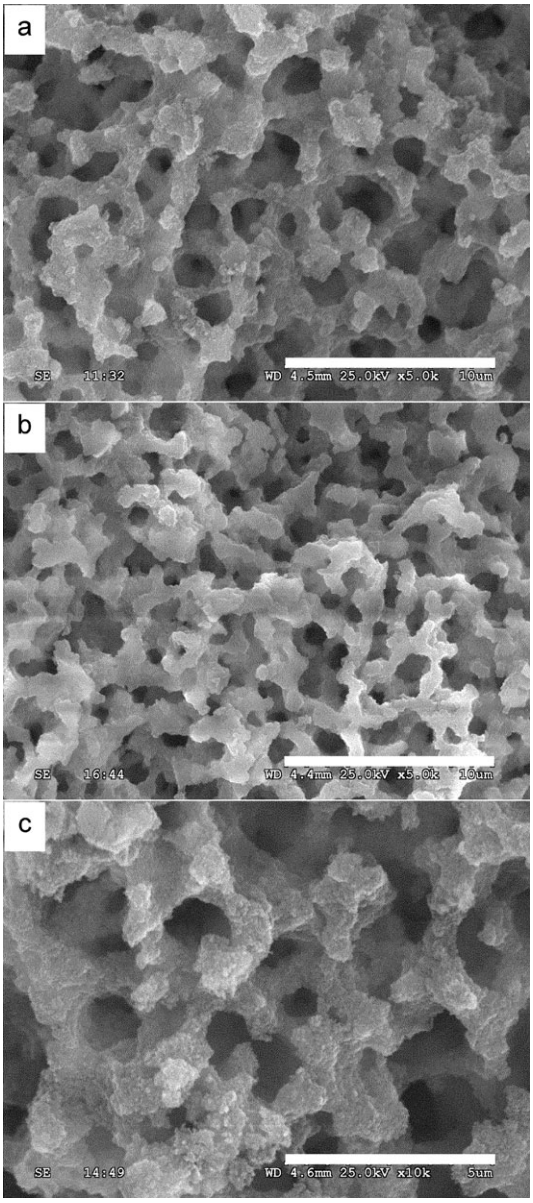

Fig. 6 SEM images of monoliths C (a), F (b) and D (c). The scale bars represent 10 μm in (a) and (b) and 5 μm in (c).

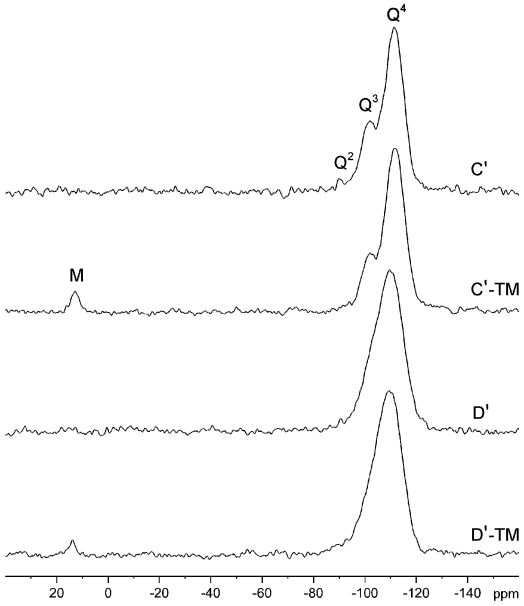

Fig. 7 ^{29}Si MAS NMR spectra of silica monoliths C′ and D′ before and after functionalization with TMCS.

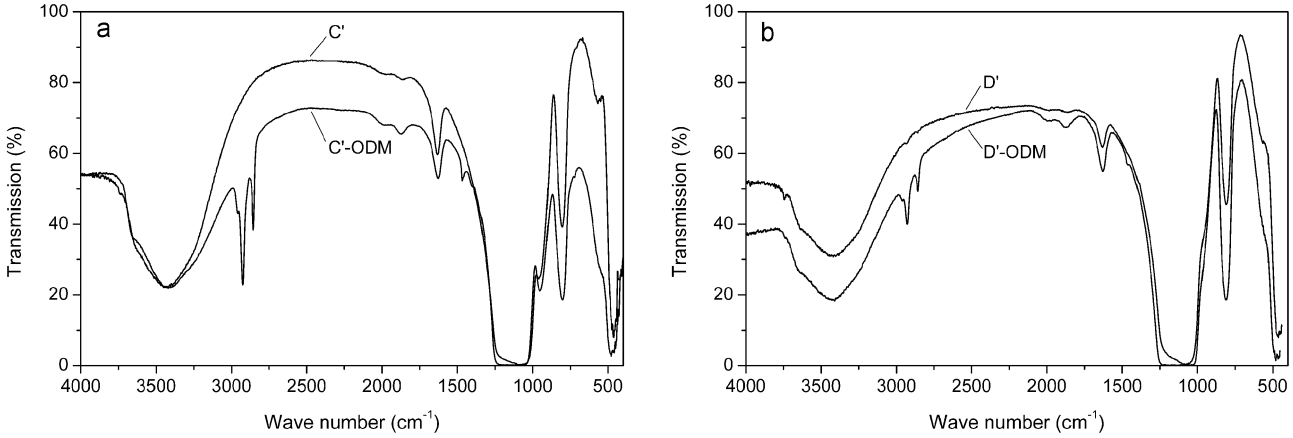

Fig. 8 FT-IR spectra of C′ (a) and D′ (b) before and after functionalization with ODMCS.

more, the thickness of the silica framework is very uniform in diameter. For the monolith directly treated with 60 wt % H_2SO_4, the macropores are also uniform in size, but are obviously smaller than for the NH_4OH-treated monoliths, in good agreement with the mercury porosimetry results.

As mentioned above, the silica monoliths firstly treated with NH_4OH, followed either by calcination or by treatment with 48 wt % H_2SO_4, were used for surface functionalization with TMCS or ODMCS. Fig. 7 shows the ^{29}Si MAS NMR spectra of monoliths C′ and D′ before and after treatment with TMCS. A new line centered at about 13.0 ppm is attributed to the anchored trimethylsilyl (TMS) species (M groups) in the functionalized monolith. The intensities of the M lines amount to about 4% and 2% of those of the Q^n lines for C′-TM and D′-TM, respectively. This indicates a higher degree of functionalization for the acid-treated silica monolith than that of the calcined one. On the other hand, the degree of functionalization with octadecyldimethylsilyl (ODMS) groups was even lower than that with TMS groups. The M species of ODMS groups in the samples C′-ODM and D′-ODM were nearly undetectable by ^{29}Si-NMR spectroscopy. The low degree of functionalization may mainly be due to steric hindrance. However, FT-IR spectra of the monoliths C′-ODM and D′-ODM, as shown in Fig. 8, suggest that C′-ODM has a higher amount of anchored ODMS groups than D′-ODM. The comparison again indicates that the acid-treated silica monolith has a higher amount of surface silanol groups than the calcined monolith, which is beneficial for further surface functionalization. It should be noted that higher loadings reported for surfactant-templated, high-surface area silica[16] can be attributed to the much higher surface-to-volume ratio of this type of materials, and is not necessarily indicative of a higher surface loading of silanes.

Conclusions

A low-temperature treatment to remove the organic polymer PEG from highly porous silica monoliths by an ether cleavage reaction with H_2SO_4 has been demonstrated. This treatment results in less shrinkage of the monoliths and larger amounts of surface silanol groups on the pore surface, as compared to the calcined monoliths. A higher degree of surface functionalization on the acid-treated monolith can be achieved.

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