

Consecutive Generation of Mesopores and Micropores in SBA-15

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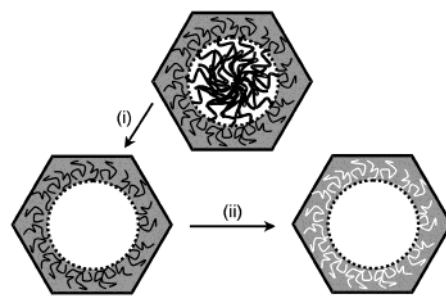
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Expansion of the functionality and improved control over the properties of ordered mesoporous solids^{1,2} are crucial for their application in various fields. Especially interesting in this respect is the dual pore system of SBA-15, which has hexagonally arranged cylindrical mesopores with micropores within the walls.^{3–5} The triblock copolymer template Pluronic P-123 (P-123) is usually removed by calcination,² microwave digestion,⁶ or extraction by solvents³ or supercritical fluids,⁷ generating both pore types simultaneously. However, making both the micropores and mesopores accessible in one step prevents independent modification of the different pores. It is therefore highly desirable for the two pore types to be formed in independent steps, making it possible to functionalize them independently. For instance, the mesopore surface could be made hydrophobic while keeping the micropores hydrophilic. This would provide a pathway for selectively depositing organic or inorganic guest species in either the one or the other pore system. Such a control over the modification would go substantially beyond what has been achieved so far.^{8–11} However, the template removal methods developed so far are not capable of accomplishing this, and a new route is necessary to achieve this goal.

With the method described in the following, the consecutive generation of mesopores and micropores in SBA-15 has been accomplished as a first prerequisite for achieving this goal. The mesopores are first vacated by partial decomposition of the template via ether cleavage by sulfuric acid. The occluded poly(ethylene oxide) chains in the silica matrix, which are less accessible to the acid, can be decomposed subsequently

Scheme 1. Schematic Representation of the Stepwise Generation of Mesopores and Micropores in SBA-15 by Treatment with (i) Concentrated H₂SO₄ at 95 °C and (ii) Subsequent Calcination at 200 °C



by thermal treatment in air to create micropores. In addition, because the entire process is based on reactions at low temperatures, the resulting SBA-15 has larger mesopores and a greater micropore volume, which is also beneficial for certain applications.

SBA-15 was synthesized starting from the preparation of a hydrochloric acid solution of P-123. Tetraethyl orthosilicate (TEOS) was then added and the mixture was stirred at 40 °C for 20 h. The molar composition was 1:5.9:193:0.017 TEOS:HCl:H₂O:P-123. The aging was performed at 65 °C for 1 day, and the solid was filtered, washed, and dried at 90 °C. For cleaving the template to generate the mesopores, 1.0 g of as-synthesized SBA-15 was mixed with 100 mL of 32–60 wt % H₂SO₄ solution and refluxed at 95 °C for 1 day. The product was recovered by washing with water and dried at 90 °C. To generate micropores, the acid-treated sample was heated to 200 °C in air. The whole procedure is illustrated in Scheme 1.

The ether cleavage of the P-123 and the effect of acid treatment on the silica were followed by solid-state NMR spectroscopy (Figure 1). In the ¹³C CP/MAS NMR spectrum of the as-synthesized SBA-15, the line at 16.6 ppm can be assigned to the methyl groups. The lines of the main-chain carbons of the propylene oxide (PO, 75.9 ppm) and ethylene oxide (EO, 70.6 ppm) blocks of P-123 partially overlap. All the lines decrease in intensity after treatment with 32 wt % or 48 wt % H₂SO₄. In addition, the ratios of the intensities of the lines at 75.9 and 16.6 ppm to that at 70.6 ppm are smaller after the treatment, implying that PO units have been decomposed preferentially and removed from the sample. This selectivity becomes even more obvious when a higher concentration of H₂SO₄ is used: the spectrum of the sample treated with 60 wt % H₂SO₄ (Figure 1b) indicates that almost complete removal of the PO blocks from SBA-15 has occurred. Such selective cleavage and removal of the PO units cannot result from the reaction between PO and H₂SO₄ being kinetically favored because EO is cleaved at a rate similar to that of PO in the absence of spatial constraints. According to the templating mechanism of SBA-15, the hydrophilic EO units interact with silica precursors and are occluded in the silica walls.^{3–5} Therefore, we assume that the occluded EO units are hindered from reacting with H₂SO₄.

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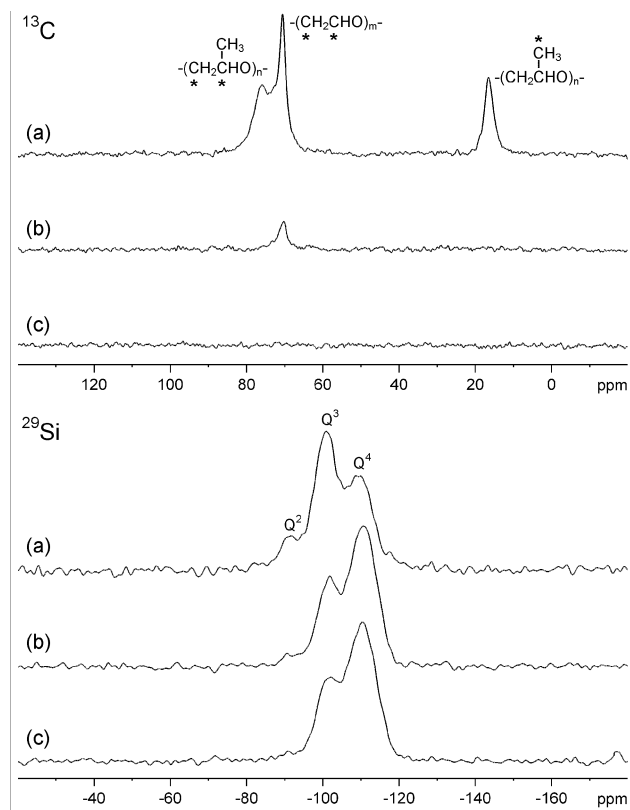


Figure 1. ^{13}C CP/MAS and ^{29}Si MAS NMR spectra of as-synthesized SBA-15 (a) and of the same sample after treatment with 60 wt % H_2SO_4 (b) and subsequent calcination at 200 °C (c).

In addition to the selective removal of the PO blocks from as-synthesized SBA-15, the acid treatment also affects the properties of the silica walls. Comparison of the ^{29}Si MAS NMR spectra of as-synthesized and H_2SO_4 -treated SBA-15 indicates that after the H_2SO_4 treatment the Q^4 line is strongly enhanced and the Q^2 and Q^3 lines are weakened. This suggests that the acid treatment at 95 °C facilitates condensation reaction of the silanol groups of the pore walls, as would be expected under strongly acidic conditions.

The H_2SO_4 -treated SBA-15 was further characterized by sorption measurements. The N_2 sorption isotherm of 48 wt % H_2SO_4 -treated SBA-15 shows a sharp step with a hysteresis loop corresponding to the filling of the ordered channel-type mesopores (Figure 2a). Compared with a calcined SBA-15 sample, the acid-treated SBA-15 has a much larger pore size (7.2 vs 4.7 nm, calculated from the desorption branch by the BJH method). The hexagonal pore structure is confirmed by powder X-ray diffraction (PXRD), which shows intense (100), (110), and (200) reflections. The cell parameter of the acid-treated SBA-15 is 11.5 nm, which is also larger than the value of 9.5 nm obtained for the calcined SBA-15. On the basis of the values of the cell parameters and BJH pore sizes, the thicknesses of the pore wall of the acid-treated and calcined SBA-15 are 4.3 and 4.8 nm, respectively. This is reasonable because almost no shrinkage should take place at 95 °C.

To investigate the microporosity of the samples, Ar sorption measurements at 87.29 K were applied. The low-pressure portion of the isotherms was evaluated by a t -plot with an empirical Harkins–Jura equation

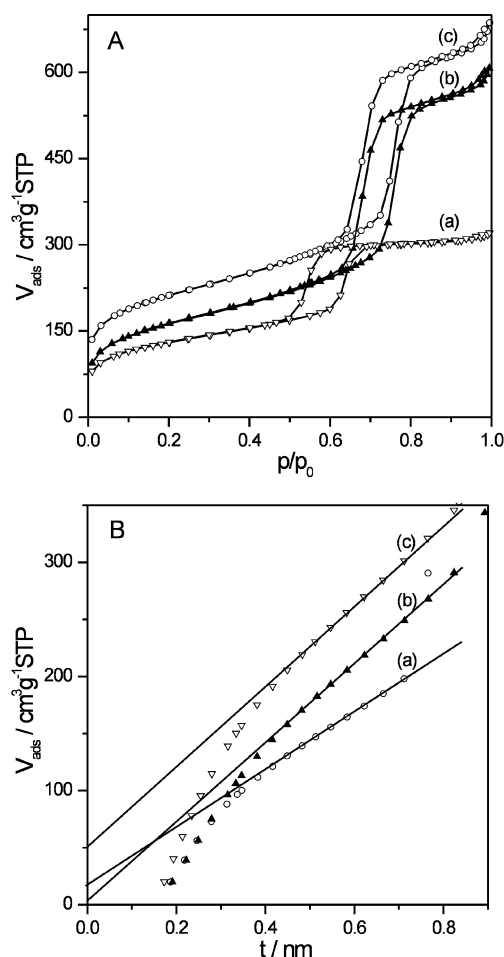


Figure 2. N_2 sorption isotherms (A) and t -plots of Ar sorption at 87.29 K (B) obtained for calcined SBA-15 (a), 48 wt % H_2SO_4 -treated SBA-15 (b), and the same sample after calcination at 200 °C (c).

(Figure 2b). The parameters in the equation were adapted from the fitted data of large-pore MCM-41 materials.¹² For the calcined SBA-15, the t -plot gives a straight line between $t = 0.4$ and $t = 0.75$ nm. The extrapolation line intercepts the y -axis above the origin, indicating the presence of micropores with a volume of $0.021 \text{ cm}^3 \text{ g}^{-1}$. On the other hand, for SBA-15 treated with 48 wt % H_2SO_4 the extrapolation of the t -plot intercepts the y -axis close to the origin, suggesting there is nearly no microporosity in the sample. The slope of the line is greater than that for the calcined SBA-15. The specific surface areas for the calcined and acid-treated SBA-15 calculated from the slopes of the t -plots are 325 and $438 \text{ m}^2 \text{ g}^{-1}$, respectively. Combined with the NMR results, this finding suggests that the remaining EO units in the H_2SO_4 -treated SBA-15 occupy and block the micropores, resulting in SBA-15 with only channel-type mesopores.

The microporosity can be generated by thermal treatment of H_2SO_4 -treated SBA-15. The ^{13}C CP/MAS NMR spectrum shows that the line from the remaining EO units in the acid-treated sample disappears after calcination in air at 200 °C (Figure 1c). That such treatment does not affect the degree of condensation of the silica matrix is indicated by the ^{29}Si MAS NMR spec-

trum. The mesopore size and the pore wall thickness remain the same, as shown by the similarity of the hysteresis loop in the N_2 sorption isotherm and by the peak position in PXRD patterns before and after the thermal treatment being the same. The t -plot of Ar sorption at 87.29 K has the same slope as that for the H_2SO_4 -treated SBA-15, which suggests that the mesopore surface area for the 200 °C-treated sample is similar ($457 \text{ m}^2 \text{ g}^{-1}$). In addition, the plot shows a pronounced increase of microporosity, as indicated by the much larger y -axis intercept. The calculated micropore volume is $0.061 \text{ cm}^3 \text{ g}^{-1}$, about 3 times larger than that for the calcined SBA-15. The reason that the micropore volume is so much larger may again be the

low temperature of the treatment, which avoids the shrinkage of the silica matrix.

In conclusion, we have demonstrated a method for the consecutive generation of mesopores and micropores in SBA-15 through ether cleavage and subsequent thermal treatment at 200 °C. The whole procedure is based on reactions at surprisingly low temperatures. The material thus prepared has larger mesopores and a greater micropore volume. This method may be advantageous for further design of advanced nanomaterials because it allows the sequential modification of mesopores and micropores of SBA-15.

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