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Mesoporous Materials with an Acidic Framework and Basic Pores. A Successful Cohabitation

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Periodic mesoporous organosilicas[1] (PMOs) opened a wide range of possibilities for the chemical design of novel nanomaterials. Indeed, these materials are formed by hydrolysis and polycondensation of bridged silsesquioxanes of the general formula $[(R'O)_3Si]_mR$ ($m \geq 2$) in the presence of a structure-directing agent. The resulting material contains the organic fragments within the framework in which they are covalently linked.

One of the major interests of the location of organic groups in the framework is the possibility to functionalize also the channel pores, which leads to bifunctional materials with distinguishable location of the functional groups.

There are few examples of bifunctional materials in which one functional group is located in the pore and the other in the framework. The first example was reported by Ozin et al. These authors described materials containing both bridging ethylene groups in the framework and terminal vinyl groups into the channel pores.[2] At the same time, Markowitz et al. reported a variety of materials containing functional groups in the channel pores and bridged ethane groups in the framework.[3] Inagaki described the synthesis of mesoporous materials with bridged phenylene groups in the framework and mercaptopropyl groups in the channel pores.[4] Recently, Jaroniec reported mesoporous materials with large heterocyclic bridging groups and mercaptopropyl ligands.[5] Indeed, this concept of bifunctional materials with one functional group in the framework and another in the channel pores is of great interest because it opens the route to an unlimited variety of nanomaterials with a possible coupling of properties.[6] However, that requires one to find the synthetic routes leading to such materials.

Here we report the synthesis of bifunctional mesoporous material containing two antagonist functions, that is, an acidic group in the framework and a basic one in the channel pores. This novel material was synthesized by co-condensation of a ternary mixture of α,ω-bistrimethoxysilyl-4,5-dithiooctane $(MeO)_3Si{-}(CH_2)_3{-}S{-}S{-}(CH_2)_3{-}Si(OMe)_3$ (**S_2**), tetraethyl orthosilicate (TEOS), and 3-*tert*-butyloxycarbonyl (aminopropyl)trimethoxysilane[7] $(MeO)_3Si{-}(CH_2)_3{-}NHBoc$ (**1**), in the presence of P123 as template under low acidic medium. The bifunctional material having an acidic framework and basic pores was obtained by post-treatments of the resulting material, such as reduction of disulfide units followed by their oxidation to SO_3H groups and deprotection of amino groups.

In a typical bifunctional material synthesis procedure, 1.58 g of $EO_{20}PO_{70}EO_{20}$ was dissolved in 0.90 mL of an aqueous HCl solution (pH 1.5); 2.08 g (10 mmol) of TEOS was then added. The mixture was stirred until a clear solution was obtained; 0.29 g (4 mmol) of *n*-butanol and 0.28 g (2 mmol) of decane were added. After 3 h of stirring, 0.38 g (1 mmol) of **S_2** and 0.28 g (1 mmol) of $(MeO)_3Si{-}(CH_2)_3{-}NHBoc$ **1** were added under stirring. The molar composition of the reaction mixture was 1 TEOS:0.1 **S_2**:0.1 **1**:0.027 P123:0.4 *n*-BuOH:0.2 decane:0.67×10^{-3} HCl:1.24 H_2O. The ethanol formed was slowly removed under vacuum. A monolith was obtained after 36 h and kept 24 h at room temperature. After filtration, the surfactant was removed by hot ethanol extraction in a Soxhlet apparatus for 12 h and then washed and dried according to the usual workup to give a white powder termed **$MS_2{-}NHBoc$** in 95% yield (Scheme 1).

The N_2 adsorption−desorption measurements for **$MS_2{-}NHBoc$** showed a type IV isotherm with a clear H_1-type hysteresis loop at relative high pressure, characteristic of mesoporous materials with a BET surface area over 588 $m^2\ g^{-1}$, a total pore volume of 1.12 $cm^3\ g^{-1}$, and a narrow pore size distribution centered at 9.6 nm (Figure S1).

Small-angle X-ray scattering pattern of **$MS_2{-}NHBoc$** exhibits a weak single diffraction peak at $q = 0.062$ Å^{-1}, characteristic of the wormlike structure (Figure S2). This type of diffraction pattern indicates a regular separation between single channel walls.[8] The corresponding *d* value was calculated to be 10.1 nm. TEM image of **$MS_2{-}NHBoc$** (Figure S3) confirms a wormlike structure as well as uniform size pores.

The incorporation of carbamate and dithioalkylene groups in the mesoporous materials and the removal of surfactant were shown by solid-state NMR spectroscopies. ^{13}C CP-MAS NMR spectrum of **$MS_2{-}NHBoc$** (Figure S4) exhibits signals at 27.08 (CH_3 resonance of *tert*-butyl), 78.59 ($C_{sp3}{-}O$), and 156.90 ppm (carbonyl resonance), proving that the carbamate group remains intact. The spectrum exhibits three additional signals attributed to the propyl spacers at 43.48 (CH_2S and CH_2N), 23.65 (CH_2), and 10.99 ppm (CH_2Si).

Solid-state ^{29}Si CP-MAS NMR spectrum of **$MS_2{-}NHBoc$** (Figure S5) displayed signals at −100.66 and −109.21 ppm attributed at the substructures Q^3 and Q^4, respectively, denoting high cross-linking of the siloxane species. Two additional peaks with minor resonance at −57.80 and major one at −65.96 ppm assigned at the substructures T^2 $[C{-}Si(OR)(OSi)_2]$ and T^3 $[C{-}Si(OSi)_3]$, respectively, indicate the cross-linking of the organosilsesquioxane species.

The Si/S and Si/N molar ratios inferred from the elemental analyses of Si, S, and N in **$MS_2{-}NHBoc$** were found to be 5.8 and 12.3, respectively, which is rather close to the theoretical ratios (6.5 and 13.0). Thus, we can conclude that 89% of **S_2** and more than 94% of **1** were introduced in the material **$MS_2{-}NHBoc$**.

The reduction of disulfide units was achieved by treatment of **$MS_2{-}NHBoc$** with an ethanolic solution of $NaBH_4$ (8 equiv per disulfide unit) at 60 °C for 12 h. The resulting material was washed and then subsequently treated with H_2O_2 solution (300 equiv) at room temperature for 2 h, then with a diluted sulfuric acid solution for 30 min to oxidize the SH group into SO_3H (Scheme 1). At this stage, the XPS measurements of the resulting material, **$MSO_3H{-}NHBoc$** (Figure S6), show that the oxidation is not complete. The conductometric titration of **$MSO_3H{-}NHBoc$** revealed that this material contains 89% of expected SO_3H groups (Figure S7).

To recover the amino groups, the carbamate deprotection was completely achieved by thermal treatment[7] of **$MSO_3H{-}NHBoc$**

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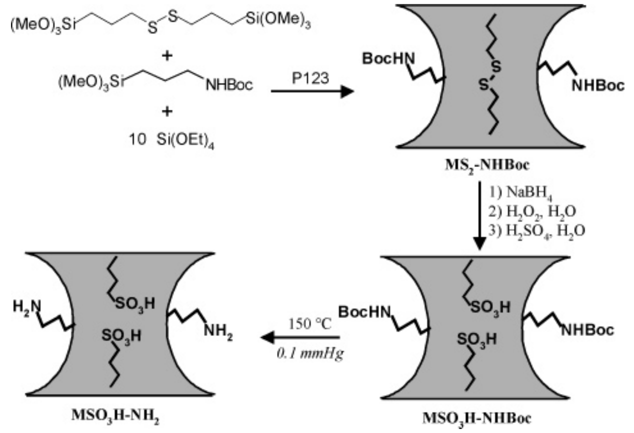
Scheme 1. Preparation of the Bifunctional Material **MSO$_3$H−NH$_2$**



at 150 °C under vacuum during 6 h to give rise quantitatively to mesoporous silica containing aminopropyl groups and sulfonic acid groups in the same material, **MSO$_3$H−NH$_2$** (Scheme 1).

Nitrogen adsorption−desorption isotherm for **MSO$_3$H−NH$_2$** (Figure S1) was very similar to that of **MS$_2$-NHBoc** with a BET surface area of 562 m^2 g^{-1}, a total pore volume of 1.06 cm^3 g^{-1}, and a narrow pore size distribution centered at 8.9 nm, indicating that the mesoporosity was maintained. Interestingly, the X-ray powder diffraction pattern of **MSO$_3$H−NH$_2$** (Figure S2) was very similar to that of **MS$_2$−NHBoc** with a weak single diffraction peak at $q = 0.060$ Å^{-1}, showing that the wormlike structure was also maintained even after chemical transformation.

The solid-state ^{13}C MAS NMR spectrum of **MSO$_3$H−NH$_2$** shows clearly the disappearance of resonances associated with the carbamate-protecting group (27.08 and 156.90 ppm), while the signals (54.21 for $-C\text{H}_2\text{SO}_3\text{H}$, 42.58 for $-C\text{H}_2\text{NH}_2$, 21.55, and 18.72 for $-\text{CH}_2C\text{H}_2\text{CH}_2-$, and 12.01 ppm for $-C\text{H}_2\text{Si}$) of propyl spacers were retained (Figure S4). In addition, the degree of polycondensation was not affected by these chemical modifications, and the ^{29}Si CP-MAS NMR spectrum of **MSO$_3$H−NH$_2$** was very similar to that of **MS$_2$-NHBoc**.

It is worth noting that Si/S (5.4) and Si/N (12.4) ratios inferred from the elemental analyses of Si, S, and N atoms in **MSO$_3$H−NH$_2$** are very close to those of **MS$_2$-NHBoc**. This result indicates that there was no carbon−silicon bond cleavage during the chemical and thermal treatments.

Conductometric titration of both functional groups (sulfonic acid and amino) in **MSO$_3$H−NH$_2$** was achieved (Figures S8 and S9) and revealed that this material contains 88% of expected amino groups and 78% of SO$_3$H (calculated from the S content in this material). This last value is slightly lower than that obtained for **MSO$_3$H−NHBoc**, indicating that most of SO$_3$H groups maintain their acid character even after deprotection of the amino groups.

The accessibility of the amino groups in **MSO$_3$H−NH$_2$** was proven by using the condensation reaction (Michael addition) between acrylamide[9] ($\text{CH}_2{=}\text{CH}-\text{CONH}_2$) and the amine function. The solid **MSO$_3$H−NH$_2$** was treated with an excess of acrylamide (15 equiv of acrylamide per NH$_2$ moiety) in anhydrous THF at room temperature for 24 h. The resulting solid, **MSO$_3$H−NHR**, was copiously washed with THF to eliminate the excess of acrylamide.

It was found that the N/S ratio in **MSO$_3$H−NHR** becomes 1.08, that is to say, twice that of **MSO$_3$H−NH$_2$** (0.56), as expected. This ratio indicates that 82% of amino groups underwent the Michael reaction. In addition, the ^{13}C NMR spectrum of **MSO$_3$H−NHR** revealed the presence of carbonyl groups at 179.89 ppm and the conservation of the sulfonic acid groups at 53.80 ppm (Figure S10).

To compare the reactivity of free amino groups in the presence and in the absence of SO$_3$H groups, **MS$_2$−NH$_2$** was prepared by thermal treatment of **MS$_2$−NHBoc**. The total deprotection of the amino groups was proven by ^{13}C NMR spectroscopy (Figure S11). The conductometric titration of the amino groups in **MS$_2$−NH$_2$** revealed that this material contains 92% of expected NH$_2$ groups (Figure S12).

Treatment of **MS$_2$−NH$_2$** with acrylamide gave rise to **MS$_2$-NHR** in which the N/S molar ratio was found to be 1.10, indicating 87% yield of Michael reaction. These results indicate that most of the amino groups are free, accessible, and remain active as nucleophile even in **MSO$_3$H−NH$_2$** when the reaction is accomplished in THF.

Finally, the condensation reaction with acrylamide was achieved in ethanol on both materials, **MSO$_3$H−NH$_2$** and **MS$_2$−NH$_2$**. While 88% yield was obtained for **MS$_2$−NH$_2$**, a dramatic decrease in the condensation yield (10%) was observed for **MSO$_3$H−NH$_2$**, indicating that, in protic solvent, most of the amino groups located in the pores can be protonated by the sulfonic acid units located in the framework. To support this result, the same reaction was achieved in water as solvent on **MSO$_3$H−NH$_2$** and gave rise to 2% condensation.

In conclusion, Avnir et al. have reported one-pot sequences of reactions with sol−gel entrapped antagonist reagents in two different materials.[10] We now describe a strategic synthesis allowing the preparation of bifunctional mesoporous material with an acidic framework and basic channel pores, with both functional groups being highly accessible. We have shown that, in aprotic solvent, both antagonist organic groups located at nanometric scale can cohabit independently without mutual destruction. In contrast, in protic solvent, there is protonation of the NH$_2$ groups, which is clear evidence of the existence of both antagonist groups in the same materials. This novel type of materials containing two antagonist groups is comparable to a semipermeable wall, depending on the solvent, and deserves to be generalized, which, in the future, could involve applications unsuspected until then.

Supporting Information Available: ^{13}C, ^{29}Si solid NMR spectra, XRD, TEM, and BET of **MS$_2$−NHBoc**. EDX and conductometric titration of sulfonic acid groups in **MSO$_3$H−NHBoc**. XRD, BET, ^{13}C solid NMR, and conductometric titration of **MSO$_3$H−NH$_2$**. Conductometric titration of amino groups in **MSO$_3$H−NH$_2$** and **MS$_2$−NH$_2$**, and ^{13}C solid NMR spectra of **MSO$_3$H−NHR** and **MS$_2$−NH$_2$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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