Synthesis and Characterization of Highly Ordered Thiophene-Bridged Periodic Mesoporous Organosilicas with Large Pores

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The first example of a highly ordered periodic mesoporous thiophene-bridged organosilica (PMO) with large pores is reported. The synthesis was carried out under acidic conditions using a polyalkylene oxide triblock copolymer (Pluronic P123) as supramolecular structure-directing agent. Materials with pore sizes between 5 and 6 nm and specific surface areas in the range of 400−550 m^2/g were obtained. The analysis of the TG/MS data demonstrates a relatively high thermal stability (up to 400 °C in air) of the mesoporous organosilica before a decomposition of the organic moieties occurs.

Introduction

Since the discovery in 1992 of ordered mesoporous M41S silica phases, a lot of effort was spent to modify and functionalize the silica network structure of the pore surfaces by introducing organic groups.[1,2] This organic functionalization gives the possibility to tune the surface properties (hydrophilicity, hydrophobicity, binding to guest molecules), alteration of the surface reactivity, protection of the surface from attack, and modification of the bulk properties (e.g., mechanical, thermal, electrical, or optical properties).[1] In general, one has to distinguish between three different synthesis approaches; each of them results in a different type of material. The first one is the grafting of the organic group onto the pore walls of the mesoporous silica in a postsynthetic treatment. Although a large number of different organic groups can be incorporated using this pathway, there are two main problems accompanied with the preparation: (i) the diffusion control during the impregnation process leads to a inhomogeneous distribution of the organic groups within the pore channels, and (ii) the organic functional groups (together with linkers) occupy the channel volume which reduces the free pore space and can finally lead to a total pore blocking. The second pathway follows a co-condensation reaction (often called “one-pot” synthesis) of a tetraalkoxysilane together with one or more organoalkoxysilanes in the presence of a supramolecular structure-directing agent. This approach is also limited by two main difficulties: (i) depending on the kind of organic group of the organoalkoxysilane, the reactivity with respect to hydrolysis and condensation reactions can substantially differ from that of the tetraalkoxysilane, resulting in an inhomogeneous distribution within the organic−inorganic hybrid network, and (ii) there is a limit of loading, as only about 25% of organic groups can be incorporated in the hybrid structure before the material loses its long-range order and structurally collapses.[3] The third synthesis approach was developed in 1999 by three different independently working research groups, who introduced a new class of mesoporous organosilica hybrid materials.[4−8] These materials, called periodic mesoporous organosilicas (PMOs), possess organic functionalities directly incorporated in the pore wall framework. This could be realized by the controlled hydrolysis and condensation of bridged organosiloxane precursors $(R'O)_3-Si-R-Si-(OR')_3$, known in sol−gel chemistry for quite some time,[9,10] in the presence of lyotropic liquid-crystals which served as structure-directing agents. This pathway permits the stoichiometric incorporation of organic groups in the silica network, leading to materials with much higher loadings and homogeneous distribution of organic functional groups than obtained by the grafting or co-condensation approach. Periodic mesoporous organosilicas are a new class of organic−inorganic hybrid materials with special properties, which should not be confused with materials prepared following the other two synthesis pathways. If the chemical reactivity and size of the organic spacer group are each in a similar range, even mixtures of two or more different bridged organosiloxane precursors can be used without forming structural and compositional heterogeneities within the hybrid material.[11] This gives also the possibility to control the concentration of a desired functional group within the hybrid

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wall structure without using tetraalkoxysilanes, for example, TEOS, which form pure silica networks. Only ordered mesoporous materials that were synthesized by using bridged organosiloxanes and supramolecular templates should be called "periodic mesoporous organosilicas". Having functional organic groups located "within" the pore walls of PMOs, rather than simply "hanging" in the channel, may be advantageous for many applications.[3] By varying the organic group, the framework density, chemical, mechanical, electrical, and optical properties would be expected to change. Currently, a lot of effort is spent to expand the pore sizes of mesoporous organosilicas by using triblock copolymer surfactants[12−19] or to synthesize materials with new morphologies, for example, thin films[20,21] and monodisperse spherical particles.[22,23] A promising way to improve the structural order of triblock copolymer templated PMOs synthesized under strong acidic conditions is the use of additional inorganic salts which have a specific effect on the self-assembly interaction between surfactant headgroups and inorganic species.[24,25] Recently, it was also possible to synthesize periodic mesoporous organosilica materials with crystal-like instead of the commonly occurring X-ray amorphous walls.[26−29] All of these PMOs have in common that their organic bridge consists of phenylene or biphenylene rings which align, probably due to $\pi-\pi$ interactions between neighboring bridges, in such an ordered fashion. In-situ synchrotron SAXS/XRD studies reveal that the formation of periodic order both on the mesoscopic scale and within the pore walls is found to occur simultaneously and in a highly cooperative process.[30] Very recently, a new archetype of PMOs was reported which was synthesized from a cyclic three-ring organosiloxane $[(EtO)_2Si(CH_2)]_3$ precursor in the presence of cationic cetyltrimethylammonium surfactants.[31] In sol−gel chemistry, the use of thiophene-bridged organosiloxanes for the synthesis of corresponding xerogels has been known for more than 20 years.[32,33] However, thiophene-bridged periodic mesoporous organosilicas are of great interest with respect to electrochemical applications, or they can serve as functionalized host materials for different types of nanoclusters. Due to their very high (maximum) concentration of coordination sites within the pores, these PMOs should possess a several times higher adsorption capacity for metal ions than comparable thiol-functionalized mesoporous hybrid materials synthesized via the grafting or co-condensation route. This makes them also very interesting for certain sensor applications. So far, thiophene-bridged PMOs have been synthesized only with low molecular weight surfactants, and the obtained products exhibited lower structural order accompanied by small pores.[7,21,34]

Experimental Section

Synthesis. The thiophene-bridged mesoporous materials were synthesized under acidic conditions starting from a 2,5-bis(triethoxysilyl)thiophene (BTET) precursor in the presence of the triblock copolymer Pluronic P123 as structure-directing agent. While BTET was synthesized in accordance with the literature,[32] the commercially available P123 was used without further purification.

In a typical synthesis, 0.512 g (0.088 mmol) of P123 was dissolved in a mixture of 19.2 g (1.067 mol) of distilled water and 0.166 g (1.5 mmol) of concentrated HCl (32 wt %). After the addition of 0.53 g (1.3 mmol) of 2,5-bis(triethoxysilyl)thiophene (BTET), the reaction mixture was kept for 20 h at 40 °C under vigorous stirring (pH value of ∼1.2). After additional hydrothermal treatment for 24 h at 100 °C in a Teflon-lined stainless steel autoclave, the obtained precipitate was filtered, washed three times with 50 mL of distilled water, and dried in air overnight to yield a fine white powder. Removal of the surfactant was accomplished by extraction with a mixture of ethanol/HCl (concentrated) (100:3; v:v) using a Soxhlet apparatus for 6 h with subsequent drying of the product in air. The molar ratios of the components in the reaction mixture were BTET:P123:HCl:H_2O = 1:0.068:1.15:821.

Characterization. Powder X-ray diffraction patterns were recorded at room temperature with a Bruker AXS D8 Advance diffractometer using filtered Cu Kα radiation.

Transmission electron micrographs were obtained with a Philips C 30 microscope operating at 300 kV.

N_2-physisorption data were recorded with a Quantachrome Autosorb 6 at 77 K.

^{29}Si MAS NMR spectra were recorded without cross-polarization to obtain a measure of the relative number of different silicon sites in the material. The spectra were acquired using a Bruker MSL-400 spectrometer. The samples were spun at 3.5 kHz. Further experimental parameters: single pulse experiment, $\pi/2$ pulse width of 6 μs, recycle delay of 300 s, 1500 scans.

Raman spectra were acquired using a Raman microscope system (Jobin-Yvon). The Ar-ion laser line 514.5 nm was used for excitation. The power on the sample was 20 mW, and the spectral resolution was 1 cm^{-1}.

TG/MS data were obtained with a Netzsch STA 409C thermobalance (heating rate in air: 10 K/min) couple with a Balzer quadrupole mass spectrometer.

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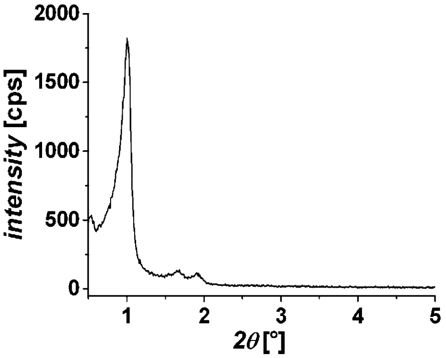

Figure 1. P-XRD pattern of a periodic mesoporous thiophene-bridged organosilica synthesized with Pluronic P123 as structure-directing agent.

Results and Discussion

The powder X-ray diffraction pattern (P-XRD) of the solvent-extracted thiophene-bridged PMO exhibits three sharp reflections in the low angle region ($2\theta < 2°$), indicating a high degree of mesostructural order (Figure 1). The pattern can be indexed as (100), (110), and (200) reflections, indicating a two-dimensional hexagonal symmetry (*p*6*mm*) of the material. The average position of the first XRD peak corresponds to the interplanar spacing of $\sim$ 9.2 nm. The unit cell dimension of the hexagonal lattice ($a = 2d_{(100)}/\sqrt{3}$) is 10.6 nm. In contrast to previous reports on the synthesis of mesoporous thiophene-bridged PMOs,[7,21,34] this is the first time it was possible to prepare such a material with high structural order and large *d* spacings using a triblock copolymer surfactant as structure-directing agent. This is also confirmed by the transmission electron microscope (TEM) images of the mesoporous material (Figure 2), which clearly reveal the hexagonal arrangement of the well-defined pores with uniform dimensions.

The nitrogen physisorption isotherm of the mesoporous product is shown in Figure 3. It reveals a typical type IV isotherm with a H1 hysteresis, which is characteristic for this type of material. Depending on the duration of the solvent extraction process, the specific surface areas vary between 400 and 550 m^2/g. The obtained narrow pore size distributions that were calculated from the desorption branch using the BJH formula exhibit pore diameters between 5 and 6 nm, which are consistent with estimations based on TEM image analyses. Framework wall thicknesses obtained by subtracting the pore size from the unit cell parameter are in the range of 4.6−5.6 nm.

One important question that has to be answered in the context of the structural homogeneity of periodic mesoporous organosilicas is whether the Si−C bond of the thiophene-bridge is still intact in the final product or not. For this purpose, ^{29}Si MAS NMR as well as Raman spectroscopic measurements were carried out. A typical ^{29}Si MAS NMR spectrum of a solvent-extracted mesoporous material is shown in Figure 4. It exhibits three characteristic T^n signals assigned to Si species covalently bonded to carbon atoms T^1 [C−*Si*(OSi)(OH)$_2$, δ −65.9], T^2 [C−*Si*(OSi)$_2$(OH), δ −74.9], and T^3 [C−*Si*(OSi)$_3$, δ −83.9)]. The absence of Q^n signals [*Si*(OSi)$_n$(OH)$_{4-n}$, $n = 2-4$] between −98 and −111 confirms the preservation of the Si−C bond during the synthesis and solvent extraction. Only after solvent extraction times longer than 48 h can one additional signal Q^3 [*Si*(OSi)$_3$-(OH), δ −102.4] with a contribution of less than 4% be observed.

Raman spectra of the PMO material display characteristic fingerprint vibrations corresponding to ν(Si−C), ν(C−S), ν_{ar}(C=C), and different C−H modes (Figure 5). The two bands at around 591 and 753 cm^{-1} are caused by the ν(Si−C) and ν(C−S) stretching modes, which clearly demonstrate that the organic moieties are still intact within the mesoporous framework structure. Additional bands can be observed at 677 and 1272 cm^{-1}, which both can be attributed to δ(C−H) out-of-plane and in-plane vibrations. The strongest band in the PMO material appears at 1414 cm^{-1}, which is assigned to the ring ν_{ar}(C=C) mode. The wavenumbers observed are in very good agreement with results obtained for thiophene-bridged PMOs with much smaller pores sizes synthesized with low-molecular weight surfactants.[34]

Another important question that always raises with respect to potential applications at elevated temperatures is the

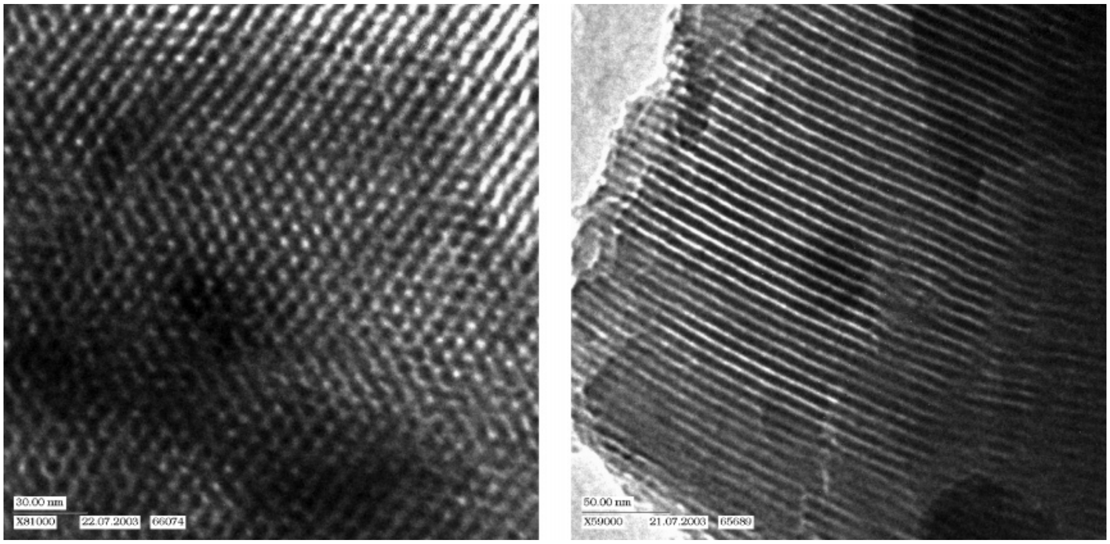

Figure 2. Representative TEM images of a mesoporous thiophene-bridged organosilica sample (view parallel (left) and perpendicular (right) to the pore axes).

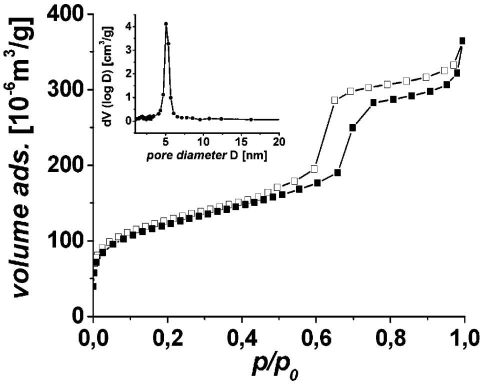

Figure 3. Nitrogen adsorption/desorption isotherm of a mesoporous thiophene-bridged organosilica (BET, 450 m^2/g; pore diameter, 5.4 nm).

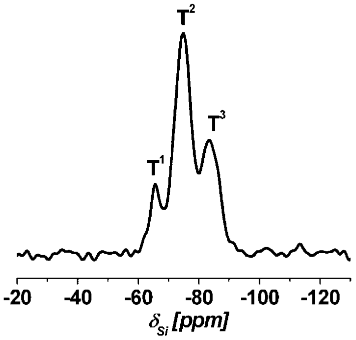

Figure 4. ^{29}Si MAS NMR spectrum of a mesoporous thiophene-bridged organosilica.

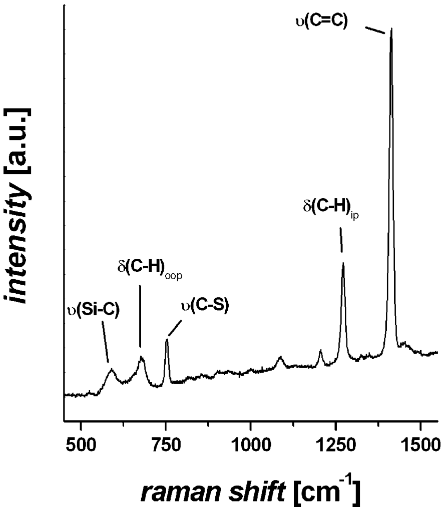

Figure 5. Raman spectrum of a mesoporous thiophene-bridged organosilica.

thermal stability of the organic−inorganic hybrid material. To answer this question, thermogravimetric measurements were carried out. Figure 6 shows typical TG/MS data of a thiophene-bridged PMO. The thermogravimetric (TG) plot reveals a total mass loss of 42.2%, which can be divided into three steps. Taking into account the combination of TG/MS, the first step (20−300 °C; mass loss: 7.8%) can be attributed to the loss of water (*m*/*z*: 18), which may be physisorbed on the inter- and intraparticle surface. In the second small step (300−400 °C; mass loss: 5.2%), additional carbon dioxide (*m*/*z*: 44) starts to become detected, an indication for the beginning oxidation of the hydrocarbons. The lack of any substantial mass loss in the range of 20−400 °C due to the oxidation of hydrocarbons (only very little proportion of the second mass loss) clearly indicates that the surfactant was successfully removed by the solvent extraction. The third and largest step (400−800 °C; mass loss: 29.2%) can be attributed to the complete oxidation of the thiophene-bridge indicated by the additional formation of sulfur dioxide (*m*/*z*: 64). The high thermal stability of this thiophene-bridged PMO is another clear indication for a real organic−inorganic hybrid character of this type of material.

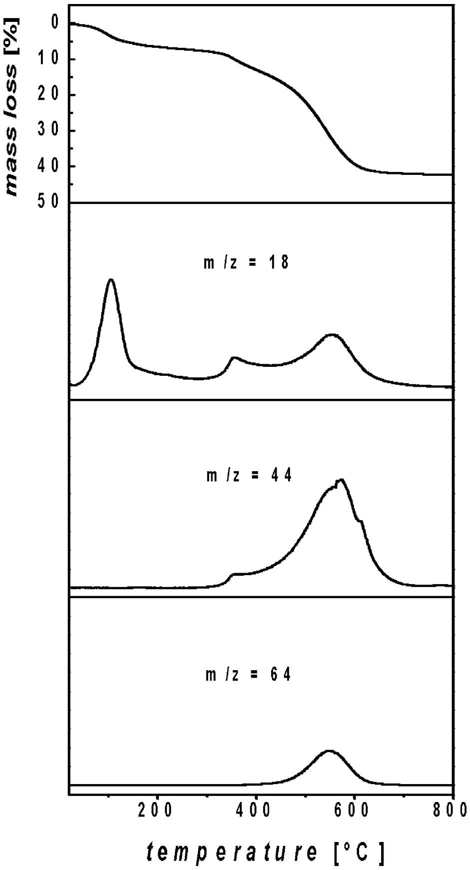

Figure 6. TG/MS data of a mesoporous thiophene-bridged organosilica (top, TG; below, mass spectra of H_2O (*m*/*z*: 18), CO_2 (*m*/*z*: 44), and SO_2 (*m*/*z*: 64)).

Conclusions

Highly ordered mesoporous thiophene-bridged organosilicas with large pores were prepared for the first time under acidic conditions using a polyalkylene oxide triblock copolymer (Pluronic P123) as supramolecular structure-directing agent. Materials with pore sizes between 5 and 6 nm and specific surface areas in the range of 400−550 m^2/g were obtained. ^{29}Si MAS NMR as well as Raman measurements clearly reveal the preservation of the Si−C bond even under strong acidic synthesis conditions. The analysis of the TG/MS data demonstrates a relatively high thermal stability (up to 400 °C in air) of the mesoporous organosilica before a decomposition of the organic moieties occurs, a property which is very promising for future applications even at elevated temperatures.

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