

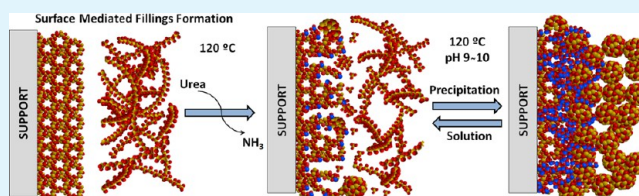
# Synthesis of Robust Hierarchical Silica Monoliths by Surface-Mediated Solution/Precipitation Reactions over Different Scales: Designing Capillary Microreactors for Environmental Applications

J. García-Aguilar, I. Miguel-García, Á. Berenguer-Murcia,\* and D. Cazorla-Amorós

Inorganic Chemistry Department and Materials Science Institute, Alicante University, Ap. 99, E-03080 Alicante, Spain

**ABSTRACT:** A synthetic procedure to prepare novel materials (surface-mediated fillings) based on robust hierarchical monoliths is reported. The methodology includes the deposition of a (micro- or mesoporous) silica thin film on the support followed by growth of a porous monolithic SiO<sub>2</sub> structure. It has been demonstrated that this synthesis is viable for supports of different chemical nature with different inner diameters without shrinkage of the silica filling. The formation mechanism of the surface-mediated fillings is based on a solution/precipitation process and the anchoring of the silica filling to the deposited thin film. The interaction between the two SiO<sub>2</sub> structures (monolith and thin film) depends on the porosity of the thin film and yields composite materials with different mechanical stability. By this procedure, capillary microreactors have been prepared and have been proved to be highly active and selective in the total and preferential oxidation of carbon monoxide (TO<sub>x</sub>CO and PrO<sub>x</sub>CO).

**KEYWORDS:** hierarchical silica monoliths, silica thin film, surface mediated fillings, solution/precipitation reactions, CO oxidation, capillary microreactors



## INTRODUCTION

Sol–gel processing is one of the most widespread methods for the synthesis of silica or titania materials. The modification of the experimental parameters, such as acid/basic hydrolysis, precursors of the materials, aging time and the temperature treatment allows preparation of a large variety of materials with different properties.<sup>1</sup> The addition of other compounds, such as surfactants, increases the amount of materials which can be synthesized by this method, performing as structure directing agents that produce controlled porosity within the material. In this direction, some silicas have been synthesized using ionic or triblock copolymer surfactants (e.g., CTAB or pluronic P123, respectively).<sup>2,3</sup>

In addition, sol–gel synthesis allows the possibility to produce silica or titania thin films with a very good control over the porosity of the film, the thickness of the layer deposited and the structure of the inorganic framework.<sup>4,5</sup> One easy alternative to produce silica thin films is by the evaporation-induced self-assembly (EISA) method. Controlling some parameters like the hydrolysis rate and the solvent and surfactant concentration in the solution, the support is introduced and withdrawn from the precursor solution (i.e., dip-coated), and dried afterward in a relative humidity controlled atmosphere. During the drying stage, the surfactant reaches its critical micellar concentration and allows the condensation of the silica within the structure.<sup>6</sup>

The general synthesis of mesoporous silica used by N. Tanaka<sup>7</sup> and G. Puy<sup>8</sup> produces silica spheres of a few microns in diameter by spinodal decomposition, as described by K. Nakanishi.<sup>9</sup> In this process, the separation between two phases

(silica gel and surfactant-rich aqueous phase) generates the spherical morphology of the silica and the macropores in the network. The spheres are formed by a process of solution/precipitation of the silica during the thermal treatment (at 120 °C), at the same time, the urea is decomposed producing ammonia. This urea decomposition takes place in the silica enriched phase, producing the mesopores inside the silica spheres. The combination between the basic medium (pH ~9–10), the temperature and the pressure enhances the solution/precipitation equilibrium giving rise to the final porous inorganic structure.<sup>10</sup>

All along the sol–gel process there are some steps where the inorganic phase can suffer a non-negligible shrinkage. The aging of the sol to produce the gel, the exchange of the solvent during hydrolysis, the solvent evaporation or the calcination of the porogen agent for its elimination are the main reasons for this shrinkage.<sup>9,11,12</sup> Generally, this shrinkage impacts negatively on the properties and the mechanical stability of the material with views toward its use as filling or as a robust monolithic unit.

Two of the most important applications where the silica must not suffer any shrinkage are when used as support of catalysts in reactors or microreactors and in the preparation of columns for chromatography.<sup>8,13</sup> Mesoporous silica is an interesting material as stationary phase in HPLC columns (e.g., capillary columns) and in reactors or microreactors (e.g., honeycomb cordierite monolith or capillaries)<sup>14,15</sup> because its properties are easy to

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modulate, such as meso- and macroporosity, pore size distribution, surface area, surface chemistry, etc.<sup>16</sup> In these applications, the silica shrinkage occurred during the synthesis produces a detachment of the silica from the walls of the support, with the gap formed between the silica monolith and the support impoverishing the properties of the final material.<sup>16</sup>

Some alternatives have proved effective to reduce or avoid silica shrinkage during the synthesis to improve its properties, such as the incorporation or combination of different silica precursors, which liberate alcohols susceptible to polymerize and that form a hybrid material between the silica gel and the polymer.<sup>17,18</sup> Another strategy to avoid the shrinkage reported by Tanaka and co-workers<sup>19</sup> consists in combining two silica precursors, TMOS and MTMS, but their results were limited to samples with dimensions below 250  $\mu\text{m}$  (inner diameter) in capillaries. This technology is applied by Merck for HPLC columns. Also, the addition of organic compounds like TMB acting as micelle-swelling reagents into the solution, has proven to effectively reduce the degree of shrinkage in the silica structure.<sup>20</sup>

Other alternatives are related to the drying and calcination steps. Some works have used a Soxhlet extraction for 1 or 2 days to remove the surfactant with acetonitrile or tetrahydrofuran,<sup>20</sup> and others have treated the silica obtained with supercritical  $\text{CO}_2$  extraction to avoid the drying step.<sup>12</sup> Combining different polymers (TMB, divinylbenzene, and styrene) has been successfully applied in capillaries of 100  $\mu\text{m}$  of inner diameter, without the need of a calcination step.<sup>21</sup> Finally, the last method found in the literature is the addition of bifunctional epoxides at the surface of the silica xerogel network to enhance the cross-linking and reduce the irreversible shrinkage.<sup>22</sup>

The main objective of this study is to develop a novel method to completely avoid the silica fillings shrinkage when synthesized inside different supports (honeycomb cordierite monolith, glass tube, steel line, and fused-silica capillaries). The deposit of a porous silica thin-film on the walls of the support by dip-coating prior to the synthesis of the silica, allows the introduction of a small quantity of silica, which is well anchored to the support. This silica thin film serves both as an anchor and a reservoir for solution and precipitation during the thermal treatment, leading to a very good interaction between the monolithic structure and the support. With this method, no shrinkage occurs in the silica fillings inside different supports over different length scales. One outstanding advantage of this method is that no additional solvents or compounds apart from those typically used to prepare hierarchical porous silica are necessary.

$\text{CO}$  emission is a relevant environmental problem due to the high toxicity of the gas at low concentrations and the diversity of the emission sources (i.e., power plants, transportation, or domestic activities). In addition, the preferential oxidation of  $\text{CO}$  in  $\text{H}_2$ -rich gas streams is one of the most important challenges for the  $\text{H}_2$  purification in fuel cells industry, due to the inhibition of the cathode for the Pt poisoning in the presence of  $\text{CO}$ . The incorporation of low loads of noble metals, such as Au or Pt, well dispersed on the silica support increases the activity and the catalytic behavior (e.g., selectivity) of the catalyst toward the oxidation of  $\text{CO}$ .<sup>23</sup>

As it has been commented, the improvement of the silica filling allows the preparation of novel microreactors, such as honeycomb cordierite monoliths and fused silica capillaries. In this work, Pt nanoparticles have been deposited on the silica

filling synthesized as a surface-mediated filling, and the performance of the microreactor has been evaluated in the catalytic oxidation of  $\text{CO}$  under different conditions ( $\text{TOxCO}$  and  $\text{PrOxCO}$ ). These reactions have been carried out in fused-silica capillaries filled with the surface-mediated filling as an example of the application of this new procedure to prepare silica-filled reactors.

## ■ EXPERIMENTAL SECTION

**Materials.** To evaluate the method developed on different size scales, four different supports with different dimensions have been used: honeycomb cordierite monoliths with a cell density of 400 cpsi (1.2 mm channel size) (cut in cylindrical pieces of 1.5 cm of diameter and 1.5 cm of height), glass tubes of 7.28 mm of inner diameter and 5 cm long (Volac), steel lines of 0.87 mm of inner diameter and 10 cm long (Swagelok) and fused-silica capillaries with an inner diameter of 250  $\mu\text{m}$  and a length of 20 cm (Agilent).

The silica precursors (TMOS and TEOS), urea, acetic acid, hydrochloric acid, CTAB, and PEG-35K were purchased from Sigma-Aldrich. Both Pluronic surfactants (F127 and P123) were from BASF. Absolute ethanol was purchased from Panreac. All reactants were used as received.

**Preparation of Silica Thin Films.** Two silica thin films (micro and mesoporous) have been prepared, adapting previously described procedures.<sup>24,25</sup>

For the mesoporous silica thin film, 5.500 g of ethanol, 0.4 g of distilled water, 0.6 g of hydrochloric acid (1 M), and 2.080 g of TEOS were stirred for 90 min. In a separate vessel, 0.700 g of CTAB were dissolved in 6.000 g of ethanol. Then, the solution with the surfactant was added dropwise to the first solution and the resulting mixture was kept under stirring at ambient temperature for 2 h. The supports (honeycomb cordierite monolith and glass tube) were dip-coated in the solution with a withdrawal rate of 1 mm/s and then dried in a humidity controlled atmosphere (RH 50%) for 24 h. The incorporation of the silicon precursor solution on the steel line and the fused silica capillaries was made by means of a syringe pump (WPI, sp210w) with a withdrawal liquid flow rate of 70  $\mu\text{L}/\text{min}$ . Both supports were then dried in the same humidity conditions. Finally, all samples were calcined. The honeycomb cordierite monoliths were calcined in a static oven at 550  $^\circ\text{C}$  for 6 h with a heating rate of 3  $^\circ\text{C}/\text{min}$ . However, the rest of the supports were calcined in a vacuum oven (Thermo Scientific) at 300  $^\circ\text{C}$  for 24 h at 3  $^\circ\text{C}/\text{min}$ .

For the synthesis of the microporous thin films, the same experimental procedure was followed, except that CTAB was not included in the Si precursor solution.<sup>26</sup> The microporous thin films were submitted to the same humidity and thermal treatments described above for the mesoporous films and calcined as previously stated. For characterization purposes, similar  $\text{SiO}_2$  were prepared as powders by the same experimental procedures.

**Preparation of Silica Fillings.** The mesoporous silica filling has been prepared adapting a synthetic protocol described in other works.<sup>8,27</sup> In this work, Pluronic F127 and P123 have been used as porosity agents, apart from the PEG used in the literature.

For the synthesis, 0.400 g of porogen agent (Pluronic F127, P123, or PEG-35K), 0.452 g of urea, and 5.052 g of acetic acid (0.01 M) were mixed under vigorous stirring for 80 min, the final pH of the solution being around 4. Then the solution was cooled in an ice–water bath maintaining the stirring and the silica precursor was added dropwise (2.030 g TMOS). This solution was kept under stirring for 40 min at 0  $^\circ\text{C}$ .

Finally, the sol was introduced in the appropriate support. For the honeycomb cordierite monolith, the support (previously washed with ethanol) and the sol were placed in a Teflon autoclave, while for the glass tube, steel line, and fused-silica capillaries, the solution was injected and sealed with high-temperature glue. To prevent the TMOS hydrolysis before the drying of the glue, the supports filled with the precursor solution were refrigerated until complete drying of the glue (around 20 min at 5  $^\circ\text{C}$ ). Then, the samples were heated at 40  $^\circ\text{C}$  for 20 h to produce the aging of the sol (the pH after this step was around

4) followed by a hydrothermal treatment at 120 °C for 6 h, to produce the urea decomposition (the final pH of the supernatant liquid was around 9–10).

The final filled support was then directly calcined as described previously.

The nomenclature of the samples indicates the porosity agent used in the silica filling, the type of thin film deposited on the support and the support used in each case. For example, the sample F127-Meso-M is prepared with honeycomb cordierite monolith (M) in which a mesoporous silica thin film was deposited, with Pluronic F127 being the porogen agent in the silica filling. All the samples prepared are shown in Table 1.

**Table 1. Samples Prepared in This Study, Indicating the Support Used in Each Case (M = Honeycomb Cordierite Monolith, T = Glass Tube, L = Steel Line, and C = Fused Silica Capillaries), the Porosity Agent Used in the SiO<sub>2</sub> Filling, the Porous Nature of the Previously Silica Thin Film Deposited, and Final Shrinkage (%) Observed in Each Sample As Estimated by SEM**

sample	porosity agent in the filling	silica thin film	support	% shrinkage <sup>a</sup>
F127-Non-M	Pluronic F127		cordierite monolith	7
F127-Micro-M	Pluronic F127	microporous	cordierite monolith	~7 <sup>b</sup>
F127-Meso-M	Pluronic F127	mesoporous	cordierite monolith	
P123-Meso-M	Pluronic P123	mesoporous	cordierite monolith	
PEG-Meso-M	PEG-35K	mesoporous	cordierite monolith	
F127-Non-T	Pluronic F127		glass tube	20
F127-Meso-T	Pluronic F127	mesoporous	glass tube	
F127-Non-L	Pluronic F127		steel line	10
F127-Meso-L	Pluronic F127	mesoporous	steel line	
F127-Non-C	Pluronic F127		silica capillary	25
F127-Meso-C	Pluronic F127	mesoporous	silica capillary	

<sup>a</sup>Estimated from SEM images observation. <sup>b</sup>No homogeneous shrinkage has been observed in the sample; 7% corresponds to the maximum shrinkage measured (see Figure 4a and 4b below).

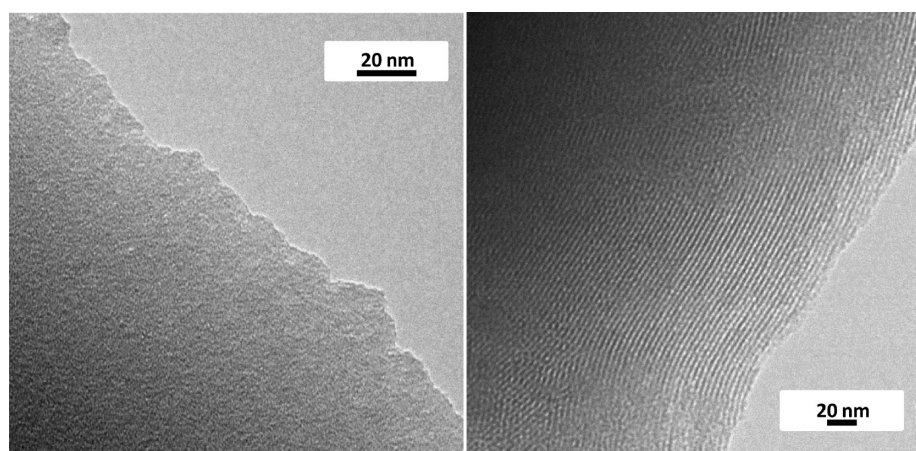
**Preparation of the Capillary Microreactor.** Pt nanoparticles were synthesized by reduction by solvent using ethylene glycol as reduction agent. The platinum precursor (Na<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Sigma-Aldrich) is dissolved in 25 mL of ethylene glycol, and the capping agent (PVP 40K, Sigma-Aldrich) is dissolved in a separate flask in 60 mL of ethylene glycol. In this synthesis 0.5 mmol of metal was used in total and the PVP/metal molar ratio was set to 10. After complete dissolution, both solutions are mixed at 0 °C under vigorous stirring, and 1 M NaOH is added to the solution to adjust the pH to 9. Then, the final solution is heated at 100 °C and formation of the metallic nanoparticles is detected when the solution changes its color to dark brown. The entire process is carried out under argon atmosphere by means of a Schlenk system. When the nanoparticles are synthesized it is necessary to do a purification stage to remove the excess of surfactant and reactants. The prepared colloids are therefore purified in an excess of acetone and redispersed in the appropriate amount of methanol, so that the final metallic concentration in this solvent is perfectly known. The nanoparticles suspension obtained by this procedure is stable against agglomeration.<sup>28</sup>

The nanoparticles were deposited over a 20 cm long silica-filled capillary with a syringe pump. The appropriate amount of Pt nanoparticles redispersed in methanol to obtain a final metal loading of 2% (w/w) with respect to the weight of the silica filling inside the capillary is flowed in the capillary with the syringe pump. Finally, the fused-silica capillary is dried to evaporate the methanol, at 150 °C (1 °C/min) for 4 h in an oven. The sample was labeled as Pt-F127-Meso-C.

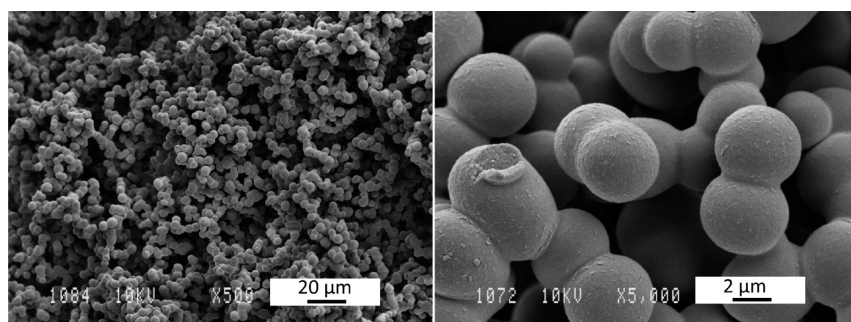
**Characterization.** Both silica thin films were analyzed by transmission electron microscopy (TEM, JEOL JEM-2010) in order to study the morphology of the coating deposited on the supports.

All silica-filled supports have been analyzed by different microscopy techniques. For the support with the largest channels (tube glass with 7.28 mm of inner diameter) two techniques were combined: optical microscopy with an image acquisition display (LEICA EZ4) and scanning electron microscopy (SEM, HITACHI S3000N and JEOL JSM-840) coupled with an X-ray analyzer (Bruker, XFlash 3001) for EDX analysis. The other supports that have significantly narrower channels have been only analyzed by SEM. In some cases, the samples were sputtered with Au to obtain images with better resolution. These techniques allow a very reliable determination of the quality of the silica filling and the shrinkage extent in the different samples. The mesoporous silica thin film was also analyzed by field emission scanning electron microscopy (FE-SEM, Merlin VP Zeiss) before and after a similar treatment in urea at 120 °C to simulate the synthesis of surface mediated fillings.

The mesoporous silica generated as a filling within the different channels and the similar SiO<sub>2</sub> deposited as thin films were also characterized as a powder by N<sub>2</sub> adsorption–desorption at –196 °C



**Figure 1.** TEM images of both silica thin films. Microporous/amorphous silica thin film (left) and mesoporous ordered structure (right).



**Figure 2.** SEM pictures of mesoporous silica powder synthesized with Pluronic F127 as porosity agent.

and by CO<sub>2</sub> adsorption at 0 °C (Quantachrome, Autosorb 6B) to analyze the porous texture of the materials.

Catalytic tests were performed under nonisothermal conditions at a heating rate of 2 °C/min. For TOxCO the gas feed composition was 3.3% CO, 10% O<sub>2</sub> using He as carrier gas with 2.5 mL/min total gas flow. Before the catalytic test, the microreactor was pretreated in a gas stream containing 10% O<sub>2</sub> (rest He) up to 220 °C. For the PrOxCO reaction the gas composition used was: 2% CO, 2% O<sub>2</sub>, 30% H<sub>2</sub> (rest He) with the same flow rate as above, and 30% H<sub>2</sub> in He was used for the pretreatment. The behavior of the catalytic reactions was evaluated by analyzing the gas composition exiting the reactor with a GC chromatograph (Agilent 6890N) working with a CTR-I column (Alltech) operating at 80 °C and a TCD detector to calculate the CO conversion and selectivity.

## RESULTS AND DISCUSSION

**Silica Thin Films.** The silica thin films obtained in this work have been studied by TEM. The TEM images are shown in Figure 1.

The microporous silica thin film prepared is a typical silica deposit without any structural order (Figure 1, left). However, when the surfactant is added (CTAB) a mesoporous network of silica is produced during the slow drying in a relative humidity controlled atmosphere by EISA (Figure 1, right). In Figure 1 it is possible to see the differences between the two silica thin films, where a higher degree of organization of the structure can be observed in the mesoporous sample. As previously reported by other authors for similarly prepared materials,<sup>29</sup> the thin films prepared by this methodology display a thickness that is around 100 nm. Another significant difference between these two materials is related to their respective specific surface area (determined from the powder materials prepared with the similar procedure), with the microporous silica thin film being significantly lower (450 m<sup>2</sup>/g) than that of the mesoporous structure (700 m<sup>2</sup>/g).<sup>30</sup>

These two porous SiO<sub>2</sub> structures have been used as seeding/anchoring surfaces for the growth of the SiO<sub>2</sub> porous fillings. These thin films have been deposited onto different surfaces (supports) with different chemical nature, that is, honeycomb cordierite monolith, glass tube, steel line, and fused-silica capillaries to evaluate the influence of the porosity of the thin film layer, and also of the nature of the support and the dimensions of the channel, on the generation of SiO<sub>2</sub> fillings on these substrates. The materials prepared by this procedure will be hereafter denoted generally as surface-mediated fillings.

**Silica Filling Analysis.** The mesoporous silica generated as a filling using the different surfactants as templates were also characterized by N<sub>2</sub> and CO<sub>2</sub> adsorption. The results indicate that there are no significant differences in the textural properties of the SiO<sub>2</sub> structures independently of the nature

of the porosity agent. In all cases, the SiO<sub>2</sub> fillings show a type I +IV isotherm typical of mesoporous materials with a hysteresis cycle which also show a certain degree of microporosity. These materials present a specific surface area of ~200 m<sup>2</sup>/g calculated by the BET method, with a relatively narrow pore size distribution (ranging from 5 to 20 nm) according to the BJH model applied to the desorption branch of the isotherm. The mesoporous silica has a very low specific micropore volume of 0.04 cm<sup>3</sup>/g calculated by the Dubinin–Radushkevich method in CO<sub>2</sub> adsorption and 0.09 cm<sup>3</sup>/g in N<sub>2</sub> adsorption.

The resulting mesoporous silica spheres were also analyzed by SEM. The images are shown in Figure 2 for the sample prepared with F127 as surfactant. The mesoporous silica spheres have a diameter between 4 and 6 μm. This morphology is due to the spinodal decomposition route synthesis and the hydrothermal treatment at 120 °C during the synthesis that allows the solution/precipitation of the silica. In this case, the use of Pluronic F127 produces also a relative amount of macropores or interparticle gaps.<sup>31</sup> This is in very good agreement with the published results for similar materials prepared with PEG-based surfactants.<sup>8,9</sup> This macroporosity, together with the mesoporosity due to the urea decomposition and the inherent microporosity of the silica, gives rise to a final silica filling that presents three levels of hierarchical structure.<sup>8,9</sup>

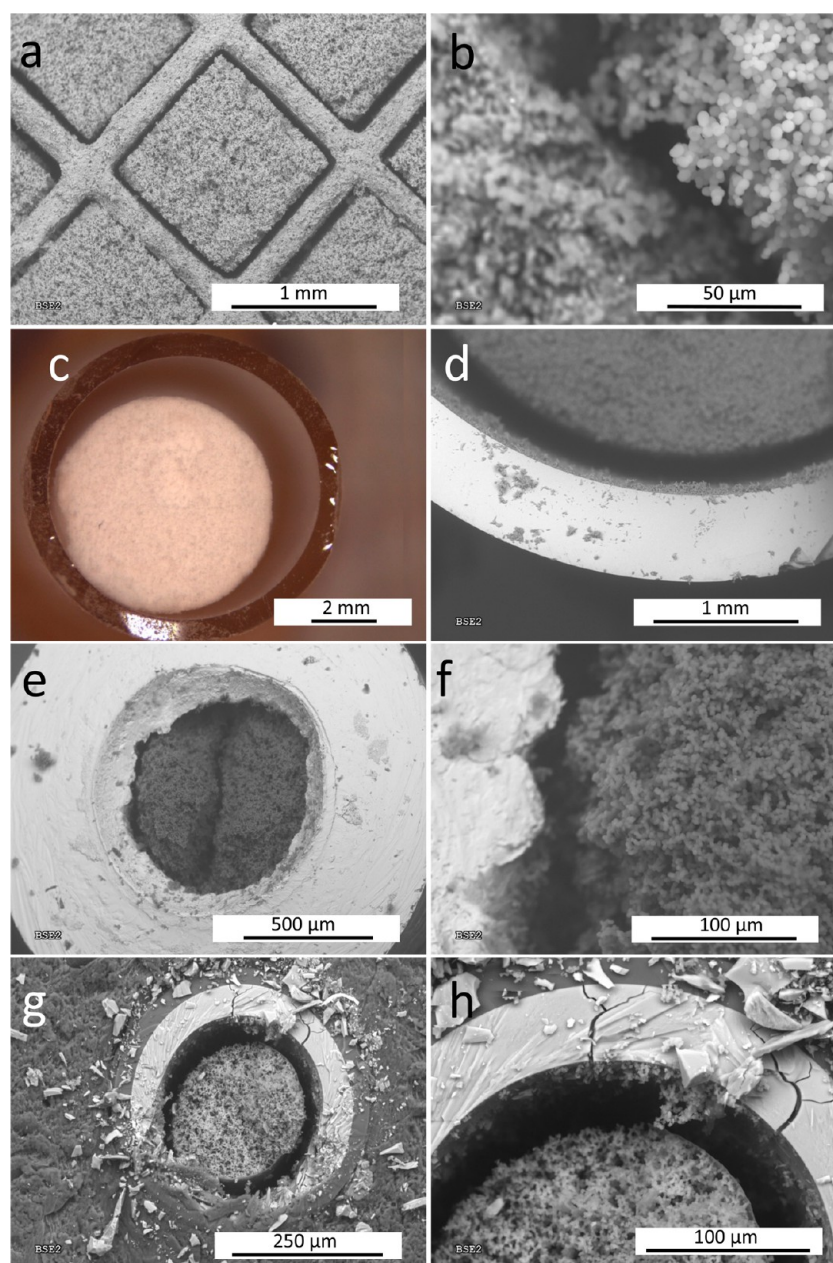
**Non-Surface-Mediated Fillings.** Prior to the surface mediated fillings, the SiO<sub>2</sub> monolithic structures have been generated within the channels in the different supports in the absence of the silica thin film. The main results are shown in Figure 3.

In all cases, a continuous filling of silica made of SiO<sub>2</sub> spheres can be seen in all the channels, regardless the size and nature of the support. However, some SiO<sub>2</sub> shrinkage can be observed in these samples.

For the honeycomb cordierite monolith synthesized with Pluronic F127 as porosity agent in the silica filling (F127-Non-M) the SEM images show a linear shrinkage (around 7%) in all directions. The pictures show that the silica filling is detached from the monolith walls, due to the weak interaction between the surface of the monolith and the fillings. In Figure 3.b a magnification of the interface is shown to demonstrate the weak interaction between these two materials.

The next example is the same filling introduced in a 7.28 mm (inner diameter) glass tube (F127-Non-T). The radial shrinkage obtained in this support is larger than the one observed in the cordierite monolith (~20%). As in the previous case, the inherent shrinkage of the silica causes the silica filling to become separated from the glass tube.

The filled-silica steel line without a silica thin film deposit (Figure 3.e and 3.f) presents the same behavior as the other



**Figure 3.** Microscopy images (optical and SEM) of non-surface-mediated fillings in the different supports tested in this research. From top to bottom, F127-Non-M (a and b), F127-Non-T (c and d), F127-Non-L (e and f), and F127-Non-C (g and h).

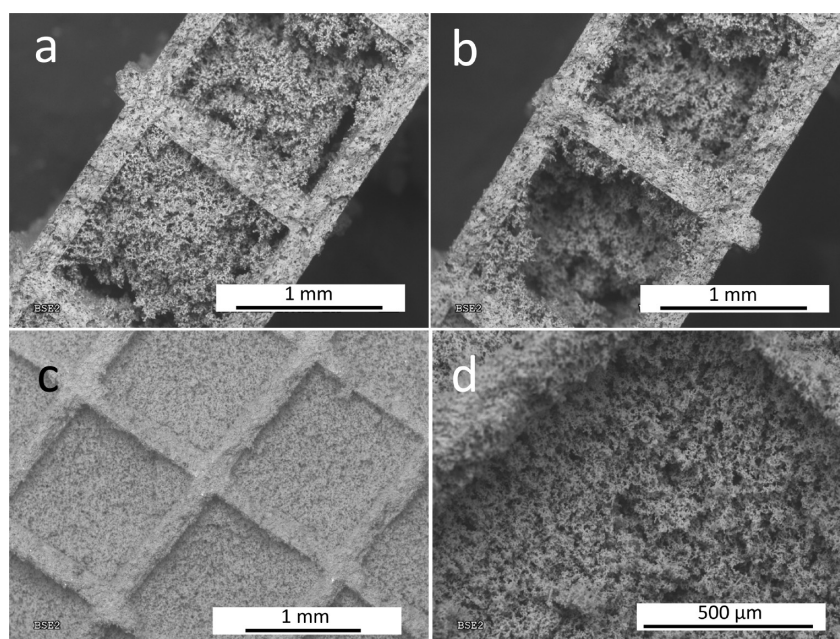
materials. A relevant shrinkage occurred during synthesis and a crack is visible in the silica filling.

The same fact is shown in the capillary sample (F127-Non-C). For this support, the most significant shrinkage of the structure is obtained (around 25%) in the silica filling. This resulted in the SiO<sub>2</sub> structure becoming completely detached from the capillary wall. This filling does not have the optimal properties for applications requiring robust materials, such as microreactors or HPLC columns.<sup>7,29</sup>

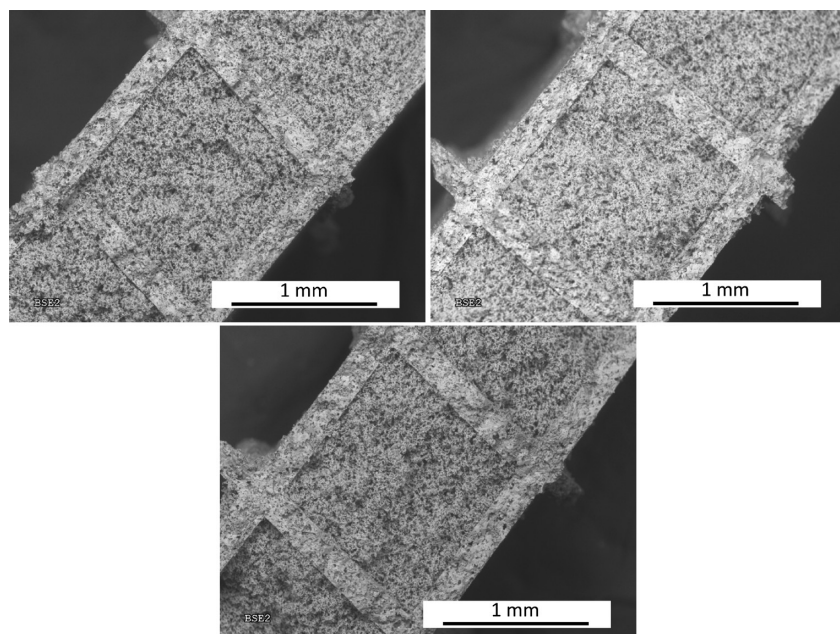
As a general feature, the poor interaction between the hierarchical SiO<sub>2</sub> filling and the supports reflects in a bad adherence of the filling to the channels. The fillings can be easily removed from the support in all cases and/or may become detached from the walls due to manipulation of the samples.

**Surface-Mediated Fillings.** To improve the silica filling adherence to the supports, we have studied the incorporation of a silica thin film on the walls of the different channels prior to the silica filling synthesis, with the idea that the silica thin film serves as a rough highly reactive surface to which the hierarchical silica filling can be anchored during the hydrothermal treatment and that can also take part in the solution/precipitation of the silica during the formation of the filling.

First we analyzed the effect of the porosity and structure of the thin film deposited. Two thin films were deposited on the honeycomb cordierite monolith, the disordered microporous thin film (Figure 1, left) and the ordered mesoporous thin film synthesized with CTAB as porosity agent (Figure 1, right). In both cases the filling was synthesized using Pluronic F127, and the samples were named F127-Micro-M and F127-Meso-M, respectively. The SEM pictures obtained for the samples are



**Figure 4.** SEM images of surface-mediated fillings, studying the effect of the porosity of the silica thin film deposited on the support. F127-Micro-M (a and b) and F127-Meso-M (c and d).



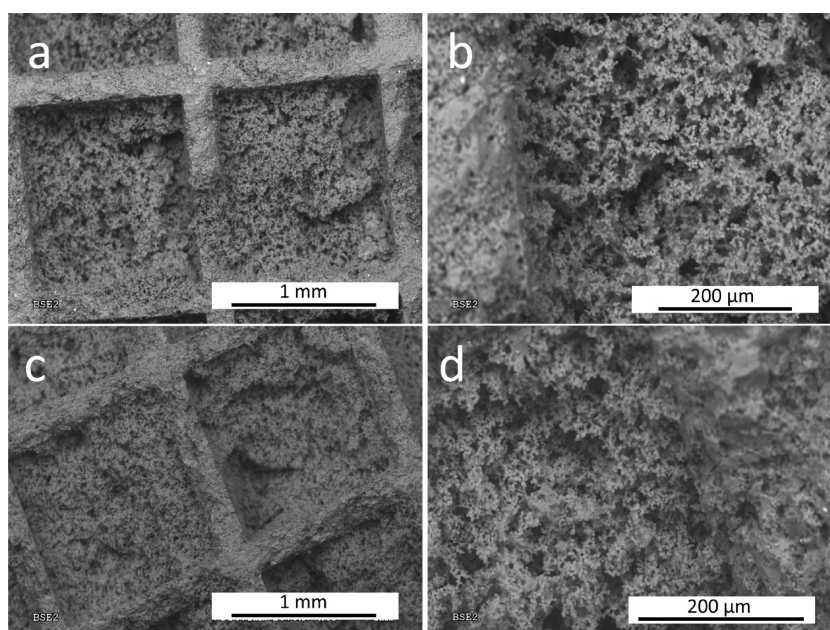
**Figure 5.** SEM pictures of different transversal sections of the honeycomb cordierite monolith surface-mediated filled with Pluronic F127 mesoporous silica (F127-Meso-M).

shown in Figure 4, to compare with their homologous Non Surface Mediated Fillings (F127-Non-M, see Figure 3.a and 3.b).

As it can be observed in Figure 4, both silica thin films deposited over the walls (microporous and mesoporous) have improved the silica filling adherence compared to the uncoated support (Figure 3a and 3b). The sample F127-Micro-M (Figure 4a and 4b), with the microporous silica thin film has reduced the lateral shrinkage in the monolith channels considerably although some cracks can still be seen near the walls. However, the F127-Meso-M Surface Mediated Filling (Figure 4c and 4d) does not present any shrinkage in any direction. The monolith

channel is completely filled with mesoporous silica because of the presence of the silica thin film previously deposited on the cordierite walls.

From these results, it can be proposed that, although the adherence of the filling to the support is improved in both cases (with respect to the uncoated support), some differences depending on the nature of the thin film can be observed. Thus, for the mesoporous coating a better interaction between the two surfaces has been found, leading to a more homogeneous SiO<sub>2</sub> filling structure and a more robust interaction with the cordierite walls, that reflects in a more mechanically stable material that withstands the manipulation of the sample for the



**Figure 6.** Scanning electron microscopy images of P123-Meso-M (a and b) and PEG-Meso-M (c and d).

analysis without a cracking of the structure and/or detachment from the walls. In contrast, when the microporous thin film is coated, the  $\text{SiO}_2$  filling seems to be more susceptible for the appearance of crevices in the structure and cracks are observed in the vicinity of the cordierite walls.

To ensure the complete and satisfactory filling of the honeycomb cordierite monolith coated with the mesoporous film along all the channels, the sample F127-Meso-M has been cut in three sections of 0.5 cm each. The SEM pictures of the different sections are shown in Figure 5, where it can be observed that the porous silica filling is totally homogeneous along the cordierite channels. The filling presents a very good adherence to the cordierite monolith in all cases, so that it can be stated that the mesoporous silica thin film incorporated before the synthesis of the filling avoids the shrinkage inherent to the synthesis and improves the properties of the final material.

For the sample with the best results obtained (F127-Meso-M), the effect of the nature of the filling was analyzed. For this, different samples were prepared using cordierite monoliths as supports and the mesoporous silica thin film previously described as coating. Then, different  $\text{SiO}_2$  porous fillings were generated in the channels, using other surfactants that are commonly used for these applications. Pluronic F127 was substituted by Pluronic P123 and PEG-35K in the synthesis of the mesoporous silica filling. The surface-mediated fillings obtained are shown in Figure 6.

In Figure 6a, some channels of the surface-mediated filling with a previous mesoporous silica thin film and using Pluronic P123 as porosity agent are presented. It can be observed that all the channels are completely filled with the silica structure and that it is also homogeneously distributed. In Figure 6b a magnification of the interface between the monolith walls and the filling is shown. A very good interaction between the support and the filling is obtained, and the filling is well adhered to the cordierite monolith. The same results are obtained for the sample prepared with PEG-35K (PEG-Meso-M) presented in Figures 6c and 6d. It should be mentioned that the use of this family of surfactants is commonly extended for

the preparation of hierarchical silica with interesting applications.<sup>32–34</sup>

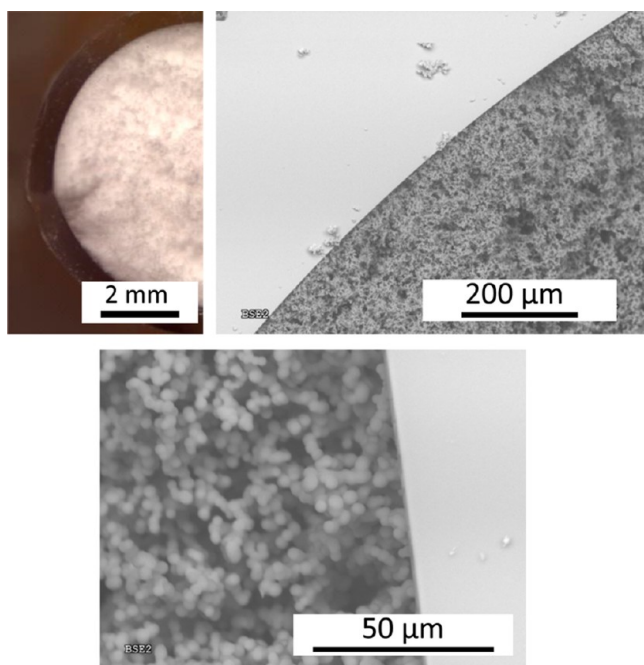
As it has been shown, the synthetic procedure described here enables the possibility to improve the adherence of the silica filling to the substrate just by the addition of a silica coating on the channel. This is very interesting because it indicates that the final properties of the material can be improved just by the addition of one step that requires the use of the same chemical reactants, with the advantage that no environmentally hazardous chemicals need to be used. Also, this result is extended not only to silica structures prepared with Pluronic F127, but also to some other materials prepared with different porogen agents, such as Pluronic P123 and the PEG family. In all samples, the continuous  $\text{SiO}_2$  monoliths suffer no shrinkage. In these cases, the adherence of the filling to the support has been proven to be highly resistant to manipulation and mechanical stress.

The amount of  $\text{SiO}_2$  contained in the samples was determined by weight difference. For these monoliths, the mass is around 1.48 mg silica/cm<sub>channel</sub>.

In order to confirm that the previous incorporation of the silica thin film improves the adherence of the later filling, the study has also included the surface-mediated filling in the rest of the supports. In all samples the silica thin film deposited is the mesoporous one and the surfactant used in the silica filling is Pluronic F127 (samples F127-Meso-X).

First of all, the glass tube of 7.28 mm of inner diameter with the filling (F127-Meso-T) is shown in Figure 7. As it can be observed, the filling again presents a very good interaction with the support, and not a significant shrinkage of the structure can be observed. The only appreciable separation between the silica and the glass in the optical image is due to the manipulation of the sample for the analysis. For this sample, the amount of silica determined inside the tube is 38.7 mg/cm.

The same experimental procedure was performed using a steel line as support. In this case, this is a very different material, with different surface chemistry properties. The sample (F127-Meso-L) is presented in Figure 8. The images show very important differences with respect to the sample without the mesoporous silica coating (F127-Non-L, Figures 3e and 3f). In



**Figure 7.** Optical and scanning electron microscopy images of the sample F127-Meso-T.

this case, the filling in the sample is homogeneously distributed inside the support and totally anchored to the walls. No shrinkage of the monolithic structure has been observed throughout the length of the line. The distribution of the filling along the length of the line has been also studied, observing that the  $\text{SiO}_2$  porous structure is continuous in the entire length of the line (results not shown). In this case, the mass incorporated in the steel line is around 3.8 mg/cm.

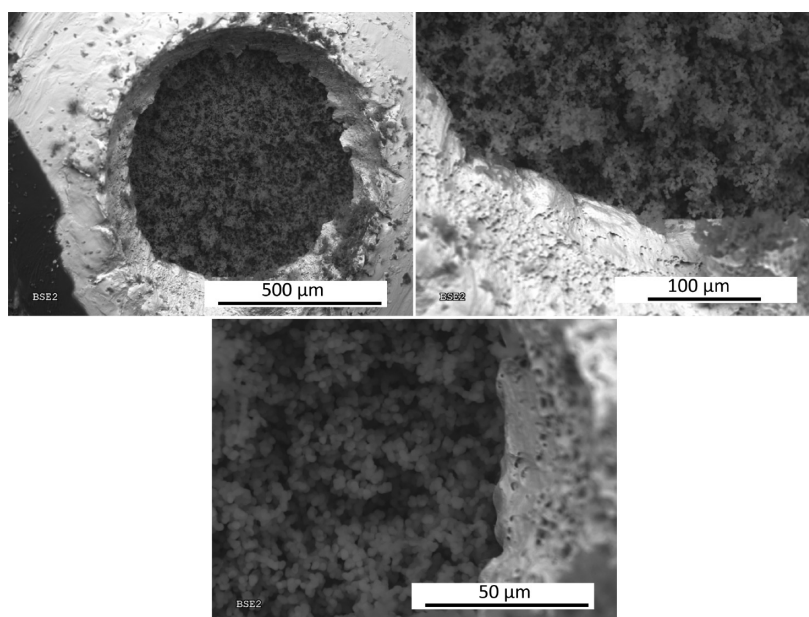
Finally, the last support studied is the fused silica capillary (250  $\mu\text{m}$  of inner diameter) because of its interesting applications in microreactors and HPLC columns. As in the previous cases, a very good interaction between the filling and

the support can be observed (Figure 9), leading to a good anchoring of the structure. In this sample, some  $\text{SiO}_2$  from the filling has been detached from the surface because of manipulation of the sample for the SEM analysis. The sample presents a silica filling density of 0.05 mg/cm.

As it has been shown, the incorporation of a silica thin film as a coating on the channels of the support, prior to the generation of the  $\text{SiO}_2$  porous filling, brings forth an enhanced interaction between the filling and the surface of the support. This has been proven for different thin films (micro and mesoporous) and also for  $\text{SiO}_2$  fillings prepared with different porosity agents. In all cases, the filling generated inside the structure maintains the dimensions of the channel, and no visible shrinkage has been determined. However, the porous nature of the  $\text{SiO}_2$  thin film plays a role on the adherence of the filling to the support and, when the mesoporous coating is performed, a more homogeneous and robust interaction between the filling and the coating is observed and a crack-free and mechanically stable material is obtained. In this case, the very good interaction between the coating and the filling might be related to the coating also playing a part in the solution/precipitation process that takes place during the formation of the silica filling. The proposed synthesis has proved to be efficient in different materials (supports) with different composition (such as cordierite, glass, stainless steel, and fused silica), and also with a large range of inner diameters (from 0.25 to 7.28 mm).

In all cases, the final materials display a highly marked hierarchical porous structure, where the filling maintains the macroporosity (related to the spheres interparticle size) and the mesoporosity within the  $\text{SiO}_2$  particles.

**Surface-Mediated Fillings Formation Mechanism.** As it has been demonstrated, the incorporation of a micro- or mesoporous silica thin film as a coating greatly improves the adherence of the filling synthesized by the sol-gel methodology to the walls of the support. However, significant differences depending on the porous nature of the coating can also be observed.



**Figure 8.** SEM images of F127-Meso-L surface-mediated filling.



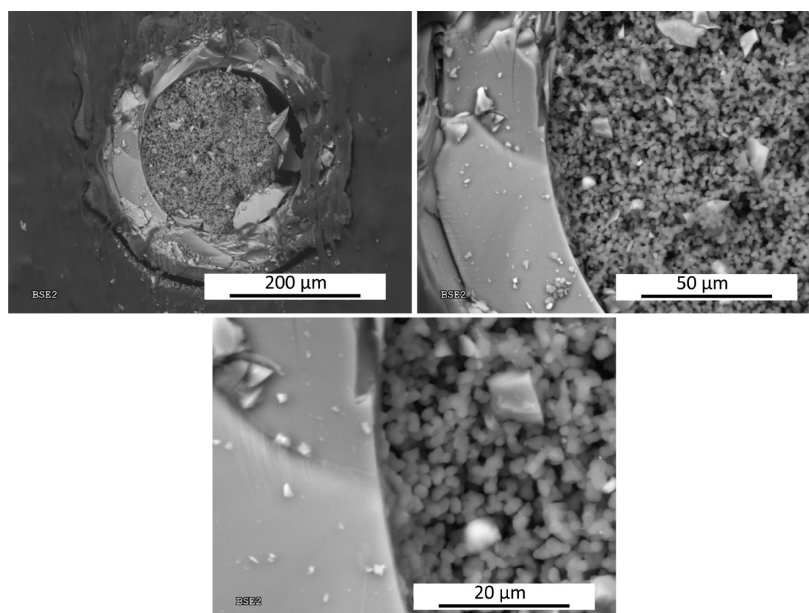
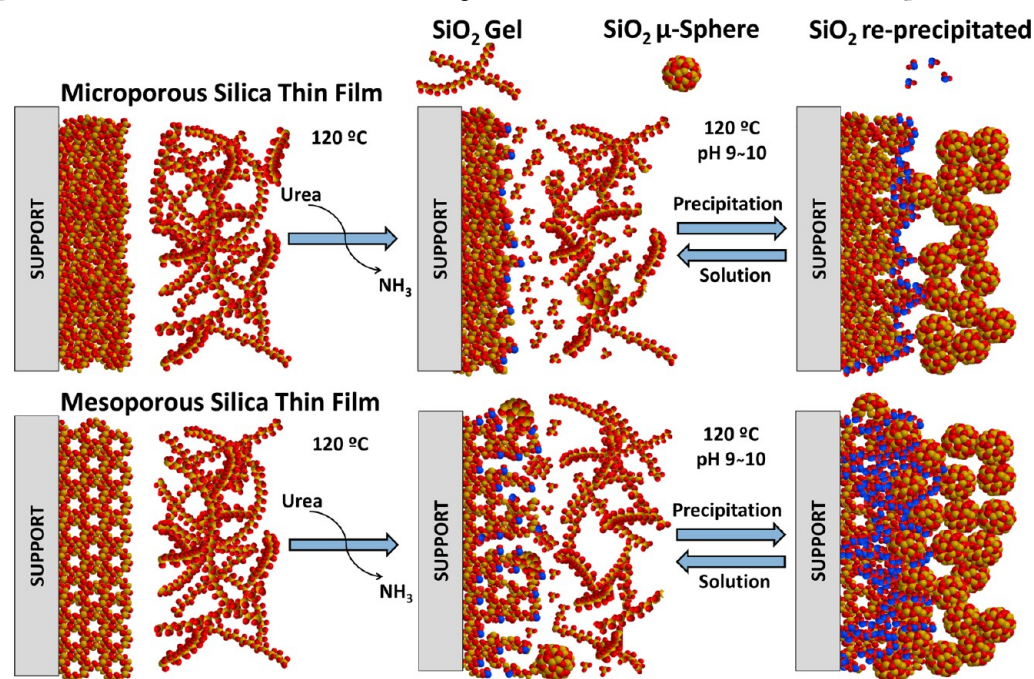


Figure 9. SEM images of the sample F127-Meso-C.

Scheme 1. Representation of the Surface-Mediated Filling Formation within the Micro- and Mesoporous Silica Thin Film<sup>a</sup>

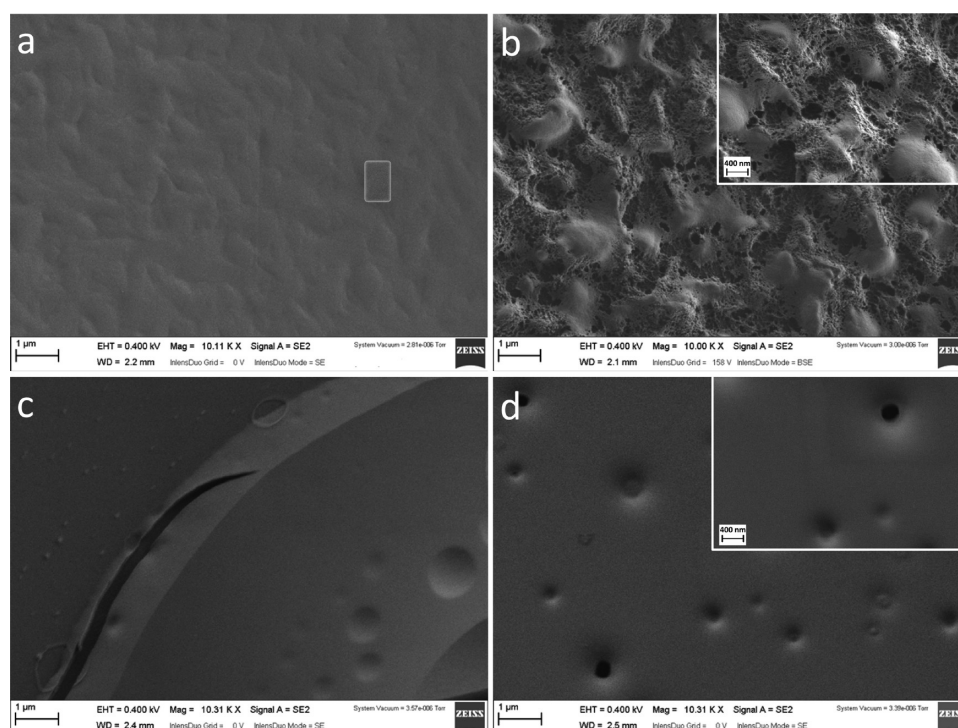


<sup>a</sup>Left: Silica thin films deposited on the walls of the support and the gel of the filling after hydrolysis. Middle: The urea decomposition at 120 °C takes place, producing the solution/precipitation reactions which produce the interaction between the partially dissolved silica thin film and the silica spheres produced by spinodal decomposition mediated by the re-precipitated SiO<sub>2</sub> (blue color). Right: The final structures are obtained, where the SiO<sub>2</sub> fillings are grown and maintain the interaction with the previously generated coating.

The first step of the synthesis is the incorporation of the silica thin film on the walls of the support. These thin films are synthesized and calcined, according to a procedure that produces silica coatings which are strongly anchored to the walls because of the thermal stabilization process.<sup>6</sup> The differences in the textural properties between the two thin films deposited on the supports (micro and meso-structured) are shown in Scheme 1.

When the silica precursor solution is submitted to the hydrolysis step, the acetic acid catalyzes the TMOS hydrolysis

and an amorphous gel is formed. This gel is not anchored to the walls or the silica thin film because no interaction takes place yet at such low temperature. The next step consists in a hydrothermal treatment at 120 °C for 6 h. The high temperature produces the urea decomposition, which increases the pH up to 9–10 and forms the mesoporous structure of the silica. The combination of the basic medium, the high temperature and the pressure inside the autoclave (or the sealed vessel) produces the solution/precipitation reactions of the silica.<sup>8,10,35</sup> At the same time, the spinodal decomposition



**Figure 10.** FE-SEM images of the mesoporous silica thin film, before (a) and after treatment with a urea solution at 120 °C (b) and the microporous thin film before (c) and after treatment with urea (d). Inset scale bars: 400 nm.

takes place in the gel. This process yields the formation of two separate phases in the system; on the one hand, one silica rich phase and, on the other hand, the water/surfactant rich one. The evaporation of H<sub>2</sub>O and the removal of the surfactant by calcination leads to the formation of the macroporous structure network and the silica spheres<sup>9</sup> which are well anchored to the walls of the support due to the chemical bonding with the reprecipitated silica.

When the solution/precipitation reactions that lead to the formation of the SiO<sub>2</sub> spheres take place in the system, we should take into account that the silica thin film deposited might also play a part in this process. In this sense, the silica layer also participates in the reactions (a part of the silica coating can be dissolved) and the porous structure can be made accessible to the synthesis solution (in samples with the appropriate porous texture).

At this point, the porosity of the thin film deposited is a critical parameter in the final material obtained. The mesoporous silica thin film presents a higher surface area than the microporous one together with a larger average pore size because of its mesoporous nature. In this case, the partial dissolution of the SiO<sub>2</sub> of the uppermost layers of the coating would make the ordered mesoporous structure of the coating more accessible for the SiO<sub>2</sub> gel to interpenetrate in it compared to the disordered microporous thin film. This would facilitate the SiO<sub>2</sub> spheres growth from the coating as well as a more firm anchoring point, generating a robust interface between the filling and the coating, as observed for sample F127-Meso-M (Figure 4.c and 4.d). In the case of the microporous coating (sample F127-Micro-M), the lower surface area of this material, together with the lower roughness would difficult the SiO<sub>2</sub> gel diffusion into the coating, generating in turn a weaker interface between the two materials (Figure 4a and 4b).

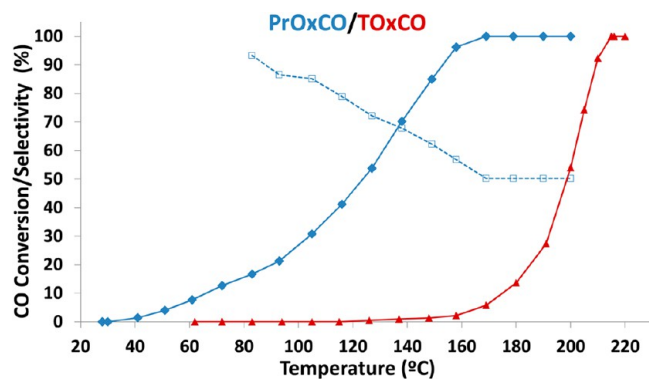
Figure 10 shows the FE-SEM images of the micro- and mesoporous silica thin film, before and after a thermal treatment in the presence of urea. The urea concentration and the temperature were the same as those used in the synthesis of the SiO<sub>2</sub> monolithic structure to evaluate the effect of the experimental conditions on the thin film previously deposited. The differences between the original silica thin films (Figure 10a and 10c for the meso- and microporous films, respectively) and the treated ones (Figure 10b and 10d) show a clear difference between the two films after undergoing the treatment with urea. In the case of the mesoporous thin film, the surface dissolution is reflected in the generation of a substantially rougher surface with an open porous structure with the appearance of large pores (macropores, of hundreds of nanometers). However, for the microporous silica thin film (Figure 10.d) the hydrothermal treatment with urea at 120 °C for the same time as its mesoporous counterpart does not produce the same effect on the silica surface. Figure 10d shows a smooth surface with a small fraction of pores created by the treatment with urea, resulting in a surface very similar to that depicted in Figure 10b. These pictures evidence that the use of a mesoporous silica thin film results in a surface with optimal textural properties for the anchoring and growth of a Surface Mediated Filling, as compared to a microporous silica thin film, which gives a surface with a comparatively smoother surface on which silica may be anchored to a lesser extent.

As evidenced in Figure 10, in both cases, while the silica thin film is being dissolved, the precipitation reaction is able to link and anchor the spheres formed in the filling and the more reactive surface (the silica coating) avoiding the silica shrinkage of the filling once the final structure is generated.

A representative scheme of the formation of these materials is shown in Scheme 1. As previously mentioned, in the case of the mesoporous coating, the SiO<sub>2</sub> gel can diffuse through the

open porous structure of the coating, whereas this diffusion is more limited for the microporous coating due to its lower surface area. Also, in the latter case, the dissolution of the outer layers of the film does not produce as significant an increase of the accessible surface as compared to the ordered mesoporous thin film, again limiting the interaction of the filling only with the external layer of the coating. As a result, when the mesoporous coating is deposited, the SiO<sub>2</sub> gel can diffuse deeper into the coating and the SiO<sub>2</sub> precipitates within the structure of the thin coating, whereas in the case of the microporous thin film this particle dissolution takes place to a much more limited extent, being detrimental for the formation of a strong interfacial binding between the deposited thin film and the grown hierarchical monolith. This process takes place for 6 h so that the system has enough time to reach equilibrium and the SiO<sub>2</sub> spheres are generated, interacting with the reprecipitated SiO<sub>2</sub> of the coating. This reprecipitated silica (blue atoms in Scheme 1) covers the spheres. Thus, the picture of the mesoporous thin film represented in Scheme 1 is in good agreement with the SEM image showed for the sample F127-Meso-C (Figure 9). For the microporous coating a weaker interface is generated and the final material presents impoverished mechanical properties.

**Catalytic Tests.** The Pt-loaded capillary with the surface-mediated filling (Pt-F127-Meso-C) has been tested as microreactor in the total and preferential oxidation of CO reactions. Pt nanoparticles have been analyzed by TEM and the average nanoparticle size is 3.3 nm. The catalytic results (CO conversion and selectivity) corresponding to both reactions are shown in Figure 11.



**Figure 11.** Catalytic performance of the Pt-loaded silica-filled capillary with the previous mesoporous silica thin film (Pt-F127-Meso-C) in TOxCO (red) and PrOxCO (blue) reactions. Solid symbols correspond to CO conversion and hollow symbols to the selectivity (for the PrOxCO reaction).

In both catalytic reactions (TOxCO and PrOxCO), the microreactor shows a good behavior oxidizing all the carbon monoxide at temperatures below 220 °C. In the TOxCO reaction (red plot in Figure 11), the catalytic conversion begins around 150 °C and has a total conversion of CO at 215 °C. However, when H<sub>2</sub> is included in the gas stream (PrOxCO reaction, blue line in Figure 11) the beginning of the catalytic activity occurs at much lower temperatures (~40 °C), and complete CO oxidation takes place at 170 °C. As it can be observed, when the total conversion of CO is achieved, the catalyst displays a selectivity value of 50%. The sample was analyzed by SEM after both catalytic tests without any noticeable detachment of the silica filling from the walls of

the capillary or change of the morphology of the micrometers silica spheres, thus indicating the robustness of the fillings.

In the case of the PrOxCO reaction, the operative temperature range for the microreactor (40–170 °C) is appropriate for the application, because the microreactor could efficiently work between the two temperatures of the low-temperature WGS reactor (200 °C) and the polymer-electrolyte membrane fuel cell (80 °C). Furthermore, it must be considered that for a CO conversion of 50% under the conditions studied, the selectivity of the microreactor is over 70%, which is remarkably high for such a system, enabling full CO abatement under the appropriate WHSV conditions at mild temperatures.

The different catalytic performance obtained in the two similar reactions studied is in good agreement with others works,<sup>36,37</sup> where the Pt catalytic oxidation of CO in H<sub>2</sub>-rich atmosphere starts at much lower temperatures than the total oxidation due to the H<sub>2</sub> promoting effect in the CO oxidation.

For this environmental applications the most widely used catalysts are based on CuO<sub>x</sub>/CeO<sub>2</sub><sup>38</sup> or noble metals supported on partially reducible oxides<sup>39,40</sup> that show a good catalytic performance both in PrOxCO and TOxCO reactions at low temperatures. These are also the active phases usually incorporated within the channels of microreactors in different structures, including stainless steel blocks<sup>41</sup> or silicon chips<sup>42</sup> where the catalyst is deposited by different methodologies. When compared to these active phases (tested as powder catalyst and also in microreactors), the Pt/SiO<sub>2</sub> catalyst of this work displays similar reaction temperatures and conversion values than these powder catalysts, with selectivity values above 50% at high conversion values, that are highly suitable for the applicability of these materials. In this respect, the sol-gel approach reported here adds the benefit of flexibility to the prepared systems, which can be grown into complex architectures (e.g., flexible tubes), facilitating their implementation in nonconventional integrated reactor configurations.

## CONCLUSIONS

In this work, we have reported a novel and straightforward methodology to improve the mechanical properties of silica fillings and completely avoid the shrinkage of the structure. Also, the materials prepared have proved to be effective and efficient when applied in different catalytic processes. This synthesis of surface-mediated fillings includes the incorporation of a (micro- or mesoporous) silica thin film over the walls of the support prior to the synthesis of the filling. It has been demonstrated that the synthesis is viable for different supports made up of different materials (cordierite, glass, steel, and fused silica) and in various configurations (honeycomb monolith, tube, line and capillaries) with a large range of inner diameters (from 0.25 to 7.28 mm) with very successful results. The fillings prepared have proven to be continuous throughout the different structures, for all the different porosity agents tested in this work, without significant differences in the textural properties of the fillings.

In all cases, a very good interaction between the thin coating and the filling has been established, with this interaction being responsible from the enhanced mechanical stability of the fillings within the channels. This interaction has been determined to be more favorable in the case where the thin film deposited has a higher surface area (mesoporous film) as compared to the microporous structure due to the open

ordered porosity of the structure and the easiness of diffusion of the SiO<sub>2</sub> precursor gel.

Finally, the process of the formation of the surface-mediated fillings is based on the solution/precipitation reactions that occur during the hydrothermal treatment and the anchoring of the silica filling to the previously deposited thin film. This methodology allows the preparation of novel materials named surface-mediated fillings with a highly ordered hierarchical structure, defined by the macroporous SiO<sub>2</sub> skeleton formed by highly mesoporous SiO<sub>2</sub> spheres of 4–6 μm. These materials are very interesting for a large number of applications, such as reactors, microreactors or HPLC columns. In this sense, successful results have been obtained for TOxCO and PrOxCO reactions performed in a capillary microreactor using the Surface Mediated Filling synthetic procedure and Pt nanoparticles as active phase of the catalyst, resulting in catalytic systems of high performance, especially in the PrOxCO reaction.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: a.berenguer@ua.es.

### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

HPLC = high performance liquid chromatography  
CTAB = cetyltrimethylammonium bromide  
TMOS = tetramethyl orthosilicate  
MTMS = trimethoxymethylsilane  
TMB = 1,2,3-trimethylbenzene  
TEOS = tetraethyl orthosilicate  
PEG = poly(ethylene glycol)

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