Synthesis of robust hierarchical silica monoliths by surface-mediated solution/precipitation reactions over different scales

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ABSTRACT: A new synthetic procedure to prepare novel materials (Surface Mediated Fillings) based on robust hierarchical monoliths has been developed. The methodology includes the deposition of a (micro- or mesoporous) silica thin film on the support followed by the growth of a porous monolithic SiO_2 structure. It has been demonstrated that this synthesis is viable for supports of different chemical nature with different inner diameters without any shrinkage of the silica filling. The mechanism of the formation 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_2 structures (monolith and thin film) depends on the porosity of the thin film and yields composite materials with different mechanical stability. The synthetic procedure described here allows the preparation of novel materials for many interesting applications, such as reactors, microreactors or HPLC columns.

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 properties¹. 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)^{2,3}.

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^{4,5}. 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like the hydrolysis rate and the solvent and surfactant concentration in the solution, the support is introduced and withdrawn from the precursor solution (i.e. dip-coated), and dried afterwards in a relative humidity controlled atmosphere.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 structure⁶.

The general synthesis of mesoporous silica used by N. Tanaka⁷ and G. Puy⁸ produces silica spheres of a few microns in diameter by spinodal decomposition, as described by K. Nakanishi⁹. 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) while, 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 around 9-10), the temperature and the pressure enhances the solution/precipitation equilibrium giving rise to the final porous inorganic structure¹⁰.

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^{9,11,12}. Generally, this shrinkage impacts negatively on the properties and the mechanical stability of the material with views towards 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^{8,13}. 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)¹⁴⁻¹⁵ because its properties are easy to modulate, such as meso- and macroporosity, pore size distribution, surface area, surface chemistry, etc.¹⁶. 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 material¹⁶.

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^{17,18}. Another strategy to avoid the shrinkage reported by Tanaka and co-workers¹⁹ consists in combining two silica precursors, TMOS and MTMS, but their results were limited to samples with dimensions below 250 μm (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 structure²⁰.

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 tetrahydrofuran²⁰, and others have treated the silica obtained with supercritical CO_2 extraction to avoid the drying step¹². Combining different polymers (TMB, divinylbenzene and styrene) has been successfully applied in capillaries of 100 μm of inner diameter, without the need of a calcination step²¹. 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 shrinkage²².

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.

EXPERIMENTAL SECTION

Materials. In order 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 μm and a length of 20 cm (Agilent).

The silica precursors (TMOS and TEOS), urea, acetic acid, hydrochloride 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^{23,24}.

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°C for 6 h with a heating rate of 3°C/min. However, the rest of the supports were calcined in a vacuum oven (Thermo Scientific) at 300°C for 24 h at 3°C/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 solution²⁵. 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 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^{8,26}. 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°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 minutes at 5°C). Then, the samples were heated at 40°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.

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 SiO₂ deposited as thin films were also characterized as a powder by N₂ adsorption-desorption at -196°C and by CO₂ adsorption at 0°C (Quantachrome, Autosorb 6B) to analyze the porous texture of the materials.

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 SiO₂ filling and the porous nature of the previously silica thin film deposited. The final shrinkage (%) observed in each sample is shown, as estimated by SEM.

Sample	Porosity Agent in the Filling	Silica Thin Film	Support	% Shrinkage*
F127-Non-M	Pluronic® F127	-	Cordierite Monolith	7
F127-Micro-M	Pluronic® F127	Microporous	Cordierite Monolith	~7**
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	-

*Estimated from SEM images observation.

**No homogeneous shrinkage has been observed in the sample, 7 % corresponds to the maximum shrinkage measured (see Figure 4.a and 4.b below).

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 materials²⁷, 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 ($450 \text{ m}^2/\text{g}$) than that of the mesoporous structure ($700 \text{ m}^2/\text{g}$)²⁸.

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

These two porous SiO_2 structures have been used as seeding/anchoring surfaces for the growth of the SiO_2 porous fillings. These thin films have been deposited onto different surfaces (supports) with different chemical nature, i.e. honeycomb cordierite monolith, glass tube, steel line and fused-silica capillaries, in order 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_2 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_2 and CO_2 adsorption. The results indicate that there are no significant differences in the textural properties of the SiO_2 structures independently of the nature of the porosity agent. In all cases, the SiO_2 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 $\sim 200 \text{ m}^2/\text{g}$ 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 $0.04 \text{ cm}^3/\text{g}$ calculated by the Dubinin-Radushkevich method in CO_2 adsorption and $0.09 \text{ cm}^3/\text{g}$ in N_2 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 $6 \mu\text{m}$. 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. This is in very good agreement with the published results for similar materials prepared with PEG-based surfactants^{8,9}. 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^{8,9}.

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

Non Surface Mediated Fillings. Prior to the surface mediated fillings, the SiO_2 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_2 spheres can be seen in all the channels, regardless the size and nature of the support. However, some SiO_2 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 ($\sim 20\%$). 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 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_2 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^{7,27}.

As a general feature, the poor interaction between the hierarchical SiO_2 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.

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).

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

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).

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 3.a and 3.b). The sample F127-Micro-M (Figure 4.a and 4.b), 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 4.c and 4.d) does not present any shrinkage in any direction. The monolith channel is completely filled with mesoporous silica due to 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_2 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 analysis without a cracking of the structure and/or detachment from the walls. In contrast, when the microporous thin film is coated, the 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.

In order 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.

Figure 5. SEM pictures of different transversal sections of the honeycomb cordierite monolith Surface Mediated Filled with Pluronic® F127 mesoporous silica (F127-Meso-M).

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 previously described as coating. Then, different SiO₂ 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 6.a, 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 6.b 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 6.c and 6.d. It should be mentioned that the use of this family of surfactants is commonly extended for the preparation of hierarchical silica with interesting applications^{29,30,31}.

Figure 6. Scanning Electron Microscopy images of P123-Meso-M (a and b) and PEG-Meso-M (c and d).

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 SiO₂ 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 SiO₂ contained in the samples was determined by weight difference. For these monoliths, the mass is around 1.48 mg silica/cm_{channel}.

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.

Figure 7. Optical and Scanning Electron Microscopy images of the sample F127-Meso-T.

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 3.e and 3.f). In 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 SiO_2 porous structure is continuous in the entire length of the

Figure 8. SEM images of F127-Meso-L Surface Mediated Filling.

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 μm of inner diameter) due to 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 SiO_2 from the filling has been detached from the surface due to manipulation of the sample for the SEM analysis. The sample presents a silica filling density of 0.05 mg/cm.

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

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 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 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 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 SiO_2 particles.

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).

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.

Here, we analyze in detail the different stages of this synthetic procedure and the chemical processes that take place, in order to deepen into the role of the silica coating and to analyze the reasons for this enhanced interaction.

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 due to the thermal stabilization process⁶. 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 (TMOS, acetic acid, urea and porosity agent) is introduced inside the support, it is submitted to the hydrolysis step, where 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^{8,10,32}. At the same time, the spinodal decomposition 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 H₂O and the removal of the surfactant by calcination leads to the formation of the macroporous structure network and the silica spheres⁹.

Scheme 1. Representation of the Surface Mediated Filling formation within the micro- and mesoporous silica thin film. 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_2 (blue color). Right, the final structures are obtained, where the SiO_2 fillings are grown and maintain the interaction with the previously generated coating.

When the solution/precipitation reactions that lead to the formation of the SiO_2 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 due to its mesoporous nature. In this case, the partial dissolution of the SiO_2 of the uppermost layers of the coating would make the ordered mesoporous structure of the coating more accessible for the SiO_2 gel to interpenetrate in it compared to the disordered microporous thin film. This would facilitate the SiO_2 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_2 gel diffusion into the coating, generating in turn a weaker interface between the two materials (Figure 4.a and 4.b).

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_2 monolithic structure, in order to evaluate the effect of the experimental conditions on the thin film previously deposited. The differences between the original silica thin films (Figures 10.a and 10.c for the meso- and microporous films, respectively) and the treated ones (Figures 10.b and 10.d) 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 10.d 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 10.b. 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.

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. Initially, the thin layer of SiO₂ (micro- or mesoporous in character) is well anchored to the substrate, while the silica gel is formed after the hydrolysis step at 40°C. Then, the hydrothermal process occurs at 120°C, producing the urea decomposition and the pH increase. At this step, the solution/precipitation reactions take place, during which the formation of the silica spheres by spinodal decomposition occurs and also the partial dissolution of some SiO₂ from the coating. In the case of the mesoporous coating, the SiO₂ 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 SiO₂ gel can diffuse deeper into the coating and the SiO₂ 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 SiO₂ spheres are generated, interacting with the re-precipitated SiO₂ of the coating. Finally, the solvents and surfactants are removed and the final structure is generated. In the case of the mesoporous coating, a good interface between the coating and the filling is obtained and a crack-free material is observed, the SiO₂ μ -spheres are well anchored to the walls of the support due to the chemical bonding with the re-precipitated silica. This re-

precipitated silica (blue atoms in Scheme 1) are covering the spheres, 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.

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. 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 SiO₂ 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 SiO₂ skeleton formed by highly mesoporous SiO₂ spheres of 4–6 μ m. These materials are very interesting for a large number of applications, such as reactors, microreactors or HPLC columns and present, as a further advantage, that no additional chemicals apart from those typically used to prepare porous silica are needed.

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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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