Foam silica films synthesized by a calcium chloride-assisted emulsification

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KEYWORDS: Macroporous, foam, silica, calcium chloride, evaporation induced emulsification, surfactant

ABSTRACT

The development of porous films presenting accessible high specific surface area is important to design new adsorbents, sensors or catalyst supports. Here, we describe a simple method to prepare a foam silica coating by using an evaporation induced emulsification method assisted by calcium chloride. An alcoholic silica sol containing calcium chloride and a poly(ethylene oxide) containing polymer is deposited on a substrate by dip-coating. The alcohol evaporation induces a phase separation between a silica-rich phase and a calcium-rich one. The droplets size increases via a coalescence process until the sol gelation, which determines the final pore size comprised between 100 nm and 3 μ m. Thermal analysis and droplet evaporation monitoring both confirm that the solvent departure is delayed by the presence of calcium chloride into the sol. Influence of the polymer nature on the porosity is discussed. Using a block copolymer such as the Pluronic F-127, which strongly stabilizes the emulsion, allows to reach a low pore size (400 nm) while on the opposite, we propose to use a short poly(ethylene glycol) (PEG) such as the PEG-400, which weakly stabilizes it, leading

to larger pores (2-3 microns). Moreover, we show that adding a zirconium salt ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) into the silica sol speeds up the condensation step of the silica network and leads to the decreasing in the pore size.

INTRODUCTION

Control of macroporosity of coatings remains a key issue to develop new chemical sensors, absorbents, stationary phases for ultrathin-layer chromatography or micro-fluidic devices.¹⁻⁴ Macroporous silica films may be helpful for the accommodation of bulky biomolecules and diffusivity of organic molecules², separation of biomolecules⁵⁻⁷ or as antibacterial coating.⁸ Some studies indicate their use as buffer layers between a glass and a polyurethane layer to depress the shear stress occurring on the glass-polymer interface.^{9,10}

Many procedures have been devised to produce porous materials including surfactant, colloidal crystal, polymer or emulsion templating, as well as phase separation, selective leaching and replication.¹¹ Macroporous silica coatings can be obtained through a templating process consisting in the condensation of the oxide framework around some hard templates.^{1,2,5,11-14} For instance, polystyrene latex spheres were first introduced into a silica sol which was spin-coated before to be dissolved to generate macropores. Macroporous silica films can also be obtained by the emulsion templating method which is an easier method compared to the hard templating process.^{13,15-30} Various silica macroporous morphologies can be synthesized by inducing a spinodal decomposition parallel to the sol-gel transition. Based on this concept, the technique of fabricating well-defined macroporous monoliths has been established in various silica-based systems by Nakanishi *et al.*¹⁵⁻¹⁶ Some reports have been published on the formation of phase-separating surface morphology during the dip-coating process of titania sols containing poly(ethylene oxide).¹⁷⁻¹⁸ By adopting methyltrimethoxysilane, as a gel-forming constituent together with low molecular poly(ethylene oxide), similar control of the macroporous morphology could be performed.¹⁹⁻²⁰ It was evidenced that the preferential evaporation of highly volatile constituents during dipping induces both the phase separation and gelation. Macroporous hydrophobic organosilicate films have been also studied by Wongcharee *et al.*²¹⁻²² using methyltriethoxysilane as precursor and some surfactants. The effects of surfactant addition, surfactant properties and atmospheric humidity have been explored. It was proved that as films dried, the preferential evaporation of the ethanol resulted in an increase of the relative water content. This explains the

development of phase separation between the hydrophobic gel and the aqueous liquid and at the end the obtention of macropores. The surfactant adsorption at the aqueous phase/gel interface has a strong influence on the extent of the phase separation and therefore on the resulting pores.²¹⁻²² Derived from the well-known emulsion templating method, the use of some salts is also reported to generate macroporous structures.²⁷⁻³⁰ This latter method was reported for the first time by Stucky *et al.*²⁷ Sponge-like silica membranes have been synthesized by a phase separation process in the presence of inorganic salts and self-assembling block copolymers. The macropore dimensions can be controlled according to the sizes of the salt solution droplets. Later, the use of alkaline earth cations with a surfactant has been reported to synthesize macroporous quartz coatings.²⁸⁻³⁰ The mechanism of porosity formation is associated to the emulsification assisted by the presence of a salt. Thus, porous silica films were obtained by dip-coating of a system composed of alkaline earth cations in amphiphilic molecular templates. By changing the surfactant and the synthesis conditions, the porosity of the silica film can be controlled, varying from a few tens of nm to 1 μm . Another effect of salt addition on the colloid aggregation has been studied and CaCl_2 is reported as an accelerator for inducing gelling in silica sols.³¹⁻³²

In this work, a similar emulsion templating induced during the solvent evaporation and assisted by the presence of a polymer and calcium chloride salt, is first described. This method allows generating macroporous silica films. The study is focused on the comparison between two polymers to generate the emulsion: a short poly(ethylene glycol) PEG-400 and a block copolymer F-127. The use of short polyethyleneglycol assisted with a salt to synthesize macroporous silica films using such emulsion templating method has never been reported before. It has been shown that the nature of polymer (PEG-400 or F-127) highly impacts the porous texture. The doping of silica with zirconia was already reported in ceramic toughening, alkaline-resistant glass and heterogeneous catalysis.³³⁻³⁹ Here, the use of a zirconium salt as a dopant is proposed for the first time to control the kinetics gelation and the resulting silica pore size.

EXPERIMENTAL SECTION

Materials

A poly(ethylene glycol) PEG-400 or a Pluronic® F-127 copolymer of ethylene oxide (E) and propylene oxide (P), were used for the emulsion formation. Reactants, Pluronic® F-127 ($\text{E}_{106}\text{-P}_{70}$ -

E₁₀₆), PEG-400 (E₉), tetraethoxysilane (TEOS) (Si(OEt)₄), calcium chloride (CaCl₂·2H₂O), and zirconium oxychloride (ZrOCl₂·8H₂O) were purchased from Sigma-Aldrich and used as received.

Silica coating preparation:

In a typical experiment, a silica sol was prepared by mixing TEOS (4 g, 19.2 mmol), in ethanol (10 g) with acidified water (HCl 0.1M, 1.8 g), and a poly(ethylene oxide) containing polymer such as PEG-400 (1 g, 2.5 mmol) or the block copolymer F-127 (1 g, 0.08 mmol). Calcium chloride CaCl₂·2H₂O (2 g, 13.6 mmol) was then dissolved into the silica sol. In some experiments, a zirconium salt ZrOCl₂·8H₂O (309 mg), corresponding to the ratio Zr/Si=0.05, was added in the sol at the end of the preparation, after one hour of TEOS hydrolysis. This ethanol/water ratio favors the homogeneity between silica and zirconia.³³ After 30 min of reaction, the sol was deposited by dip-coating on an aluminum or glass substrate with a speed rate of 1 mm.s⁻¹. The films were, then, aged under ambient conditions (T = 23 °C, RH = 30-40%) for 24 h. The films became white during this drying stage. Then, they were calcined at 350 °C for 2 h, with a heating ramp of 10 °C min⁻¹ to eliminate the polymer. A washing step in water for 30 min was finally used to eliminate the calcium salt.

Characterization:

Scanning electron microscopy SEM images were obtained using a Zeiss Merlin Compact SEM with an SE2 detector at a low acceleration voltage up to 5 kV. Energy dispersive X-ray analysis (EDX) was used to determine the ratio Ca/Si within the film.

Observations of the evaporation were done with a Kruss EasyDrop goniometer. Droplets (10 µL) of solutions used to prepare the films were deposited on a PTFE substrate. Contact angle have been measured using the Young-Laplace model. Surface tension measurements of polymer aqueous solutions have been done with the Kruss EasyDrop goniometer at room temperature and at a polymer concentration of 12.5 g/L without salt or with salt at concentration of 15 g/L. Others measurements have been done at higher concentration in polymer (250 g/L), without salt. Image J has been used to perform SEM analysis and to obtain the pore size distribution. Infra-red spectra of the solids were recorded on a Safas Monaco IR700 spectrometer. Thermogravimetric analysis TGA were performed with a Mettler Toledo TGA/DSC 2 instrument under the following conditions. Around 10 mg of the solution used to prepare the film were placed inside a 150 µL alumina crucible with a pre-pierced cover. Temperature was increased from ambient up to 150 °C at 5°C/min. Air of

high purity was used as reactive gas at a rate of 50 mL. min⁻¹. The evolved gases (EtOH, H₂O) were analysed with a portable micro-gas chromatograph micro GC (SRA Instruments) coupled to a mass spectrometer detector Agilent 5975 Network. The micro GC is equipped with 3 modules, each one composed of a column and a thermal conductivity detector (TCD). Water was separated and followed on PPU (PoraPlot-U) capillary column, while EtOH on OV1 (Ohio Valley, 100% dimethylpolysiloxane) capillary column.

Differential scanning calorimetry DSC analyses were performed on a DSC1 Mettler-Toledo apparatus. The solution used to prepare the film (ca. 10 mg) was placed in a 40 µL aluminium pan, with a pierced lid and sealed before introduction into the DSC cell. The temperature was increased from 5°C to 100°C at 5°C.min⁻¹, under nitrogen, then cooled down to room temperature. Standards used for the control calibration test were indium and mercury. The calibration tests for Hg and In melting temperatures showed errors below 0.3%.

RESULTS

Macroporous silica film prepared with PEG-400

By using a single block polymer such as the PEG-400, the as-prepared films present a macroporous morphology, constituted of large pores with a size measured between 2 and 3 µm (Fig. 1a & 1b). The macroporous morphology is explained by a phase separation occurring during the dipping process between two liquid phases, one silica-rich phase which transforms into a gel and a calcium-rich aqueous phase, generating the pores. The pore size distribution was estimated thanks to an image analysis by using Image J (Fig. 1c). The curve has been fitted using a normal distribution function allowing to estimate the mean diameter at 2757 nm with a 442 nm standard deviation. Previous steps of the process have also been observed. The coating morphology by SEM as well as its elemental composition by EDX have been observed on the sample shaped by dip-coating before the thermal treatment (Fig. 2). After the dip-coating process (Fig. 2a), the porosity is already created, as shown by the silicon repartition on the corresponding mapping (Fig. 2a3). The calcium mapping shows as for it that the largest cavities contain a lot of calcium, while the smallest ones are bordered with the calcium salt (Fig. 2a2). This feature tends to indicate that a phase separation process occurred during the solvent evaporation step. After the thermal treatment (Fig. 2b), the crystallized calcium chloride is only present at the periphery of the pores (Fig. 2b1 and 2b2). This buildup of

calcium at those areas may be explained by the localization of the calcium chloride inside the former liquid droplets. After the washing step (Fig. 2c), the calcium is almost undetectable, and the atomic Ca/Si ratio initially measured at 0.6 decreases to 0.1 (Table S1). These whole observations prove that the calcium chloride salt, soluble in ethanol, is then mainly located in the liquid phase which doesn't contain silicon.

Observation of the solvent evaporation step using Optical microscopy

The solvent evaporation step has been monitored over time by using optical microscopy at room temperature and at a relative humidity of 60% (Fig. 3). The water droplets nucleation is first occurring and followed by their coalescence, this phenomenon is observed to be fast during the first minute (Fig. 3a to 3c) and slower during the second one (Fig. 3d to 3f), as the silica sol becomes a gel. After 2 minutes, the film appearance remains unchanged. This observation tends to show that the emulsification occurs during the solvent evaporation and that the calcium-rich liquid droplets size rapidly increases due to the coalescence phenomenon until the silica condensation stops the destabilization process. It is worth mentioning that by suppressing either the polymer or the calcium chloride within the sol, a non-porous silica coating is obtained, meaning that the emulsification process which determines the foam formation needs both the polymer and the calcium salt to occur.

Observation of the solvent evaporation step using thermal analysis

The sol evaporation has also been followed using DSC analysis (Fig. 4a). Both DSC curves (Fig. 4a) recorded on two sol systems incorporating or not a calcium salt displays an endothermic peak related to the solvent evaporation. By comparing both graphs, this peak appears shifted by a couple of degrees within the calcium salt system. Likewise, comparison of both associated thermograms (Fig. 4b) shows the weight loss associated to the solvent evaporation. It confirms that the solvent departure is delayed in the case of the sol containing the calcium salt. Indeed, the total weight losses at 105°C are of 74 % vs 84%. These weight losses are due to the complete departure of water and ethanol from the sols and coincide with the theoretical losses. In the calcium containing sol, the loss (74%) is, as expected, below the loss of the sol without calcium (84%). To compare more easily the evaporation process in the two sols, we have calculated the relative weight loss (weight loss%/total weight loss%). This value corresponds to the evaporation rate curves shown

in Fig. 4c. At 80°C, the sol without calcium has already lost 90% of its total loss; while the calcium containing sol has lost only 75% of its total loss. This difference is due to the solvent retention induced by the calcium salt. Finally a micro GC experiment coupled with TGA allows to analyze the gas evolved during the evaporation (Fig. 4d). This analysis allows to observe in both cases, expected ethanol and water removing. The red curves showing ethanol evaporation are similar for both sols, but a small delay is noted in the calcium containing sol. The two green curves showing water evaporation are strongly different (Fig. 4d). The green filled curve (calcium chloride containing sol) is delayed compared to the green dotted curve (without calcium chloride sol). Water evaporation is drastically postponed in the sol containing calcium chloride.

Macroporous silica film prepared with a block copolymer F-127

Silica coatings have been also obtained by using triblock copolymer F-127 instead of the PEG-400. SEM pictures (Fig. 5a) obtained on samples after thermal treatment and washing, show that silica films display a foam morphology, with submicrometric pore size. By using an image treatment, the pore size distribution is measured to be between 200 nm and 600 nm (Fig. 5b). The curve fitting using a normal distribution function leads to a 401 nm mean diameter (MD) with a 144 nm standard deviation (SD). An observation of the section of the film (about 1 μm) confirms its porous nature (Fig. 5c).

Surface tension measurements and monitoring of the droplet evaporation with the goniometer

Experiments have been done to characterize the surface tension of the different polymer aqueous solutions (12.5 g/L) without salt by using a pendant drop test at room temperature (20°C). PEG-400 has a small effect on tension surface of water that slightly decreases from 72 to 65 dyne/cm. The block copolymer F-127, as expected for a classical surfactant, is much more efficient to decrease the surface tension of water from 72 to 40 dyne/cm. With a higher polymer concentration (250 g/L) without salt, a decrease of surface tension is also observed (from 72 to 59 dyne/cm for PEG-400 and to 37 dyne/cm for F-127). This analysis could explain why both polymers are able to stabilize the emulsion. Indeed, the PEG-400 is known as an hydrophilic polymer but it can display a “surfactant-like” behavior as it decreases the surface tension of water.⁴⁰⁻⁴⁸ These observations may also explain the differences observed in the obtained porous structures, and how a classical surfactant like F-127 can stabilize for a longer time smaller droplets, delaying the

coalescence, while the PEG-400 has a weaker ability to stabilize the droplets. Contact angles measurements (on PTFE substrate) have also been done using water. In the aqueous solution of PEG-400 (12.5 g/L), the contact angle is around 101°, while for the F-127, this angle is around 82° (Fig. S1). This result confirms the surface tension measurement, showing that F-127 strongly decreases the contact angle while the PEG-400 has a small impact. We have tried to observe the influence of the salt on the surface tension in the presence of polymers. After adding salt (at a concentration 15g/L), the measured surface tension does not seem to change, neither the contact angle. A lot of studies are relative to the salt influence on the behavior of PEG or block copolymers.⁴⁵⁻⁵⁵ PEG tends to form complex with salts and these complex are considered to have cations trapped within the PEO helices. Salts decrease the cloud point of PEG containing polymers and favorise their phase separation process.⁴⁵⁻⁵⁵ By considering the concentration of salt and polymer used in this study (ratio PEO/Ca 1.25 for F-127 and 1.6 for PEG-400), the salt could be linked to the polymer and could participate to the phase separation process. But this interaction is probably not determinant in the emulsion formation since the use of a cationic surfactant instead of a poly(ethylene oxide) containing polymer also leads to similar foam morphologies.

The droplet evaporation within the sols at 20°C and 60% of relative humidity has been followed using a goniometer instrument (Fig. 6). It confirms that calcium salt prevents the water evaporation, since water is still clearly present after 5 min (Fig. 6b) while it has totally disappeared when the calcium salt is not used (Fig. 6a). It also shows that the surfactant nature has an impact on the gelation process since the droplet containing F-127 rapidly becomes a solid at room temperature. The picture of the Fig. 6d is frozen after 2 minutes and do not change anymore. The gel formation is confirmed after contact with a tip. While PEG-400 containing droplet remains a liquid (Fig. 6c). Solvent evaporation from solutions containing PEG-400 leads to liquid droplets after 5 min (Fig. 6e & g) while the same experiment with solutions containing F-127 leads to gels after 5 min, as shown with the images of Fig. 6f & h which remain frozen (pictures in insert show the droplet after tip contact). Then, F-127 contributes to a more rapid gelation of the sol. The main parameter explaining the formation of larger pore obtained with a poly(ethylene oxide) could be related to the low decrease of the surface tension and to what happen during the first two minutes of the solvent evaporation. Using a poly(ethylene oxide) of higher molecular weight such as PEG-6000, solid at room temperature instead of the PEG-400 does not have a great impact on the pore size. The initial contact angles are

comprised between 41 and 48°, since solutions contain alcohol. During the solvent evaporation process, the contact angle increases progressively in the case of the P-400 containing solutions reaching around 60°. On the opposite, for the F-127 containing solutions, the contact angle decreases during the solvent evaporation. The higher wettability on the PTFE substrate of F-127 containing sol compared to the PEG-400 containing sol, already noted in Fig S1, is confirmed. Moreover, salt seems to induce an increase of the contact angle (Fig. 6c & 6e).⁵⁶

Influence of a zirconium salt addition in the sol

By introducing a zirconium oxychloride salt in the sol, the condensation kinetic is changed with a silica sol gelation noted within 24 h for both surfactants. This modification of the gelation kinetics has a major influence on the film morphology as it can be observed in the case of zirconium oxychloride salt / PEG-400 containing film, in Fig. 7. The pore size in the formed macroporous film strongly decreases (Fig. 7a). An image analysis with Image J allows giving a broad pore size distribution between 200 to 400 nm, centered on 300 nm (Fig. 7c). The fit of the curve using a normal distribution gives a 306 nm mean diameter and a 47 nm standard deviation. The morphology in all the thickness of the film is also impacted as noted on the image Fig. 7b, in which the porous film appears to be constituted of several layers presenting a foam like morphology. In the case of F-127 containing film (Fig. 5d), the zirconium salt addition also leads to a pore size decreasing below 100 nm. A consequence of the zirconium salt addition is also to produce an important increase of the acidity which can also promote the silica condensation. If, instead of ZrOCl_2 , an equivalent amount of HCl is added in the silica sol, at the end of the preparation, a macroporous film is still obtained with similar pore size, but the pore's density is considerably reduced (Fig. 7d). This feature tends to indicate that kinetic of the silica gelation has a direct influence on the foam pore size. If the silica gelation is speed up, the duration for the destabilization of the emulsion between the calcium-rich phase and the silica-rich phase is shorter, which allows a lower calcium-rich liquid droplet size and then a lower pore size within the final film. To better understand the role of zirconium oxychloride, other analyses have been done. First, SEM/EDX analysis performed on the film after thermal treatment shows that zirconium is homogeneously distributed and that its distribution coincides with the silicon one (Fig. 8). Besides, FTIR analysis confirms that zirconium is fully integrated inside the

silica network since the vibration characteristic of Si-O-Zr bound is seen at 960 cm^{-1} in the zirconium containing gels obtained from the sols with calcium (Fig. S2b) and without calcium (Fig. S2a).³³⁻³⁹ Water vibrations at 1620 cm^{-1} are very strong in the calcium containing samples (Fig. S1b), showing that calcium salt maintains water in the sample.

The sol evaporation was followed with the goniometer by depositing one droplet on a PTFE substrate (Fig. 9). When ZrOCl_2 is introduced into the sol, the droplet evaporation is strongly modified. After 4 minutes, gelation has occurred in the PEG-400 containing sol (Fig. 9b), while the sol without zirconium is still liquid after 30 minutes (Fig. 9a). In the case of F-127 containing sols, the same observation is done within shorter times. The sol with zirconium salt gelifies in one minute (Fig. 9d) while the sol without zirconium needs about 5 minutes to gelify (Fig. 9c). This analysis clearly confirms the influence of zirconium salt on the gelation kinetics. The HCl addition instead of ZrOCl_2 also induces an acceleration of the silica gelation, but the gelation time remains clearly higher. Then, ZrOCl_2 probably acts both as a network modifier and as an accelerator of gelation.

To resume, the Figure 10 illustrates that foam silica film of $1\text{ }\mu\text{m}$ thick can be easily deposited on a glass or aluminum substrate, by using a silica sol containing calcium chloride and a poly(ethylene oxide) containing polymer (Fig. 10). The solvent evaporation begins with the departure of an ethanol-rich gaseous phase and induces an emulsion formation between a silica-rich phase and a calcium-rich one. The presence of the calcium salt allows preserving an emulsion onto the silica film. The calcium-rich liquid droplets become larger and larger by a coalescence process. The coalescence process is stopped when the silica sol is turned into gel. After the thermal treatment, the water and ethanol are removed while the calcium salt is still present. The washing step with water allows the calcium salt elimination from the pores, even if some small quantity of calcium may be still observed within the silica phase. Thermal analysis (Fig. 4) and droplet evaporation monitoring (Fig. 6) have shown that the calcium salt presence delays the solvent evaporation. It explains how calcium chloride is an efficient salt to design such foam silica coatings, the hygroscopic character of the salt could be an essential feature involved in this emulsification templating process.^{53,57} Another parameter is the solubility of the salt in ethanol. Optical microscopy monitoring (Fig. 3) suggests that coalescence may occur during the first few minutes of the emulsion formation, while the solvent evaporates and the silica sol progressively condenses into a gel.^{58,59} This coalescence slows down as the silica condensation

occurs and the sol viscosity increases. The addition in the sol of a poly(ethylene oxide) containing polymer (F-127 or PEG-400) is necessary to stabilize the emulsion. By using a block copolymer F-127, a classical surfactant, droplets can be stabilized with a size around few hundreds of nanometers. We have seen that the F-127 surfactant induces a strong decrease of the measured surface tension and then a low pore size. On the contrary, the use of a poly(ethylene glycol) which decreases moderately the surface tension, leads to the formation of some larger micrometric porosity.

Addition of a zirconium oxychloride salt into the silica sol allows increasing the gelation kinetics and consequently decreasing the droplet size. As the condensation kinetics of silica is increased in presence of ZrOCl_2 , the coalescence process inducing the droplet size growth could be stopped earlier and a silica foam with smaller pore size is obtained. FTIR (Fig. S2) and EDX analyses (Fig. 8) have shown that zirconium is homogeneously distributed inside the silica. The emulsification process described in this paper allows creating silica films with macropores of controlled size. The described emulsion templating process involves complex interactions between both a silica precursor involved in sol-gel hydrolysis and condensation reactions, a hygroscopic salt soluble in ethanol and a poly(ethylene oxide) polymer.

CONCLUSION

Silica foam coatings were synthesized using an emulsion templating process induced by solvent evaporation and assisted by a calcium chloride salt. The presence of a hygroscopic salt, such as calcium chloride, favours the formation of an emulsion in the silica sol, which is stabilized by a surfactant or a poly(ethylene oxide) polymer. By modifying the nature of the polymer, a control of the pore size distribution can be adjusted from 100 nm to 3 microns. The block copolymer F-127 has a stronger ability to decrease the surface tension compared to the PEG-400 polymer and leads to silica films with a smaller porosity (400 nm). Using a silica sol doped with a zirconium oxychloride salt, the gelation kinetics of silica can be speed up as the coalescence of the droplets is stopped more rapidly, leading to a better control of the porosity.

ASSOCIATED CONTENT

Supporting Information

Table S1: EDX elements content (%atom) of a silica coating, on an aluminum substrate (error bars of 5%), prepared with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and PEG-400 during the different steps of the process. **Fig. S1:** Contact angle on PTFE substrate of aqueous solutions of PEG-400 and F-127 (12.5 g/L) without CaCl_2 . **Fig. S2:** FTIR spectra of the gels obtained from the sols containing PEG-400 and the silicon precursor without (black) and with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (blue), without CaCl_2 (a) and with CaCl_2 (b).

ACKNOWLEDGMENT

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors gratefully acknowledge the Ctμ platform of electronic microscopy (University Lyon 1).

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Figure Caption

Fig. 1: SEM images of the silica coating (after thermal treatment and washing) with the polymer PEG-400 (a) and (b), and pore size distribution from the picture a (c).

Fig. 2: SEM images (a1, b1, c1) and EDX Ca maps (a2, b2, c2) and Si maps (a3, b3, c3) of the silica coating (PEG-400) before thermal treatment (ai), after thermal treatment (bi) and after the washing step (ci).

Fig. 3: Optical microscopy images of the silica film during the solvent evaporation step (PEG-400) every 30 seconds at 20°C and 60% RH; t=0 s (a); t=30 s (b); t=60 s (c); t=90 s (d); t=120 s (e); t=150 s (f).

Fig. 4: DSC on sols without CaCl_2 (black) and sols with CaCl_2 (red) (a), TGA (b), evaporation rate from TGA vs temperature (c) and micro GC (d) curves of the gaz (EtOH in orange and H_2O in green) evolved during the solvent evaporation step (PEG-400) from room temperature to 110°C (dotted line for sol without CaCl_2 , full line for sol with CaCl_2).

Fig. 5: SEM images of the silica coating (after thermal treatment and washing) obtained with the block copolymer F-127: a: top view; b: profile view, and pore size distribution from the picture a, MD = mean diameter; SD= standard deviation (c), with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (d).

Fig. 6: Observation (at 20°C and 60% RH) of the solvent evaporation in a droplet deposited on PTFE substrate of the alcoholic solutions, at two times (t =0 min and t= 5 min) with pure EtOH/ H_2O (a), with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (b), with PEG-400 (c), with the block copolymer F-127 (d), with PEG-400 and CaCl_2 (e), with F-127 and CaCl_2 (f), with PEG-400, CaCl_2 and TEOS (g), with F-127, CaCl_2 and TEOS (h). Insert represents droplet after contact with a pipette tip to discriminate between gel and liquid states.

Fig. 7: SEM image of the silica coating (after thermal treatment and washing) with the polymer PEG-400 and with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ($\text{Zr}/\text{Si}=0.05$) (a), image of a default of the coating (b), and pore size distribution from the picture a, MD = mean diameter; SD= standard deviation (c), SEM image of the silica coating with the polymer PEG-400 and with HCl (d).

Fig. 8: SEM image (a) and EDX maps of the silica coating (after thermal treatment) with the polymer PEG-400 and with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ($\text{Zr}/\text{Si}=0.05$): EDX Cl, Zr and Si maps (b, c, d).

Fig. 9: Observation of the solvent gelation in a droplet deposited on PTFE substrate of the alcoholic solutions without $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, with PEG-400 (a,b) or with the block copolymer F-127 (c,d), without $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (a & c) and with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (b & d).

Fig. 10: Illustration of the process of emulsification induced by the solvent evaporation assisted by the salt presence and leading to macroporosity formation in the silica film.

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