Highly ordered hybrid mesoporous bifunctional thin films†

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Highly ordered mixed framework mesoporous cubic (*Im3m*) thin films of $(M_{1−x}(Si–R)_x)O_2$ bearing organic groups (M = Ti or Zr, R = propylamine, propylthiol or phenyl, $x \leqslant 0.2$) are obtained by one-pot dip-coating; a second organic function (R′ = hexadecyl, phenyl, thiol) can be added by post-grafting with a molecule presenting a group capable to anchor to the M sites, thus leading to bifunctional accessible mesopores.

Mesoporous hybrid materials are one of the most promising features in the so-called "Organised Matter chemistry" field.[1] Among these, mesoporous hybrid thin films (MHTF) are especially interesting for their possible applications in sensors, analytical devices (separation or chromatography), and advanced optoelectronics. Silica, transition metal oxide or metal films have been synthesised by following different chemical routes[2] and a general Evaporation Induced Self Assembly (EISA) procedure.[3] Silica-based MHTF bearing one organic function have been recently synthesized by co-condensation or post grafting routes.[4]

Incorporation of multiple functions to mesostructures is a step beyond towards multifunctional tailored porous systems which can mimic biological systems. Although inclusion of two or more organic functions in mesoporous silica powders has been reported in previous works,[5] no results have yet been presented on multifunctionalised films to the authors' knowledge. Furthermore, there are scarce examples of functionalised transition metal (TM) oxides, which are interesting for their electronic, mechanical, optical and chemical stability properties, although the feasibility of producing zirconia-based MHTF by post synthesis grafting was demonstrated by the Sanchez group.[6]

In this work, we report for the first time a strategy leading to bifunctional hybrid mesoporous films with mixed oxide frameworks, by using a two-step strategy. In the first step, mixed oxide MHTF are obtained by co-condensation of R–Si(OEt)₃ and a TM centre (Ti or Zr). Organic functions included (amino, thiol or phenyl) are conserved after template removal and free M(IV) sites are left behind in the pore surface. A second function (R′ = alkyl, phenyl, sulfonate…) can be then added by post-functionalisation with molecules containing the desired R′ and a suitable grafting group (phosphate, carboxylate…) able to perform selective complexation of the TM centres. This procedure leads to highly ordered hybrid mesoporous films presenting two different functions at the pore surface.

Hybrid mesoporous $M_{1−x}(SiR)_xO_2$ (M = Ti, Zr; $x \leqslant 0.2$) films have been synthesised by dip-coating glass, silicon, polymer substrates or KBr pellets into a water/ethanol solution containing MCl₄, R–Si(OEt)₄ and triblock copolymer F127 $(EO)_{106}(PO)_{70}(EO)_{106}$ (EO = –OCH₂CH₂; PO = –OCH(CH₃)CH₂) as templating agent. The starting sol ratios were M : Si : EtOH : H₂O = $1−x : x : 40 : 5–20$; s = [F127]/[M + Si] = 5×10^{-3}. The M(IV) Lewis acid species in solution and the H⁺ liberated by the hydrolysis of MCl₄ control the Si hydrolysis and Zr condensation.[7]

Highly ordered optical quality films containing amine (*e.g.*, denoted ZSA91 or ZSA82 for Si/(Si + Zr) = 0.1 or 0.2, respectively) phenyl or thiol groups (ZSP or TSP series, depending on M = Zr or Ti, respectively) were synthesised from fresh solutions in a two step procedure (dry atmosphere RH < 20%, followed by exposure to water vapours).[8] The films were stabilised by post treatment at RT and 20 to 50% RH, followed by heating at 60–130 °C for 3–96 hours. Stabilised films were thermally treated (250–300 °C) for 1–3 hours to eliminate the template while conserving the R function in ZS films. Higher temperatures lead to total phenyl or thiol, and partial amino loss. In the case of TS films, decomposition of the organic functions is almost complete at 300 °C; thus, templates must be extracted from stabilised TS films by treatment in acidic ethanol (0.01 M HCl).[4] Multilayer films can be obtained by sequential dip-coating onto films stabilized at 200 °C, allowing for thicker films to be produced, and ensuring a homogeneous mesostructure along the film thickness.

2D-SAXS (LNLS SAXS line, Campinas, Brazil, $\lambda = 1.608$ Å) and TEM images of stabilised and calcined ZSA films (Fig. 1) show large-pore *Im3m* cubic mesostructures for $x < 0.2$ ($a = 240–250$ Å) with thick amorphous walls; samples tend to be unstable under the TEM beam, possibly due to the presence of organics and transition metal centers. Thermal treatment leads to uniaxial contraction, which is lower for higher Si contents, as observed in mixed oxide mesoporous films.[7]

FTIR spectra of ZSA91 films deposited on KBr pellets and thermally treated (Fig. 2 and ESI†) show that vibrations corresponding to the template (ν_{CH} at 2850–2920; $\nu_{C–O–C}$ at 1038 and 1118 cm⁻¹) are lost upon thermal treatment, while NH (ν_{NH} at 3200 cm⁻¹, δ_{NH} at 1570 cm⁻¹; broad primary amine band at 650–895 cm⁻¹)[9] and a fraction of the CH species are conserved; this indicates that the propylamino dangling groups are kept at least until 350 °C. Si–O–Zr bands[7] are observed at 960–1000 cm⁻¹ and no Si–O–Si bands (1000–1200 cm⁻¹) are observed, ruling out phase segregation. The intimate Zr and Si dispersion throughout the sample is confirmed by EDS analysis of the calcined films (Si : Zr ∼ 0.25 for ZSA82, ESI). The pore system of ZSA hybrid films is further accessible to Cu(II) cations, as confirmed by the Cu/Si = 0.25 atomic ratio found by SEM-EDS of a calcined ZSA82 immersed in a 150 ppm Cu(II) solution (pH = 5) for 200 minutes
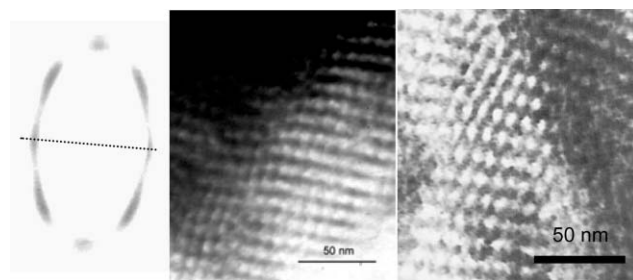

Fig. 1 A. 2D-SAXS of a ZSA91 thin hybrid film. The dotted line represents the film orientation; B TEM image of ZSA 82 cubic film along the [100] projection. C. TEM image of an amino-functionalised TSA 91 cubic film ([110] projection).
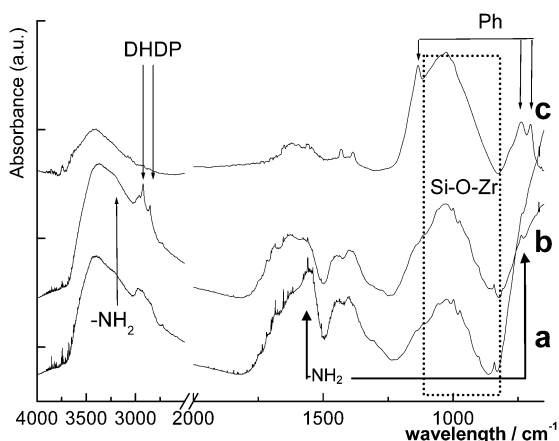
Fig. 2 FTIR spectra of silica–zirconia hybrid films a) ZSA 91 calcined to 300 °C, b) film in a) after second functionalisation with DHDP, c) ZSP 82 calcined to 300 °C. Typical function and skeleton bands are indicated.

(ESI). This is an indirect indication that the amino groups are conserved after thermal treatment. No Cu(II) is incorporated in these conditions in non-functionalised ZrO_2 or SiO_2 mesoporous films of similar pore features; amino groups are essential to trap the Cu(II), as has been shown previously.[10] For ZSP films, phenyl vibrations (weak $\nu_{=C-H}$ at 3056 and 3079 cm^{-1}; X-sensitive Si–Ph at 1133 cm^{-1}, C–H out of plane deformation at 704 and 740 cm^{-1}) suffer no significant degradation until 200 °C and they are clearly observed until 300 °C (ESI†), when the template is totally eliminated.

The organic groups seem to have a significant influence in the organisation of these films at the mesoscale, as has been observed before for one-pot synthesised hybrid films with CTAB template.[11] Amino terminal groups lead to a highly organised cubic mesostructure, while locally ordered pore structures are observed in systems containing phenyl or thiol groups.

These differences can be attributed to different interactions of the R-groups with the inorganic skeleton and/or the organic groups attached to the siloxane centres.[11] Significant differences in the 3000–3500 cm^{-1} region of the FTIR spectra are observed. In the case of ZSA films, the ν_{C-H} and ν_{N-H} bands are large and ill-defined, suggesting a high degree of hydrogen bonding for the N–H fragments with the EO blocks, with the resulting spreading of the C–H frequencies. This interaction might favour the hydrophilic framework–template matching,[2] leading to the development of a high curvature hybrid interface (*i.e.* metal oxide/template), and a better mesophase definition. Interestingly, for ZSA systems, *Im3m* cubic phases are obtained even under low humidity (RH < 20%) post treatment; for related systems,[6-8] a low RH treatment results invariably in the formation of a 2D-Hexagonal (*p6mm*) mesophase. For ZSP systems, this R-template hydrophilic interaction which favours order is absent, and local order porous structures are obtained.

A second organic function was added to the template-free films by post grafting. The MHTF obtained in the first step were immersed in dilute solutions (10^{-2}–10^{-4} M) of R′–G, where R′ is an organic residue such as alkyl, aryl, sulfonate, thiol… and G can be an anchoring group such as phosphate, biphenol, carboxylate, acetylacetonate, *etc.* FTIR spectra of KBr-supported MHTF dipped for 2 hours in a 0.01 M dihexadecyl-phosphate (DHDP) solution in THF present intense bands in the ν_{C-H} region (Fig. 2), in addition to those previously found in the monofunctional films. This result implies a high incorporation of the second molecule, which is in the order of 5% atP/at(M + Si), as obtained in related systems.[6,12] Adsorption kinetics of DHDP on ZSA films‡ show a fast DHDP incorporation (80% of the total amount within 5 minutes), in a lower quantity than in cubic ZrO_2 films with comparable thickness and accessibility (ESI†). This suggests that a

fraction of the surface sites is not available for complexation, and it should be thus occupied by the R functions. In addition, leaching experiments‡ show that more than 95% of the DHDP remains attached to the pore surface after 5 hours leaching (ESI†).

In summary, we present a two-step chemical strategy permitting the creation of mesoporous hybrid thin films (MHTF) with accessible multifunctional cavities. In the first step, the co-condensation of an M(IV) chloride and a silane function carrier afford a hybrid mesoporous film with a mixed oxide framework, in which Si and M(IV) are intimately dispersed. This strategy should be easily adapted to Si-rich systems.[7] A second step permits to position a second function (R′) on the pore surface by selective complexation of the M(IV) sites with a phosphate anchoring group carrying the R′. This is interesting in the design of ceramic-embedded biomimetic systems, where a functional or binding group can be dispersed in an accessible pore where the environment features can be modulated by a second organic function incorporated within the pores and/or embedded in the ceramic framework.

Notes and references

‡ A typical functionalisation kinetics experiment was performed by dipping a calcined mesoporous film in a continuously stirred 0.01 M solution of DHDP in THF for variable periods. After immersion, the film was rinsed with THF and dried in air. Leaching experiments were performed by introducing a functionalised film in THF or water while stirring. DHDP leaching was evaluated from 5 minutes to several days by analysing the evolution of the ν_{C-H} band (%ν_{C-H} area loss relative to the total ν_{C-H} initial area).

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