Mesoporous organosilicas with Pd(II) complexes in their framework

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ABSTRACT

Incorporation of various Pd(II) complexes into the framework of mesoporous organosilica materials has been achieved by co-condensation, using a facile solvent-free one-pot method. The synthesis of Pd(II) complexes using ligands with triethoxysilyl terminal groups allowed for their homogeneous in situ incorporation into the organosilicicous structure. Organic/inorganic precursor bis(triethoxysilyl)ethane was used both, as silica source and as solvent for the synthesis of the complexes, avoiding the use of any other organic co-solvent and making the synthesis more environmentally friendly. The mild synthetic conditions used such as neutral pH, room temperature and ethanol extraction of the surfactant, allowed for a cleaner route for the preparation of hybrid organic/inorganic mesoporous materials with Pd(II) complexes covalently bounded to the support. The chemical integrity of the metal complexes after the synthesis of the hybrid material, [trans-PdCl2L2] (L = 4-C5H4N-(CH2)2Si(OEt)3 and PPh2(CH2)2Si(OEt)3), was confirmed by several spectroscopic techniques. A systematic study of the role of the different parameters involved in the synthesis of these materials and their relation with the final morphology of the catalysts is herein described.

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1. Introduction

Among the different techniques used for the immobilization of metal complexes, the covalent anchoring of their ligands on nanostructured supports has proved to be a very versatile and useful technique [1–7]. The covalent bonding of organic species on preformed inorganic nanostructured materials and the subsequent reaction of these ligands with the metal to finally obtain the desired complex has become the most common approach for the covalent immobilization of metal complexes on porous supports [8–15]. By this method, host–guest complexes have been synthesized from mesoporous silica materials for their application in catalysis [16], sensors [17], adsorption [18] and drug delivery systems [19]. Main drawbacks of this approach include the difficulty to prepare and control certain structures, as well as the characterization of the final complex obtained.

In the last few years, an alternative in situ approach has been developed [20–26]. The synthesis of metal complexes using terminal trialkoxysilyl groups in their ligands allows first the control and characterization of the homogeneous catalysts and their subsequent incorporation to the walls of the mesoporous materials by co-condensation with the material precursor. Recently, Li and co-workers [20–22] have used this approach to incorporate different metal complexes of Au(I), Ru(II), Rh(I) or Pd(II) with diphenylphosphine ligands in mesoporous silicas and organosilicas. The corresponding hybrid materials showed similar activity and selectivity to the related homogeneous catalysts. However, in all these cases the synthesis includes an organic solvent for the addition of the metal complex, very low pH conditions (1–2) and hydrothermal treatment (100 °C) for the formation of the mesoporous materials, which limits this method to very stable complexes.

As a more versatile alternative, our group reported in 2011 a new method based in the use of a neutral surfactant at room temperature and neutral pH for the incorporation of various Pd(II) complexes containing amine, pyridine and phosphine ligands into the silica framework [23]. The use of organic solvents was avoided by using the inorganic precursor tetraethylorthosilicate (TEOS) as solvent for the synthesis of the Pd(II) complexes.

Herein, our method is extended to the incorporation of metal complexes in the framework of organosilica materials. Since periodic mesoporous organosilica materials (PMOs) were reported in 1999 [27], great attention have attracted as promising materials for various applications. In these hybrid materials, organic species are integrated into the walls of a mesoporous silica matrix through covalent Si–C bonds and the hydrophobicity/hydrophilicity can be easily tuned. Comparing with mesoporous silica materials functionalized with organic species, mesoporous organosilica materials can be prepared at higher organic contents more homogeneously...
distributed [28]. Nevertheless, the nanostructuration of organosilica materials involves a greater synthetic challenge than in mesoporous siliceous materials. The higher enthalpy of dispersion of the organosilica precursor in the aqueous environment, combined with the steric and conformation constraints imposed by the carbon backbone, makes the templating process more challenging for organosilicas [28]. For this reason, few examples of mesoporous organosilicas synthesized under neutral pH conditions and room temperature can be found in the literature [29].

In this regard, the work here reported shows the incorporation of Pd(II) complexes in organosilicas under mild conditions of pH (close to neutral), temperature (as close as possible to RT) and atmospheric pressures, and studies the different synthetic parameters involved in their preparation. This strategy could potentially extend the scope of the synthesis of novel mesoporous materials with metal complexes incorporated into their framework to a number of complexes which could not be utilized under acidic or high temperature conditions.

2. Experimental

2.1. Synthesis

Two neutral surfactants Triton X-100 (Alfa-Aesar) and Brij-56 (Aldrich) were used as templates for the mesoporous solids, biss(triethoxysilyl)ethane (BTEE, Gelest Inc.) as organosilica source and ammonium fluoride (NH₄F, Aldrich) as nucleophilic catalyst for the condensation of the network.

Complexes [trans-PdCl₂L₂]⁻ (L = 4-C₅H₄N-(CH₂)₂Si(OEt)₃ (PETS), PPPh₂(CH₂)₂Si(OEt)₃ (PPETS)), [trans-PdCl₂L₂]⁻ (L = PETS, PPETS) with BTEE in the presence of neutral surfactants, namely Triton X-100 or Brij-56, using NH₄F as catalyst for the condensation of the network. This strategy could potentially extend the scope of the synthesis of novel mesoporous materials with metal complexes incorporated into their framework to a number of complexes which could not be utilized under acidic or high temperature conditions.

Complexes [trans-PdCl₂L₂]⁻ (L = 4-C₅H₄N-(CH₂)₂Si(OEt)₃ (PETS), PPPh₂(CH₂)₂Si(OEt)₃ (PPETS)) were synthesized by a similar method to that described previously by us [23], by reacting suspensions of [PdCl₂(PhCN)]₂ (15 mg, 0.04 mmol) in BTEE (0.91 g, 2.56 mmol, 1 wt. % Pd:organosilica) and the adequate amount of ligand PETS or PPETS (1:2 Pd:l molar ratio) with orbital stirring until total solution of the formed complex (≈15 min). In a typical synthesis of the Pd(II) complexes–mesoporous organosilica hybrid materials, the yellow palladium complex solution was added dropwise to a clear solution of the surfactant, obtained by solving 0.46 g (0.7 mmol) of Brij-56 in 23 g of distilled water, being the two phases obtained vigorously stirred (400 rpm). To induce the silica precipitation, 1 ml of a solution 0.55 M NH₄F was added. The mixture was reacted at room temperature or 45 °C during 24 h maintaining the stirring. The obtained solid was washed with water, ethanol and acetone, filtered off, and air dried at 40 °C. Finally, the surfactant was removed by ethanol extraction (0.2 g catalyst/50 ml ethanol) at room temperature for 12 h.

A systematic study was carried out in order to analyze the role in the formation of the hybrid materials of the following synthetic parameters: (i) neutral surfactant, (ii) temperature of synthesis, (iii) pre-hydrolysis of the inorganic precursors, (12 h) before the addition of the nucleophilic catalyst (NH₄F), and (iv) molar ratio of reagents in the synthetic gel: (RT) 1 BTEE:0.11 Surfactant:0.02 F⁻ :210 H₂O and (R2) 1 BTEE:0.27 Surfactant:0.21 F⁻ :520 H₂O.

Table 1 shows the synthetic conditions of representative samples (1 wt.% nominal Pd:organosilica) and their textural and structural properties. For comparison purposes, samples of organosilica materials, without Pd(II) complexes in their framework, were also synthesized. The samples were labeled as ORCXN_PdCl₂L₂_T, where: X = 1 or 2 depending the molar ratio employed; N = T or B depending the neutral surfactant used (T = Triton X-100 and B = Brij-56); L = the ligand of the Pd(II) complex incorporated (PETS or PPETS) and T indicates the temperature during the synthesis, 25 or 45 °C. The experiments in which inorganic precursors were pre-hydrolyzed are marked with an ‘h’.

For comparison purposes, the same complexes were incorporated into mesoporous silicas following the procedure previously reported [23], using TEOS (Aldrich) as inorganic precursor, Triton X-100 as neutral surfactant and the molar ratio R2 (1 BTEE:0.27 Surfactant:0.21 F⁻ :520 H₂O). In that case, samples are denoted MSU_PdL₂, L = PETS or PPETS.

2.2. Characterization

IR spectra were recorded on a Nicolet Nexus FT-IR Spectrometer. All the mesoporous materials samples were prepared as pure material pellets and KBr diluted pellets. Diffuse reflectance UV-Vis (DRUV) data of pressed pure powder were recorded on a Shimadzu UV-3600 spectrophotometer with a Harrick praying mantis accessory, and recalculated following the Kubelka Munk function. Palladium content was determined by ICP-OES on a Perkin Elmer 7300 DV spectrometer, with the samples dissolved in aqua regia and the undissolved siliceous matter filtered off prior to analysis. Transmission electron microscopy (TEM) studies were carried out on a JEOL JEM-2010 microscope (200 kV, 0.14 nm of resolution). Samples for TEM studies were prepared by dipping a sonicated suspension of the sample in ethanol on a carbon-coated copper grid. Porous texture was characterized under high vacuum conditions, using a Micromeritics ASAP 2020 apparatus, operating in the nitrogen adsorption mode.

3. Results and discussion

3.1. Synthesis of the hybrid mesoporous organosilica materials

Co-condensation of palladium(II) complexes [trans-PdCl₂L₂]⁻ (L = PETS, PPETS) with BTEE in the presence of neutral surfactants, namely Triton X-100 or Brij-56, using NH₄F as catalyst for the condensation of the network, gave yellow solid materials as corresponding to the color of the Pd(II) complexes used in their synthesis. After removing the surfactant with EtOH extraction during 12 h at room temperature, the obtained materials kept their initial color, remaining the extraction solutions uncolored. The amount of Pd incorporated into the networks was determined by ICP-OES. For the materials prepared with a target Pd content of 1 wt.%, the obtained values were around 0.75–0.85 wt.% loading of Pd for materials prepared with the pyridine ligand and 0.50–0.60 wt.% for materials with diphenylphosphine ligand. Regarding the textural properties of Pd(II) complexes organosilica materials, all of them show type IV isotherms, from which textural parameters were calculated (Table 1). The incorporation of the metal complexes into the organosilica frameworks entails the apparition of a second adsorption process (with the exception of the pre-hydrolyzed materials), which is characteristic of textural interparticle meso-/macroporosity [31]. The bimodal porosity of the catalyst, with small mesopores and large interparticle mesopores/macropores, can be observed in both, isotherms and pore size distribution (see Fig. 1).

The open bimodal structure of these materials was confirmed by TEM studies, see Fig. 2. Hybrid materials present a continuous organization built from irregular mesoporous nanoparticles. The growth and nucleation of these primary nanoparticles and their
subsequent aggregation result in a non-ordered system of large interparticle mesopores. Although all mesoporous organosilicas prepared displayed similar architectures, there are appreciable differences among them in terms of average size and shape of the nanoparticles. While the pure organosilica materials (without Pd(II) complexes) are formed by particles around 200 nm (Fig. 2(a)), materials incorporating Pd(II) complexes present smaller and more irregular shapes. Fig. 2(b) and (c) show TEM images of ORG1T_PdCl2(PPETS)2_25 and ORG1B_PdCl2(PPETS)_25 materials with [trans-PdCl2(PPETS)]2− in their structure, which present an average particle size of 60 nm and less than 40 nm, respectively. The smaller and more irregular the particles are, the higher interparticle volume the material has, see Table 1.

In some cases, the architecture of some solids resembles to that observed in porous xerogels prepared without template synthesis [32]. Under the same synthetic conditions, materials prepared using the Pd(II) pyridine complex show smaller primary particles and, consequently, higher interparticle volume. As has been already reported for mesoporous silica materials [33], an increase in the pH during the preparation of mesoporous materials by the neutral route causes a diminution in the mesoporous volume, while the interparticle volume increases. The use of a pyridine ligand in the synthesis (weak base, pKb = 8.79) entails a slight increase of the initial solution pH, which results in less sharp nitrogen-uptake steps in the small mesoporosity region with higher second adsorption steps regarding materials prepared from the

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>S BET (m² g⁻¹)</th>
<th>V mes (cm³ g⁻¹)</th>
<th>V mes (cm³ g⁻¹)</th>
<th>V mp (cm³ g⁻¹)</th>
<th>Ø mp (nm)</th>
<th>Ø ipart (nm)</th>
<th>d 100 (nm)</th>
<th>Ø part (nm)</th>
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<td>–</td>
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<td>–</td>
<td>5.88</td>
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</table>

* Out of range of nitrogen adsorption technique.

* Very small particle size, almost xerogel architecture.

a The BET surface area was estimated by using multipoint BET method in the adsorption branch of the nitrogen isotherm in the relative pressure (P/P0) range of 0.05–0.30.

b Mesopore volume, V mes, was calculated from the adsorption branch of the nitrogen isotherm using the BJH method, the volume was measured at the plateau of the cumulative adsorption pore volume plot. The total pore volume, V t, was measured at P/P0 = 0.95. The pore volume of the interparticle pore, V ipart, was estimated subtracting both values.

c Average mesopore, Ø mp, and interparticle sizes, Ø ipart, were estimated from the adsorption branch of the nitrogen isotherm using the BJH method.

d 100 spacing calculated from the main peak of XRD applying the Bragg’s law.

e Primary particle size of the material determined from TEM images (measurement of more than 100 particles).
Pd(II) diphenylphosphine complex. This trend was not observed in our previous studies based in mesoporous silica materials with Pd(II) complexes in their framework [23]. Mesoporous solids prepared using the Pd(II) pyridine and Pd(II) diphenylphosphine complexes showed similar textural properties in silica based materials, confirming the more challenging templated synthesis in the case of organosilica materials [28].

3.1.1. Influence of the temperature during the synthesis

The effect of the temperature during the synthesis in the final properties of the material was analyzed for the different surfactants, Pd(II) complex and composition in the synthetic gel. The temperature was varied from room temperature (~25 °C) to 45 °C. Higher temperatures gave as result the decomposition of the complex and consequently the formation of Pd aggregates. In all cases, the increase in the temperature produces a diminution in the BET surface area, together with an increase in the interparticle volume, suggesting the formation of smaller primary particles, see Table 1.

Moreover, the average mesopore diameter of the materials increases when temperature raises. As shown in Fig. 3(a), for any surfactant and molar ratio of reagents, the materials obtained present a higher average mesopore size when the synthesis was carried out at 45 °C. This effect has been previously described for mesoporous silica materials prepared by neutral surfactants [34], where it has been proven that non-ionic surfactant micelles increase in size when raising the temperature. In aqueous media, the hydrophilic shell of these micelles increases its volume by the incorporation of water molecules trapped in the PEO chains by hydrogen bonds. The degree of hydration of the micelles decreases with the temperature, as well as the hydrophilic nature of the PEO groups [35]. The dehydration of the hydrophilic chains produces their stretching by expelling the water trapped in the micelles’ shell (see a schematic representation in Fig. 3(b)), and subsequently an enlargement in the average pore size of the organosilica materials.

3.1.2. Influence of the surfactant: hydrophobic character

In order to study the effect of the neutral surfactant employed in the synthesis, two types of non-ionic PEO derivatives were used as surfactants, Brij-56 and Triton X-100. Triton X surfactants have structures given as \((\text{CH}_3)_3\text{CCH}_2\text{CH(CH}_3)\text{-C}_6\text{H}_4\text{(CH}_2\text{CH}_2\text{O)}_x\text{H}\), where \(x = 10\) (for TX-100); while surfactant Brij-56 has the following structure: \(\text{C}_{16}\text{H}_{33}\text{(OCH}_2\text{CH}_2\text{)}_{10}\text{OH}\). The main difference between these two non-ionic surfactants lies in the hydrophobic part; Brij type surfactants possess a longer hydrophobic tail than other neutral surfactants (Triton in this case) and for this cause are less hydrophilic.

When comparing materials prepared with the same Pd(II) complex and different surfactants the results obtained are strongly dependent of the temperature of synthesis. Fig. 4 shows the N\(_2\) adsorption/desorption isotherms of hybrid materials prepared with the different surfactants and using the molar composition
R1 in the synthetic gel (1 BTEE:0.11 Surfactant:0.02 F :210 H2O), the Pd phosphine complex and different temperatures, 25 °C, Fig. 4(a), and 45 °C, Fig. 4(b). Materials prepared at 25 °C show significant differences with regard to the surfactant employed, when Triton X-100 is used as template mainly porosity in the range of the mesoporous was found and the interparticle volume was low. Whereas Brij-56 surfactant at this temperature gave solids less structured and with high interparticle volume, indicating a worse porogene effect of Brij-56 at 25 °C.

However, when the temperature increases up to 45 °C materials prepared with both surfactants showed similar properties, see Fig. 4(b). The solids have similar total pore volume for both neutral surfactants at 45 °C and the distribution between mesoporosity and interparticle porosity is the same in both cases. The longer hydrophobic tail in Brij-56 makes this surfactant less soluble in aqueous solutions [36], therefore an increase in the temperature during the synthesis favors the solubility of the surfactant and, subsequently, a better templating effect can be found at this temperature. For this reason, mesopore size distributions (not showed here) are narrower for materials prepared with Brij-56 at 45 °C than for those prepared at lower temperature.

3.1.3. Influence of the molar ratio of the precursors

The effect of the molar composition in the synthetic gel, R1 (1 BTEE:0.11 Surfactant:0.02 F :210 H2O) or R2 (1 BTEE:0.27 Surfactant:0.21 F :520 H2O), was studied for materials prepared with Brij-56 as surfactant and both temperatures of synthesis, 25 °C and 45 °C. Higher concentration of surfactants and the addition of fluoride catalyst in the synthetic gel are expected to improve the final textural properties of the mesoporous solids. Since the neutral surfactant acts as template for the generation of mesopores and the organization of the mesostructured material, higher concentration of surfactant should lead to an increasing in both the BET area and the pore volume. In a similar way, when the preparation of mesoporous materials takes place at neutral pH, the fluoride ion increases the reaction rate and gives as result better structured materials than those prepared without fluoride-assisted synthesis [37].

Nevertheless, similar textural properties have been obtained for the mesoporous materials prepared using pyridine as ligand and the different molar composition in the synthetic gel evaluated, see Fig. 5(a) and textural properties in Table 1. The expected beneficial effect of the higher concentration of neutral surfactant and fluoride ion in the textural properties of the final materials seems not to take place when the pyridine was used as ligand. As it has been abovementioned, the use of a weak base (pyridine ligand) produces a slight change in the pH during the synthesis of the mesoporous solids, which results in less structured materials. This change in the pH results in poor structured materials even using the molar composition R2, where the molar ratio surfactant:BTEE (n(surfactant):n(BTEE) = 0.27:1) increases up to 2.5 times the initial one (R1, n(surfactant):n(BTEE) = 0.11:1) and using 10 more times of fluoride catalysts regarding the organosilica precursor, molar ratio n(F-):n(BTEE) in R2 = 0.21:1 and in R1 = 0.02:1.

As expected, in the case of the Pd(II) complex prepared using the phosphine as ligand the molar composition R2 clearly improves the textural properties of the final materials (see Fig. 5(b) and Table 1). Materials synthesized using higher surfactant/BTEE and F / BTEE molar ratios present higher BET surface areas and slightly higher mesoporous volume.

3.1.4. Influence of the pre-hydrolysis of the organic/inorganic precursors

The effect of the pre-hydrolysis of the organosilica precursors (BTEE and Pd(II) complexes) before the addition of the nucleophilic catalyst (NH4F) used for the condensation of the silica network was studied using the R2 molar composition in the synthetic gel and Brij-56 as template at 45 °C.

The pre-hydrolysis of the precursors during 12 h before the addition of the NH4F has a drastic effect in the morphology and textural properties of the materials. Fig. 6 shows the nitrogen adsorption/desorption isotherms of these materials and their corresponding pore size distributions. Contrary to that observed for materials prepared without the pre-hydrolysis step, these materials have a monomodal small mesoporosity with very narrow mesoporous size distributions. The smaller average pore size of the materials with pre-hydrolysis is likely to be due to the hydrophobicity of the organosilica precursor and the weak interaction between the precursors and the micelles shell of the neutral template. The combination of these two effects can result in the penetration of some precursor molecules into the hydrophobic core of the surfactant micelles, which entails the reduction of the average mesoporous size, as it has been explained for functionalized mesoporous silica materials prepared by neutral routes [36]. The penetration of the precursor into the surfactant micelles was higher in the pre-hydrolyzed materials probably due to the higher reaction time employed in their synthesis.

Typically, mesoporous materials prepared with neutral surfactant and neutral pH present wormhole like structures with disordered mesoporous [38]. In this case, as expected, hybrid
mesoporous materials prepared with the pre-hydrolysis step do not present XRD spectra of ordered hexagonal mesoporous materials (three peaks in the 2θ range between 1° and 8°), see Fig. 7(a), but TEM studies showed the presence of hexagonally ordered particles in these materials, Fig. 7(b). Under the synthetic conditions in which these materials are prepared, organosilica precursors are in neutral state (not charged) and have a weak interaction with the non-ionic surfactants by hydrogen bondings.
The pre-hydrolysis step and, consequently, the higher reaction time between the organosilica precursors and the neutral surfactant improves their interaction, thus provoking a better nanostructuration, narrower pore size distributions and higher BET surface areas in the final hybrid materials, see Table 1.

3.2. Organosilica mesoporous materials with Pd(II) complexes in their framework

The mutually trans disposition of the ligands in the Pd(II) complexes has been already studied and reported elsewhere, and their incorporation to the organosilica mesoporous materials has been inferred by spectroscopic means (NMR, FT-IR and DRUV spectroscopies). Thus, the $^{29}$Si CP NMR spectra for all the hybrid materials (see Figs. 8(a) and S1 in SI, for the materials prepared with both Pd(II) complexes) show signals characteristic of $7^m$ \([\text{RC-Si(OSi)}_{m}(\text{OH})_{3-m}]\) sites of PMOs type materials. The deconvoluted peaks can be assigned to the organic ethyl fragments of the organosilica precursor; $T^3$, $\delta = -66$ ppm; $T^2$, $\delta = -59$ ppm and $T^1$, $\delta = -50$ ppm [39] and to the organic ligands of the complexes; $T^2$, $\delta = -72$ ppm. Moreover, no signals due to $Q^n$ species \([\text{Si(OSi)}_{n}(\text{OH})_{4-n}]\) were observed in the range 90 to $-120$ ppm, showing that all silicon are covalently bonded to carbon atoms. With regard to the infrared spectra, Fig. 8(b) shows FT-IR spectra of selected organosilica hybrids with [trans-PdCl$_2$(PPETS)$_2$] in their frameworks. These spectra display two weak signals at 1437 and 1480 cm$^{-1}$ characteristics of the diphenylphosphine ligands, $\nu$(P–C) and $\nu$(C=C) stretching vibrations, respectively [21,40]. Unfortunately, in the FT-IR spectra of [trans-PdCl$_2$(PET)$S_2$] derivative mesoporous materials, the absorptions corresponding to the Pd(II) complex are obscured by the bands due to the organosilica mesoporous material.

Finally, the correct incorporation of the Pd(II) complexes into the mesoporous organosilica supports was also confirmed from the DRUV spectra of pressed pure powders of the extracted materials (see Fig. 8(c) and (d)). These spectra show similar features to those observed for the Pd(II) complexes [23], being practically identical in the case of the broad high energy band (230–250 nm), typical of intraligand transitions. The less intense low energy features (330, 400 nm for [trans-PdCl$_2$(PET)$S_2$]; 270, 340 nm for [trans-PdCl$_2$(PPETS)$_2$]) are most likely associated to metal perturbed intraligand transitions.

3.3. Mesoporous materials with Pd(II) complexes into their framework: silica versus organosilica

Mesoporous silica materials with the Pd(II) complexes incorporated into their frameworks were synthesized using the procedure abovementioned and incorporating 0.5 and 1 wt.% nominal of Pd(II) into the different supports. The synthetic conditions used in this case include Triton X-100 as neutral surfactant and the R$_1$ molar ratio of reagents (1 TEOS:0.11 Surfactant:0.02 F:$\cdot$210 H$_2$O).

Fig. 8. (a) Solid-state $^{29}$Si CP NMR spectrum (blue) and simulated one (red) of ORG2B_PdCl$_2$(PPETS)$_2$-45 material and its deconvoluted peaks (dotted lines); (b) FT-IR spectra of the [trans-PdCl$_2$(PET)$S_2$] complex (black line) and different organosilica hybrid materials (colored lines) with this complex in their framework; and DRUV spectra of pressed pure powders of the (c) [trans-PdCl$_2$(PPETS)$_2$] and (d) [trans-PdCl$_2$(PET)$S_2$] (black lines) and their derivative mesoporous materials (colored lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
In a similar way than in the organosilica materials the samples were labeled as MSU1T_PdCl2(L2), where L indicates the ligand of the Pd(II) complex (PETS or PPETS). Textural parameters of the samples and the Pd loading measured by ICP-OES are shown in Table 2. Under the same synthetic conditions, materials prepared using silica precursors result in higher BET surface areas and total pore volumes, indicating a better interaction between the neutral surfactants and inorganic precursors. The same conclusion can also be inferred by TGA analysis of the samples. The organic content due to the surfactant calculated from the thermogravimetric curves (see S2 in SI) was around 40% for silica materials and only 20% for the organosilica ones, confirming a smaller incorporation of surfactant in the organosilica materials, which gives smaller pore volumes in these solids as result. Furthermore, small angle XRD analysis of both kinds of materials showed that, under the same synthetic conditions, silica catalysts present sharper and more intense peaks than organosilica catalysts, probably due to the higher regularity of the mesoporous in the silica solids consequence of a better templating effect of the neutral surfactant in the silica materials, see Fig. 9.

The average pore size in the organosiliceous hybrids is smaller in any case than in the siliceous materials. As it was abovementioned, the weak interaction between the precursors and the hydrophilic heads of the neutral templates micelles, joined to the hydrophobic character of the organosilica precursors, result in the penetration of some precursor molecules into the hydrophobic core of the surfactant micelles, entailing the reduction of the average mesoporous size. This effect was not observed in the case of silica precursors due to their more hydrophilic character. Moreover, the increasing in the concentration of Pd(II) complex into the organosilica materials entails an increasing of the average mesoporous size, see Table 2. This fact suggests that the incorporation of the Pd(II) complexes to the organosilicieous solids hinders the penetration of the BTEE precursors into the surfactant micelles.

The Pd content was determined by ICP-OES. In the case of the Pd(II) phosphine complexes, yields higher than 70% of incorporation were obtained in the silica materials, while only the 50% of the Pd used in the synthesis of the organosilica materials was incorporated to the final material, see Table 2.

Finally, Mesoporous Pd(II) complexes-silica and organosilica materials were tested for the oxidation of terminal double bonds using styrene as substrate (Table S1). Reactions were performed at 65 or 80 °C using both different solvents and solvent-free conditions under magnetic stirring. Preliminary results indicate the catalytic activity of these complexes in styrene oxidation and show the accessibility of the substrate to the active site incorporated to the framework of the material; however, not significant differences in terms of the support used were found. The results with (acetonitrile) and without solvent indicate a better conversion using solvent-free conditions but with a broad number of by-products. Using acetonitrile as solvent media, the conversion was remarkable lower, but very good selectivities to the benzaldehyde product (near 70% for the phosphine ligand and ca. 85% for the pyridine one) can be reached. Experiments under the same conditions but using water as solvent showed very low conversion.

4. Conclusions

Different hybrid mesoporous materials-Pd(II) complexes were prepared, using a neutral and environmentally friendly route, by co-condensation of two metal complexes containing trialkoxysilane terminal groups with BTEE and TEOS in the presence of neutral structure directing agents, Triton X-100 and Brij-56. This synthetic technique was carried out at mild conditions (neutral pH and room temperature), which preserve the integrity of the metal complexes in the mesoporous frameworks. The surfactant was easily removed by ethanol extraction at room temperature and the chemical integrity of the metal complexes was confirmed by spectroscopic techniques after extraction.

This study with metal complexes shows that it is possible to extend the in situ incorporation of chemical functionalities into
the structure of different mesoporous materials, as our groups have previously described for metal nanoparticles [41], metal complexes [23] and metal clusters [26] in mesoporous silicas. Furthermore, this incorporation method is general and should also serve to incorporate other metal complexes in organosilica matrices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2012.03.036.