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# A periodic mesoporous organosilica containing a carbapalladacycle complex as heterogeneous catalyst for Suzuki cross-coupling

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## Abstract

A series of periodic mesoporous organosilica with varying contents of a carbapalladacycle complex forming part of the walls of the hybrid material has been prepared. These solids have a very large surface area (ca.  $1000 \text{ m}^2 \text{ g}^{-1}$ ), a mononodal pore size distribution (ca. 3 nm), and a periodic hexagonal structure typical for MCM-41 materials. The fresh solids exhibit high activity for the Suzuki cross-coupling of phenylboronic acid with bromobenzoic acid and bromoacetophenone. The initial catalytic activity of these PMO materials is significantly higher than that of a related amorphous silica catalyst containing the same complex. Leaching studies, either filtering the solid in hot solution or three-phase-test attaching one of the reagents to a solid, demonstrate that there is a contribution to the catalysis of leached species from the solid into the solution. The solid can be reused although a progressive deactivation caused by complex degradation, and mesopore collapse has been observed.

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## 1. Introduction

Heterogeneous catalysis in which the catalyst is in a phase different from that of reactants and products has the advantage of easy separation of the catalyst from the reaction mixture, allowing its reuse and the possibility of designing a continuous-flow process [1-3]].

A general methodology for transforming a successful transition metal complex catalyst into a heterogeneous catalyst consists of covalently anchoring the ligand to a large-surface-area inorganic oxide [4,5]. In addition to amorphous metal oxides, structured mesoporous silicas have frequently been the supports of choice because of their large specific area, which makes these solids among those with the highest surface area. Transition-metal complexes anchored into mesoporous silicates have been demonstrated to be useful heterogeneous catalysts [6]. In this case, the metal complexes are predominantly located inside the channels connected to the internal surface silanol groups through the

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linker chain. The degree of freedom and co-conformational mobility with respect to the solid surface depend on the chain length and on the interaction of the complex with the surface functional groups.

More recently, a new concept of structured mesoporous hybrid organic–inorganic materials has been developed in which the walls of the mesoporous material contain a relatively small organic functional group such as methylene, ethylene, and phenylene [7–9]. These solids, known as periodic mesoporous organosilicas (PMOs), are structured like MCM materials by the templating effect of surfactants, but the source of silicon is an organosilicon compound with two or more terminal trialkoxysilyl groups instead of inorganic tetraethyl orthosilicate (TEOS).

When a functionality is desired, the complexity and molecular size of the organic component must increase. The use of large organosilanes as the exclusive silicon source under PMO synthetic conditions leads generally to amorphous materials; it is necessary to add a certain amount of TEOS to obtain structured PMOs. Co-condensation of the organosilicon compound and TEOS under conditions that avoid phase separation or preferential self-condensation permits suffi-

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cient framework flexibility to accommodate a certain proportion of a large organic component. PMOs prepared from TEOS and large organosilicon compounds have a periodic mesoporous channel structure with the organic functionality covalently grafted to the walls. These solids constitute a logical evolution of those in which MCM-41 has covalently anchored an organosilicon compound by just a single tether. Although there must be common properties between these two solids, PMOs may have larger surface areas and pore volumes, and the organic component should experience a larger degree of immobilisation than post-synthetically modified MCM-41.

We have contributed to the development of functional PMOs by preparing solids that exhibit a photochemical response [10,11] or that are catalytically active [12,13]. In some cases, the organic precursor was initially enantiomerically pure, and the resulting solid (termed ChiMO, from Chiral Mesoporous Organosilicas) exhibits optical activity towards polarised light [14]. In these examples, however, the content of organic component that can be tolerated in the solid while it is still forming a MCM-41-like structure is limited to a level typically below 20 wt%. However, this content is sufficiently high for most of the applications.

As a continuation of this line of research, we report here the synthesis and catalytic activity of a PMO containing a carbapalladacycle complex of the type of compound **1**. These palladium complexes have been reported to be highly active catalysts for Suzuki–Miyaura cross-coupling in aqueous solution and supported in amorphous inorganic oxides [6,15–20].

# 2. Experimental

The reagents and solvents were obtained from commercial sources and were used without further purification. Gas chromatographic analyses were performed on a HP 5890 instrument equipped with a 25-m capillary column of 5% phenylmethylsilicone. GC/MS analyses were performed on a Agilent 5973N spectrometer equipped with the same column and operated under the same conditions as the GC. HPLC-UV analyses were performed with a Varian instrument with an UV diode array detector separating the mixture through a Kromasil-C<sub>18</sub> column ( $0.4 \times 25$  cm, pore diameter 5 µm). CH<sub>3</sub>CN:H<sub>2</sub>O was used as the mobile phase  $(50:50 \text{ v/v}, \text{ flow: } 0.7 \text{ ml} \text{min}^{-1})$ . <sup>1</sup>H- and <sup>13</sup>C-NMR were recorded in a 300-MHz Bruker Avance instrument, with CDCl<sub>3</sub> or CD<sub>3</sub>OD as the solvent and TMS as the internal standard. Diffuse reflectance UV-vis spectra were recorded on a Cary 5G adapted with a praying mantis accessory, with BaSO<sub>4</sub> as a reference. IR spectra were recorded on a Jasko 460plus spectrophotometer, with the use of sealed greaseless quartz cells with CaF<sub>2</sub> windows. IR spectra were recorded in transmission mode using self-supported wafers of the PMOs prepared pressing the solid at 2 tons  $cm^{-1}$  for 15 s. Thermal treatments were carried out in situ inside the sealed IR cells,

and the spectra were recorded in a Nicolet 710 instrument at room temperature after outgassing at the corresponding temperature under  $10^{-2}$  Pa. BET surface area and micropore volume were measured by isothermal nitrogen adsorption with a Micromeritics ASAP2000, with the use of samples that were previously sieved (particle size  $0.2-1 \mu m$ ). X-ray diffraction spectra were recorded in a X'Pert Philips analyser with a curved monochromator for Cu X-ray radiation, with the use of automatic divergence and anti-scatter slits and a mini-proportional Xe detector. The C and N content of the solids was determined by combustion chemical analysis with a Fisons CHNSO analyser. We determined the Pd content by dissolving the silicate in a mixture of HF:HCl:HNO<sub>3</sub> conc. (30 mg of solid in ca. 1:1:1 ml), diluting the solution in water (30 ml), and measuring by quantitative atomic absorption spectroscopy (Varian SpectrAA 10 plus). Quantification was achieved by a comparison of the response with a calibration plot. MCM-41 was prepared by hydrothermal crystallisation at 100 °C, with cetyltrimethyl ammonium bromide as a structure-directing agent and Aerosil as a silica source, following a procedure described in detail elsewhere [21,22].

# 2.1. Synthesis of the silylated carbapalladacycle precursor 2

The carbapalladacycle oxime complex was synthesised as described in Ref. [7]. The complex (730 mg, 2.5 mmol) was placed in a previously dried double-necked roundbottomed flask. Then anhydrous THF (25 ml) was added under a nitrogen atmosphere, and the mixture was magnetically stirred in a preheated oil bath at 65 °C under a nitrogen atmosphere until a dark yellow solution was observed. 3-Isocyanatepropyltriethoxysilane (1.875 ml, 7.5 mmol) was slowly added, and the reaction was left to react at 65 °C under an inert atmosphere for 24 h. We monitored the course of the reaction by periodically taking aliquots (0.5 ml) and following the decrease of the isocyanate band at 2275  $\rm cm^{-1}$ together with the appearance of the amide bands by IR. At the final time the mixture was concentrated, hexane (500 ml) was added, the solution was cooled, and the precursor started to precipitate as a black solid. The solid was isolated by filtration in vacuo under a nitrogen atmosphere and stored in a screw-capped vial under argon (1.2 g, 61%). [IR (CDCl<sub>3</sub>, cm<sup>-1</sup>): 3315, 2975, 2930, 2885, 2275, 1768, 1745, 1580, 1580, 1550, 1525, 1460, 1440, 1390, 1375, 1340, 1280, 1235, 1200. <sup>1</sup>H NMR  $\delta_{\rm H}$  (ppm, 300 MHz, CDCl<sub>3</sub>): 8.15 (bs), 6.95 (1H, d), 6.7 (1H, s), 6.55 (1H, d), 5.85 (bs), 3.75 (10H, q), 3.25 (H, s), 2.2 (3H, s), 1.7 (4H, s), 1.25 (15H, t), 0.75 (4H, bs). <sup>13</sup>C NMR  $\delta_{\rm C}$  (ppm, 300 MHz, DMSO- $d^6$ ): 180.1, 158.2, 154.6, 154.1, 130.6, 120.8, 113.0, 58.9, 44.1, 26.0, 23.1, 18.5, 13.2, 7.9. MS (FAB): isotopic distribution recorded for 2 compatible with 1 Pd (relative % with respect to the major peak of the peak cluster): m/z 719 (41), 721 (41), 722 (81), 723 (100), 725 (96), 727 (44); other peak clusters at 645, 503 (loss of one propyldiethoxysilyl group) and 423 daltons. Anal. Calcd. for  $C_{28}H_{50}N_3O_{10}ClSi_2Pd$  (786.5): C 42.72; H 6.35; N 5.34; Pd 13.47. Found: C 42.06; H 6.25; N 5.27; Pd 14.21.]

#### 2.2. Synthesis of PdL × PMO: general procedure

Compound 2 was used in combination with tetraethylorthosilicate (TEOS) in the synthesis of PdL $\propto$ PMO, and cetyltrimethylammonium bromide (CTABr) was used as the structure-directing agent. The molar proportions of the components in the precursor gel were

## 1.0 Si:0.12 CTABr:8.0 NH<sub>3</sub> (20%):114 H<sub>2</sub>O:10 EtOH.

TEOS and compounds **2** were used as sources of Si. Several TEOS:**2** molar ratios were tested, and highly structured materials can be obtained below a molar ratio of 95:5, corresponding to a weight ratio of 73:17. After we mixed the reactants at 20 °C and stirred the mixture for 2 h, the resulting gel was transferred to a polyethylene container and heated at 90 °C for 4 days. The solid obtained was washed with water and dried in air at 60 °C. The structure-directing agent was removed by extraction of the solid with dilute ethanolic HCl acid solution at 40 °C for 2 h (20 ml of 0.5 M ethanolic HCl for 0.5 g of solid).

#### 2.3. Kinetics experiments in water

*p*-Bromobenzoic acid (804 mg, 4 mmol), phenylboronic acid (732 mg, 6 mmol), and potassium carbonate (2.208 g, 8 mmol) were dissolved in neat water (100 ml) at 100 °C. The solid catalyst (0.005 mol% in Pd) was placed in a 250-ml double-necked round-bottomed flask in a preheated bath oil at 100 °C, the aqueous solution was added, and the suspension was magnetically stirred. We followed the course of the reaction by taking aliquots (50 µl) periodically, cooling them in an ice bath, diluting them in CH<sub>3</sub>CN (1 ml), analysing them by HPLC-UV (injected volume: 20 µl), and measuring the absorbance for *p*-bromobenzoic acid at  $\lambda = 239$  nm and for *p*-phenylbenzoic acid at  $\lambda = 273$  nm.

#### 2.4. Typical procedure for Suzuki reactions

*p*-Bromoacetophenone (19.9 mg, 0.1 mmol), phenylboronic acid (18.3 mg, 0.15 mmol), and potassium carbonate (27.6 mg, 0.2 mmol) were dissolved in water (2.5 ml) and stirred magnetically in the presence of PdL37 $\propto$ PMO (270 mg, Pd 10 mol%) at reflux temperature for 24 h. Then the mixture was allowed to cool and was extracted with ethyl acetate (2 × 20 ml). The organic phases were concentrated under reduced pressure and analysed by GC and GC-MS, with nitrobenzene as an external standard.

#### 2.5. Leaching tests

We studied leaching of catalytically active species from the solid to the solution (in where the bleeded species would act as homogeneous catalysts) by taking a 5-ml sample from the reaction at 35% conversion. Filtration was carried out in hot to avoid reprecipitation of palladium in case of a temperature decrease, in a 5-ml glass syringe coupled with a swinney 13-mm filter (Millipore). Then the clear solution was allowed to react for additional 22 h. We followed the course of the reaction by periodically analysing the reaction mixture by HPLC-UV. The results were compared with those obtained in a twin reaction under the same conditions, without removal of the solid catalyst from the reaction mixture.

### 2.6. Recovery and reuse of PMO

*p*-Bromoacetophenone (19.9 mg, 0.1 mmol), phenylboronic acid (18.3 mg, 0.15 mmol), and potassium carbonate (27.6 mg, 0.2 mmol) in neat water (2.5 ml) were stirred magnetically in the presence of PdL37 $\propto$ PMO (135 mg) at reflux temperature for 24 h. Then 2.5 ml of water was added, and the mixture was filtered in hot under vacuum. The solid was washed with water (2.5 ml) and ethyl acetate (20 ml), the liquid phase was extracted in ethyl acetate to obtain the conversion result, and the dry solid was weighed and reused in a next run; proportional amounts of reactants were added to keep the substrate-to-catalyst and the solvent-to-catalyst ratios constant throughout the series of reuses. The palladium content of the solid was measured in the first and last reuses.

# 2.7. Procedure for the synthesis of aminopropyl modified silica

After dehydration of the high-surface-area silica (1 g at 200 °C under  $10^{-2}$  Torr for 2 h), the required amount of 3-aminopropyltriethoxysilane (3 ml) in dry toluene (10 ml) was added, and the suspension was stirred at reflux temperature under a nitrogen atmosphere for 48 h. The solid was filtered and Soxhlet was extracted with dichloromethane for 24 h. After the solids were dried (at 45 °C under  $10^{-1}$  Torr for 2 h), the density of the 3-aminopropyl groups anchored in the solid (1.05 mmol N g<sup>-1</sup>) was estimated from combustion chemical analysis.

# 2.8. Procedure for the synthesis of BrPhCONH@SiO<sub>2</sub>

To anchor the *p*-bromo benzamide to silica, a solution of the corresponding acyl chloride (575 mg, 2.6 mmol) in dry THF (10 ml) was placed in a previously dehydrated round-bottomed flask in the presence of aminopropyl-modified solid (0.5 g) and pyridine (202  $\mu$ l, 2.5 mmol) under a nitrogen atmosphere. The suspension was stirred magnetically at 40 °C under a nitrogen atmosphere for 12 h. The solid was separated by centrifugation and washed with 10 ml of HCl/H<sub>2</sub>O (5% v/v, three times), 10 ml of K<sub>2</sub>CO<sub>3</sub>/H<sub>2</sub>O (0.02 M, two times), neat water (two times), and ethanol (two times). Then the solid was soxhlet extracted with

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CH<sub>2</sub>Cl<sub>2</sub> for 24 h. After the solids were dried (at 45 °C under  $10^{-1}$  Torr for 2 h), the anchored amount was determined by combustion chemical analysis and confirmed by thermogravimetric analysis (BrPhCONH@SiO<sub>2</sub>: 0.54 mmol g<sup>-1</sup>).

#### 2.9. Three phase tests

A solution of 4-bromoacetophenone (0.1 mmol), phenylboronic acid (0.3 mmol, 3 equivalents), and K<sub>2</sub>CO<sub>3</sub> (0.4 mmol, 4 eq.) in water (2.5 ml) was magnetically stirred in the presence of PdL37 $\propto$ PMO (135 mg) and BrPhCONH@SiO<sub>2</sub> (185 mg) at 100 °C for 24 h. At this time, the supernatant was analysed by GC (conversion > 99%), and the solid was separated by filtration under vacuum in hot, washed with ethanol, and soxhlet-extracted with ethanol for 24 h. After that, the solid was hydrolysed in a 2 M solution of KOH (1.68 g) in ethanol:water (10:5 ml) at 90 °C for 3 days. The solution was neutralised with HCl (10% v/v) (9.1 ml), extracted with CH<sub>3</sub>CN, and analysed by HPLC.

# 3. Results and discussion

#### 3.1. Synthesis of PdL × PMO

In considering the structure of the carbapalladacycle 1, we devised a simple derivatisation strategy for the introduction of two terminal triethoxysilyl groups the oxime and phenolic hydroxyl groups. A convenient disilane derivative can be obtained in a single step by reaction of complex 1 with 3-isocyanatepropyltriethoxysilane. Scheme 1 depicts the route followed to obtain the precursor 2. Alternative routes in which palladium atom was introduced after the hydroxyacetophenone oxime ligand was derivatised with triethoxysilyl groups were less successful and apparently produced the reduction of Pd(II) with the formation of black palladium metal.

Formation of precursor **2** can be followed by IR monitoring of the disappearance of the isocyanate band at  $2300 \text{ cm}^{-1}$  and observation of the concurrent growth of the two carbamate carbonyl vibrations at 1760 and 1730 cm<sup>-1</sup> (Fig. 1). The silanised carbapalladacycle **2** can be obtained with high purity by quenching of the reaction after disappearance of the characteristic isocyanate band with hexane, whereby precipitation of compound **2** occurs. The



Fig. 1. IR spectra of 3-triethoxysilylpropylisocyanate (a, dotted line), reaction mixture after 24 h (b, dashed line) and carbapalladacycle precursor **2** precipitated from hexane (c, solid line).

bis-carbamate 2 was characterised by analytical and spectroscopic means that were in agreement with the proposed structure. In addition to IR spectroscopy, precursor 2 shows in the UV–vis spectrum a ligand-centred band at 260 nm, together with a broader, less intense LMCT band at 350 nm characteristic of the complex. In <sup>1</sup>H NMR the most salient features are the signals of the three aromatic protons of the carbapalladacycle appearing around 7.0–6.4 ppm together with the signals of the methylene groups between the uretane and the silane groups, whose integral indicates the double functionalisation at the phenolic and oxime hydroxyl groups.

The corresponding PdL $\propto$ PMO was obtained by cocondensation of the precursor **2** and TEOS in the presence of cetyltrimethylammonium bromide (CTABr) following the conventional procedure for preparing MCM-41 silicates (Scheme 2). Blank control with the use of **1** shows that the complex can stand the treatment at 100 °C at pH 10 for 3 days with only partial decomposition, as evidenced by the electrospray mass spectrum of the reaction mixture. Three PMOs containing different proportions of compound **2** in the synthesis gel were prepared. After the synthesis, the assynthesised PdL $\propto$ PMO contained channels full of CTABr, which acted as a structure-directing agent. The template was removed by exhaustive solid–liquid extraction with ethanol and *n*-heptane–ethanol mixtures containing HCl as reported [14].



Scheme 1. Synthesis of precursor 2.





Scheme 3. Procedure of post-synthetic anchoring of the carbapalladacycle precursor 2 to pre-formed MCM-41.

As controls to compare the catalytic activity of the PdL xPMO, we prepared two other solids. One of them was a pre-formed all-silica MCM-41 that after synthesis and CTABr surfactant calcination was submitted to postsynthetic treatment with 2 to graft the complex covalently (Scheme 3). The periodic structures of PdL x PMO and PdL MCM-41 must be very similar, with an array of parallel hexagonal channels containing the complex 2 covalently linked by two tethers. The third solid,  $PdL \propto SiO_2$ , was a material prepared under the same conditions as PdL xPMO, except that no CTABr was added as a structure-directing agent. This synthesis will lead to a palladium complex catalyst anchored on an amorphous silica, in contrast to the periodic structure of PdL xPMOs. Comparison of the catalytic performance of PdL xMCM-41 and PdL xSiO<sub>2</sub> with that of PdL $\propto$ PMO should provide information about the role of the structure, porosity, and synthetic procedure in the activity of the solid.

# 3.2. Characterisation data for the palladium-containing solids

The series of catalysts prepared and their main analytical, textural, and porosity parameters are summarised in Table 1. The Pd content of the series of solid catalysts was determined by quantitative atomic absorption spectroscopy after the solid silicates were dissolved with HF/HNO<sub>3</sub>/HCI (1:1:1). The nomenclature of the samples indicates the mmol Pd content of each sample. On the other hand, C and N content was determined by combustion chemical analysis. The experimental C/N atomic ratio agrees with that expected for the composition of extracted PdL $\propto$ PMO, and the Pd/C atomic ratio is in accordance with that of the precursor complex **2**, suggesting that the palladium complex has survived the treatment required for the synthesis of the periodic silicate.

Most of the transition-metal complexes have characteristic absorption UV-vis spectra originating from ligand-tometal or metal-to-ligand charge transfer transitions. As mentioned above, carbapalladacycle **1** has a characteristic band at 350 nm in solution. It is reasonable to assume that this band will be preserved in PdL $\propto$ PMO, although it may unRelevant analytical, textural and porosity data of the catalyst prepared for the present work

Solid	$\begin{array}{c} \text{BET} \\ \text{surface} \\ \text{area} \\ (\text{m}^2  \text{g}^{-1}) \end{array}$	Micropore volume $(cm^3 g^{-1})$	Average pore diameter (Å)	Elemental analysis (mmol g <sup>-1</sup> )	Pd analysis $(\text{mmol g}^{-1})$
PdL04∝PMO	729.6	0.43	31.0	N: 0.03 C: 1.20	0.004
PdL08∝PMO	848.3	0.56	28.8	N: 0.04 C: 3.53	0.008
PdL37∝PMO	1033.5	0.71	32.3	N: 0.40 C: 2.46	0.037
PdL73∝PMO	847.4	0.45	34.5	N: 0.57 C: 3.09	0.073
PdL88∝PMO	1026.0	0.66	29.5	N: 1.13 C: 4.92	0.088
PdL∝MCM-41	715.8	0.47	29.8	N: 0.15 C: 1.30	0.014
$PdL \propto SiO_2$	155.5	0.02	_	N: 0.03 C: 0.20	0.011

dergo solvatochromic shifts, depending on the polarity of the medium. Fig. 2 shows the diffuse reflectance UV-vis spectra of PdL x PMO before and after removal of the CTABr template, where the broad-band characteristic of 1 can be seen. The absorption band of PdL xPMO is shifted with respect to  $\lambda_{max}$  of precursor **1** in solution. Moreover, there is a variation in  $\lambda_{max}$  and a decrease in intensity upon CTABr extraction. The variation in  $\lambda_{max}$  can be interpreted as reflecting the polarity change from hydrophobic to hydrophilic experienced by the palladium complex upon removal of the surfactant, and the decrease in the intensity can be due to the removal of the fraction of 2 that was not successfully covalently grafted to the silica walls during the synthesis. Powder X-ray diffractions of the PdL 
PMOs show the characteristic diffraction pattern of MCM-41-like solids, exhibiting an intense peak at  $2\theta = 2^{\circ}$  and other, less intense peaks corresponding to diffraction in the [1.1.0] and [2.0.0] planes. The crystal structure of the PdL xPMO remains after removal of the CTABr, although the decrease in the number of counts



Fig. 2. Diffuse reflectance UV–vis spectra (plotted as the Kubelka–Munk function of the reflectance, R) of as-synthesized PdL37 $\propto$ PMO (a) and after removal of the template (b).



Fig. 3. Powder XRD of PdL08 $\propto$ PMO before (a) and after surfactant removal (b) and of PdL88 $\propto$ PMO before (c) and after surfactant removal (d), showing the periodic MCM-41 like structure of the solids.

may indicate that solid–liquid extraction introduces some degree of disorder in the material. Fig. 3 shows the X-ray diffraction of some of the samples before and after removal of the template to illustrate the quality of the PdL $\propto$ PMOs used in this work.

Isothermal gas adsorptions also agree with the formation of a well-crystallised mesoporous material with a large BET surface area of about 850 m<sup>2</sup> g<sup>-1</sup> and micropore volumes close to 0.5 ml g<sup>-1</sup>. The average pore size diameter is in the mesopore range, about 3 nm. For the sake of comparison we also determined the mesoporosity and surface area of the sample in which the palladium ligand was introduced by post-synthetic grafting on a highly crystalline *all-silica* MCM-41 that gives values smaller than some of those measured for PdL $\propto$ PMOs. Also as expected, the material PdL $\propto$ SiO<sub>2</sub> prepared as PdL $\propto$ PMOs with precursor **2** in the absence of structure-directing agents gave a very low surface area with a considerably smaller pore volume. The relevant porosity parameters are included in Table 1.

In addition to powder X-ray diffraction, the MCM-41-like structure of the PdL $\propto$ PMOs is also revealed in the TEM images of the solids. Fig. 4 shows two different images recorded for PdL88 $\propto$ PMO in which the pore openings with hexagonal array and the channel structure of the material can clearly be seen.

#### 3.3. Catalytic activity of PdL CPMO

The series of PMOs prepared were tested as heterogeneous catalysts for the Suzuki cross-coupling of 4-bromobenzoic acid with 1.5 eq. of phenylboronic acid in neat water (Eq. (1)). All of the solids exhibit catalytic activity, and, in all cases, the only product observed was the corresponding 4-carboxybiphenyl; the formation of biphenyl arising from homocoupling or debromination to form benzoic acid is not detectable under reaction conditions.



The results obtained are summarised in Table 2. First, we proceeded to determine the influence of Pd content on the catalytic activity. For these experiments we kept the 4-bromobenzoic acid/Pd ratio constant, thus varying the weight of solid catalyst in the reaction according to the Pd loading. In principle, it should be expected that the catalytic activity is the same for all of the materials if the intrinsic activity of the complex is constant, since the experiments are performed at the same substrate/Pd ratio. This was not the case, and from the results it is clear that carbapalladacycle complex loading has a remarkable influence in the catalytic activity; the highest turnover frequency was observed for the PdL08 x PMO, with an intermediate Pd content. Lower or higher Pd content leads to a decrease in activity; the lack of proportionality is particularly remarkable for PdL88 PMO, in which the Pd content is the highest. PdL88 CPMO should exhibit an order-of-magnitude higher turnover frequency than the other catalysts, but its activity was actually lower than that for PdL08 CPMO. At this point it is worth mentioning that the reported activity in the homogeneous phase for the cross-coupling of phenyl boronic acid and 4-chloroacetophenone of parent oxime carbapalladacycle at 0.1 mol% in water at 100 °C in the presence of K<sub>2</sub>CO<sub>3</sub> and tetrabutylammonium bromide in 1 h is higher than 99%.

This variation in the intrinsic activity of 2 could reflect interactions with spurious silanol groups of the support or the preferential location of the complex at high loading in framework positions that are not accessible to the substrates.



Fig. 4. Two transmission electron microscopy images of PdL88 PMO in where the hexagonal arrangement and channel structure of the PMO can be clearly seen.

Kinetic data at 6 h for the Suzuki reaction of *p*-bromobenzoic acid (804 mg, 4 mmol), phenylboronic acid (732 mg, 6 mmol) and potassium carbonate (2.208 g, 16 mmol) in neat water (100 ml) at reflux temperature in the presence of the corresponding amount of solid catalyst (Pd 0.005 mol%)

Catalyst	Pd analysis	Final vield	Initial rate	TOF (h <sup>-1</sup> )
	$(\text{mmol g}^{-1})$	(%)	$(\% h^{-1})$	( )
PdL04∝PMO	0.004	60	54	10843
PdL08∝PMO	0.008	86	175	34979
PdL88∝PMO	0.088	84	85	17009
PdL  MCM-41	0.014	88	182	36314
$PdL \propto SiO_2$	0.011	84	64	12900

#### 3.4. Influence of the structure in which PdL is embedded

To demonstrate the beneficial influence of porosity and regular arrangement of the Pd complex through the mesopores, we proceeded to compare the catalytic activity for the Suzuki-Miyaura cross-coupling of 4-bromobenzoic acid and phenylboronic acid of three related solids containing the carbapalladacycle complex. One of them was PdL08 CPMO, in which the PdL complex is incorporated into the solid during the synthesis of the material. A second catalyst used was PdL MCM-41, in which the synthesis of the structure and the subsequent grafting of the complex were performed successively and independently. The third catalyst used was PdL SiO<sub>2</sub>, which was obtained by co-condensation of precursor 2 and TEOS in the absence of a structure-directing agent and where no mesopores are present. The three solid catalysts have a similar palladium content. For the sake of comparison we have also included in our study a reaction in the homogeneous phase with a soluble oxime carbapalladacycle complex. The final yields, initial rates, and turnover frequencies are collected in Table 2. The results obtained with the catalytic test are shown in Fig. 5, where the time conversion using of the set of three catalysts is presented. From this figure it is clear that, although the final conversion at long reaction time is very similar for the three solids and independent of the structure of the catalyst, the initial activity at short reaction times is significantly lower for



Fig. 5. Time conversion plot for the Suzuki reaction of *p*-bromobenzoic acid (804 mg, 4 mmol), phenylboronic acid (732 mg, 6 mmol) and potassium carbonate (2.208 g, 16 mmol) in neat water (100 ml) at reflux temperature in the presence of PdL08 $\propto$ PMO (a, 25.0 mg), PdL $\propto$ MCM-41 (b, 14.3 mg) and PdL $\propto$ SiO<sub>2</sub> (c, 18.2 mg) as catalyst.

 $PdL \propto SiO_2$  compared with PdL08 $\propto$ PMO and PdL $\propto$ MCM-41; the latter two show very similar reaction rates. These catalytic data nicely illustrate the beneficial influence of porosity and regular distribution of the active sites, which makes PdL08 $\propto$ PMO and PdL $\propto$ MCM-41 catalytically superior to PdL88 $\propto$ SiO<sub>2</sub>.

To determine the scope of our PdL $\propto$ PMO catalysts, we selected the most active and studied its catalytic activity for other substrates. The results for PdL37 $\propto$ PMO as a catalyst are summarised in Table 3. As can be seen there, although bromo-substituted halobenzenes give high yields of the corresponding biphenyl, this mesoporous solid was inefficient in catalysing the coupling of chloro-substituted derivatives. This is in accord with the lower reactivity of the chloro aromatics with respect to bromo compounds.

# 3.5. Leaching studies

When one works with heterogeneous catalysts, an important issue is to determine the degree of leaching of the active sites from the solid to the solution. In these cases, the solid behaves like a reservoir of catalytically active species, but the reaction may occur in the liquid phase. To address

Results of the Suzuki coupling of *p*-bromoacetophenone (19.9 mg, 0.1 mmol), phenylboronic acid (18.3 mg, 0.15 mmol) and potassium carbonate (27.6 mg, 0.2 mmol) dissolved in water (2.5 ml) in the presence of the PdL37 $\propto$ PMO (270 mg, Pd 10 mol%) at reflux temperature for 24 h



this point, we compared the time conversion plots of twin reactions; in one of them the solid was removed at the reaction temperature at about half-conversion, and the resulting liquor was allowed to react further in the absence of the solid catalyst. Fig. 6 shows the time conversion plot for these experiments, from which it can be concluded that part of the catalytic activity is due to some palladium species that, under the reaction conditions, migrate from the solid to the solution. From a comparison of the conversion increase since the catalyst filtration time for a reaction in which the solid has not been filtered with that in which the solid catalyst has been filtered (see Fig. 6), it can be estimated that 50% of the overall catalytic activity of  $Pd \propto PMO$  is due to leached palladium species.

To better address the occurrence of leaching and particularly to overcome the filtration in hot at the reaction temperature, Davies and Lipshutz [23,24] have developed a



Fig. 6. Time conversion plot for the Suzuki reaction of *p*-bromobenzoic acid (804 mg, 4 mmol), phenylboronic acid (732 mg, 6 mmol) and potassium carbonate (2.208 g, 16 mmol) in neat water (100 ml) at reflux temperature in the presence of PdL08 $\propto$ PMO as catalyst (a, 25.0 mg) and a twin run in which the solid was filtered in hot at 10 min (ca. conversion 34%) and allowing the clear solution to continue the reaction (b).

so-called three-phase-test methodology for activated carbonsupported palladium catalyst in which the halogenated reactant is covalently immobilised on an insoluble support; after the reaction with the solid palladium catalyst the solid containing the reagent is surveyed for the presence of the corresponding C-C coupling product by hydrolysis. We adapted this methodology and proceeded to anchor 4-bromobenzoic acid to an aminopropyl-modified silica (Scheme 4). The success of the covalent bonding between 4-bromobenzoic chloride and the aminopropyl-modified silica was demonstrated by recording the IR spectra of the solid and observing of the presence of the amide bands around  $1700 \text{ cm}^{-1}$ . Independent controls show that hydrolysis of the amide bond of inmobilised 4-bromobenzoic acid can be achieved quantitatively under strong basic conditions. Thus, we proceeded to perform the Suzuki coupling of 4-bromobenzoic acid with an excess of phenylboronic acid (3 eq.) catalysed by PdL37 CPMO in the presence of 4-bromobenzoic acid bound to silica. After the reaction the solids were filtered, washed, and submitted to hydrolysis under basic conditions, where 4carboxybiphenyl accompanied by benzoic acid arising from the debromination was observed (Scheme 5).

The three-phase-test experiment and the observation of reaction conversion in the absence of solid are clear indications that some active Pd species is in solution. It may be that part of the palladium complex is decomposed in the course of the reaction, forming palladium nanoparticles or any other species that dissolves and becomes active during the reaction.

### 3.6. Reusability

A second issue that has to be addressed for heterogeneous catalysts is their reusability. Thus we proceeded to study the catalytic activity of PdL $\propto$ PMO solid upon reuse. These experiments were undertaken by recovery of the solid at the end of the reaction by filtration, washing with ethanol and



Scheme 4. Anchoring procedure of the *p*-bromo-N-butyl benzamide onto the aminopropyl modified high surface silica.



Scheme 5. Study of the leaching by the three-phase test experiment for the Suzuki reaction of *p*-bromoacetophenone (20.1 mg, 0.1 mmol), phenylboronic acid (36.6 mg, 0.3 mmol) and potassium carbonate (55.3 mg, 0.4 mmol) in neat water (2.5 ml) at reflux temperature in the presence of PdL37 $\propto$ PMO as catalyst (135 mg) and BrPhCONH@SiO<sub>2</sub> (185 mg, 0.1 mmol haloaryl) as solid reactant.

Reusability of PdL37 $\propto$ PMO for the Suzuki reaction of *p*-bromoacetophenone (20.1 mg, 0.1 mmol), phenylboronic acid (18.3 mg, 0.15 mmol) and potassium carbonate (27.6 mg, 0.2 mmol) in neat water (2.5 ml) at reflux temperature in the presence of solid catalyst (137 mg)

Use	Conversion <sup>a</sup> (%)	Palladium content <sup>b</sup> (%)	
1	92 (1)	0.037	
2	95 (0.2)	0.037	
3	80 (-)	0.037	
4	88 (-)	0.037	
5	73 (-)	0.037	
6	68 (-)	0.037	

<sup>a</sup> Percentage of homocoupling is given in parentheses and these values are included in the total p-bromoacetophenone conversion.

<sup>b</sup> Pd content (in percentage and measured by quantitative atomic absorption spectroscopy) of the recovered solid catalyst after being used. The initial Pd content of the fresh catalyst was 0.037%.

then ether, and undertaking a new reaction with fresh solvent and reactants under the same conditions. The substrateto-catalyst ratio was maintained throughout the reuses. The results obtained are summarised in Table 4.

As expected in view of the general behaviour of supported complexes, the catalytic activity of PdL37 $\propto$ PMO decreases progressively upon reuse, the diminution in activity being significant under our reaction conditions after the fourth use. To gain insight into the deactivation of the catalyst, palladium analyses of the solid catalyst were performed after each experiment. These analyses show that within the analytic error  $[3 \times 10^{-5} (Pd \text{ mmol})(\text{g of solid})^{-1}]$ , there is no significant variation in the palladium percentage upon reuse. However, diffuse-reflectance UV-vis spectroscopy of the solid shows that the carbapalladacycle complex gradually decomposes during the reactions, and its presence is undetectable at the end of the second use. In addition, X-ray diffraction of the used catalyst after the sixth use shows that the PMO structure has completely collapsed, and the material has become an amorphous solid.

In view of these data, the most reasonable deactivation process for PdL $\propto$ PMO consists of the progressive transformation of PdL complex into Pd metal particles and the increasing loss of porosity of the material. In accord with this interpretation, the BET surface area of the catalyst after the sixth use was 213 m<sup>2</sup> g<sup>-1</sup>, which corresponds to a remarkable decrease with respect to that of fresh catalyst (see Table 1). Given that leaching is already observed in the first use of the catalyst, there has to be an initial leached species, probably in very low amounts, with a high activity. Nanometric palladium metal clusters of very small size are the most reasonable proposal for the leached species, in

view of the tendency of palladium to become reduced and the formation of nanoparticles. After being used, the overall activity (leaching plus heterogeneous catalysis) of the palladium decreased significantly, thus leading to the conclusion that the leached species are also being transformed. Palladium particle size increase can explain this remarkable activity diminution. Thus, although the total palladium content remains constant, the activity and turnover number of the site decrease as a consequence of the transformation of the catalyst, that is, both disappearance of the carbapalladacycle complex and a gradual increase in palladium particle size, starting from a few nanometers.

#### 4. Conclusions

Periodic mesoporous organosilicas incorporating a carbapalladacycle complex were synthesised, and the resulting materials showed the ordering and structure expected for an MCM-41 silica. The periodicity of the PMOs is largely maintained upon removal of the cetyltrimethylammonium surfactant. These solids exhibit catalytic activity for the Suzuki-Miyaura cross-coupling of bromobenzenes with phenylboronic acid. There is an optimal palladium loading with which to achieve the highest efficiency. These structured PMO materials have an activity similar to that of related solids in which crystallisation of the MCM-41 and covalent grafting have been made stepwise and independently. The activity of these mesoporous catalysts is much higher than that of analogous amorphous solids. However, further work is still necessary to improve the durability of the PMO catalyst in aqueous medium upon reuse and to reduce palladium leaching during the reaction. Although the total palladium content of the PMO solid is maintained upon reuse, there is a gradual decomposition of the initial oxime carbapalladacycle complex with the formation of palladium metal that partially migrates to the solution under the reaction conditions, but is re-adsorbed to the solid upon cooling and filtering.

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