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Palladium supported on polyether-functionalized mesoporous silica. Synthesis and application as catalyst for Heck coupling reaction

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A new catalytic system based on Pd supported on polyether-functionalized mesoporous silica was prepared. This material was obtained by co-hydrolysis and polycondensation of tetraethylorthosilicate and a bis-silylated triblock copolymer P123 ($M_w = 5800$) followed by the decomposition of Pd(OAc)₂ salt. We have shown that this material can be applied as powerful heterogeneous catalyst for the Heck coupling reaction. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: organosilicon; sol-gel; hybrid material; Heck reaction

Introduction

Organic-inorganic hybrid materials based on silica and obtained by sol-gel process have attracted considerable attention during the last decades, as they constitute a unique class of materials combining the properties of organic moieties and inorganic matrix.^[1] They are obtained by hydrolysis and polycondensation of bis-or poly(trialkoxysilyl)organic precursors of general formula $\{[(R'O)_3Si]_m R (m \ge 2)\}\$ leading to materials in which the organic fragments are integrated into the silica matrix by covalent bonds.^[2] The interest of this class of materials resides in that their properties can be modified by changing the nature of the bridging organic groups, which renders them very attractive offering a wide range of possibilities in terms of chemical or physical properties.^[3] Thus, numerous organic groups have been silylated, such as ferrocene for electrochemical properties,^[4] diazo units for nonlinear optical properties^[5] or tetra-azamacrocycle for chelating properties towards transition metal centers.^[6] The corresponding materials are amorphous with often low surface area. Amorphous and non porous hybrid organic-inorganic materials containing polyethylene glycol (PEG) chains were previously reported. Nanocomposite materials were prepared starting from a mixture of tetraethoxysilane and PEG of low molecular mass.^[7] PEG-functionalized materials for catalysis,^[8] ionic conductivity^[9] or optic^[10] properties have been obtained by hydrolysis and polycondensation of silylated PEG with short chains. Recently, mesostructured materials containing PEG chains as conducting polymers were prepared by grafting of short monosilylated-PEG into pores of mesoporous silicas MCM-41^[11] and SBA-15.^[12] This last method does not allow the control loading of organic groups in the silica. In addition, grafting method led to inhomogeneous distribution of the functional groups onto the inner pores surfaces.[13] In order to avoid these drawbacks, one alternative approach has consisted in the introduction of the organic groups during the synthesis of the material by co-condensation of tetraethylorthosilicate (TEOS) and an organotriethoxysilane $RSi(OEt)_3$ in the presence of a structuredirecting agent.^[14]

More recently, periodic mesoporous organosilicas (PMOs) have constituted a real advance in materials science. Indeed, it was shown that the hydrolytic polycondensation of bridged organosilica precursors in the presence of a structure-directing agent allows the integration of organic groups into the walls of mesoporous silica through covalent Si–C bonds. A large number of papers concerning PMOs have appeared due to the great interest in the fuctionalization of the framework to tailor the properties of mesoporous silica.^[15–19]

The immobilization of homogeneous catalysts on polymeric organic^[20] or inorganic^[21] supports offers the advantages of easy product separation and catalyst recycling. The Heck reaction has been extensively used as a test reaction for the evaluation of Pd based-catalyst.^[22] The hybrid organic–inorganic materials formed by catalytic species covalently anchored to silica have chemical, mechanical and thermal stability superior to that of organic polymers. In the course of our investigations in this field, we found an original and efficient route to an immobilized palladium catalyst for Heck coupling reaction.

Herein, we report the synthesis of bis-silylated triblock copolymer Pluronic P123 ($M_w = 5800$) [PEO₂₀PPO₇₀PPO₂₀ with PEO = poly (ethylene oxide) and PPO = poly (propylene

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oxide)] followed by the preparation of two-dimensional hexagonal mesoporous silica containing tunable amount of polyether groups covalently bonded to the silica matrix. Thanks to polyether groups, $Pd(OAc)_2$ was impregnated within and the resulting materials were tested in heterogeneous Heck coupling reaction. A practical heating technique was used in this study was microwaves, known to reduce reaction time.^[23,24]

Experimental

General Procedures

The triblock copolymer $[PEO_{20}PPO_{70}PEO_{20} \text{ with } PEO = poly$ (ethylene oxide) and PPO = poly (propylene oxide)], Pluronic P123, TEOS, triphenylphosphine and phenyl iodide were purchased from Aldrich and used as supplied. 3-Isocyanatopropyltriethoxysilane was purchased from ABCR. Triethylamine and DMF were purchased from Fluka, N-methylpyrrolidone (NMP) from Merck and Pd(OAc)₂ from Janssen Chimica. The ²⁹Si CPMAS NMR spectra were recorded on a Bruker FTAM 300 as well as ¹³C CPMAS NMR spectra, in the latter case using the TOSS technique. The repetition time was 5 s (for ¹³C) and 10 s (for ²⁹Si) with contact times of 3 ms (for ¹³C) and 5 ms (for 29 Si). The duration of the ¹H pulse was 4.2 μ s (for 13 C) and 4.5 μ s (for ²⁹Si) and the rotor spin rate was 10 kHz (for ¹³C) and 5 kHz (for ²⁹Si). Chemical shifts (δ , ppm) were referenced to Me₄Si (13 C and 29 Si). Q^n and T^n notations are given respectively for $[(SiO)_n SiO_{4-n}]$ and $[R(SiO)_n SiO_{3-n}]$ environments. Specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method on a Micromeritics Tristar 3000 analyzer (using 74 points and starting from 0.01 as value for the relative pressure) and the average pore diameters were calculated by the BJH (Barret, Joyner and Handela) method and using the desorption branch. Powder X-ray diffraction patterns were measured on a Bruker D5000 diffractometer equipped with a rotating anode (Institut Européen des Membranes, Montpellier, France). Transmission electron microscopy (TEM) observations were carried out at 100 kV on a Jeol 1200 EXII microscope. Samples for TEM measurements were prepared using ultramicrotomy techniques and then deposited on copper grids. Thermogravimetry analysis (TGA) measurements were carried out under air from 20 to 600° C (5 $^{\circ}$ C min⁻¹) on a thermobalance Netzsch STA 409. Microwave-assisted reactions were performed with a Biotage Initiator 60 EXP[®]. Temperature was measured with an IR sensor on the outer surface of the reaction vial. The starting heating power was set to the maximum level (400 W) in order to obtain reproducible results.^[22]

Synthesis of Si-P123

A solution of 10 g (1.72 mmol) of P123 in CH₂Cl₂ (200 ml) was dried with magnesium sulfate and filtered. CH₂Cl₂ was removed and polymer was heated (100 °C) under vacuum for 12 h. Dry P123 was then silylated with 3-isocyanatopropyltriethoxysilane (ICPTES). To a solution of P123 (0.1 M) in dry THF (100 ml), an excess of ICPTES (4 equiv.) and Et₃N (2 equiv.) were added at room temperature. The mixture was stirred at reflux for 72 h under argon. After removal of THF and Et₃N, the obtained crude was washed with pentane four times and dried, giving rise to 9.39 g (1.50 mmol, 87%) of Si-P123 as colorless oil. ¹H NMR (200 MHz, CDCl₃): 0.60 (t, 4H, CH₂Si); 1.10 (d, 210H, CH₃CH); 1.16 (t, 18H, CH₃CH₂OSi); 1.51 (m, 4H, CH₂CH₂Si); 3.09 (q, 4H, CH₂NH); 3.42 (m, 70H, CH₃CH); 3.53 (m, 140H, CH₂CH); 3.59 (s, 156H, CH₂CH₂O); 3.68 (t, 4H, CH₂OC=O); 3.74 (q, 12H, CH₃CH₂OSi); 4.16 (t, 2H, NH).

¹³C NMR (50 MHz, CDCl₃): 8.01 (s, *CH*₂Si); 17.75, 17.87 (2s, *CH*₃);
 18.51 (s, *CH*₃CH₂OSi); 23.71 (s, *CH*₂CH₂Si); 43.84 (s, *CH*₂NH); 58.83 (s, *CH*₃*CH*₂OSi); 69.02 (s, *CH*₂OC=O); 70.98 (s, *CH*₂*CH*₂O); 73.32 (s, *CH*₂CH); 73.78 (s, *CH*₃*CH*). ²⁹Si NMR (40 MHz, CDCl₃): -45.73.

Synthesis of M50

This material was named M50 (M for material and the followed number to indicate the molar percent of Si-P123 introduced during the synthesis). Aliquots of 1.02 g (0.175 mmol) of P123 and 1.11 g (0.177 mmol) of Si-P123 were dissolved in an aqueous HCl solution (80 ml, pH \sim 1.5). The resulting clear solution was poured into 4.67 g (22.45 mmol) of TEOS at room temperature. The mixture was stirred for 2 h, giving rise to a perfectly transparent microemulsion. After heating at 60 °C, a small amount of NaF (40 mg) was added to induce polycondensation. The molar composition of the final mixture was 0.04 F-: 1 TEOS:0.01 P123:0.01 Si-P123:0.12 HCl:220 H₂O. After 72 h of stirring at 60 °C, the resulting solid was filtered and wash with ethanol and acetone. The P123 was removed by hot ethanol extraction in a Soxhlet apparatus over 24 h. After filtration and drying at 120 °C under vacuum, 2.30 g (0.166 mmol, 94%) of M50 was obtained as a white solid.

Synthesis of M50^{Pd}

General procedure for the preparation of palladium impregnation

Pd(OAc)₂ (5.6 mg, 0.025 mmol) was dissolved in 15 ml of THF and stirred for 5 min, before addition of 100 mg of **M50**. Then, the mixture was refluxed for 24 h. After filtration, washing with THF and drying at 100 °C under vacuum, **M50^{Pd}** was recovered quantitatively as a gray solid. Elemental analysis was used to determine the quantity of palladium contained in **M50^{Pd}**: 1.6 equiv. of palladium for 1 equiv. of silica was present in the material.

Heck Coupling Reaction

A mixture of **M50^{Pd}** (20.6 mg, 0.01175 mmol of Pd), tert-butyl acrylate (64.35 mg, 0.5 mmol), phenyl iodide (20.4 mg, 0.1 mmol), triethylamine (15.18 mg, 0.15 mmol) and DMF or NMP (0.5 ml) as solvent was heated under microwaves at a temperature of 100 °C and a reaction time between 30 to 60 min. After the reaction, the product was recovered by filtration, washed with dichloromethane, evaporated and then analyzed by ¹H NMR using CH₂Br₂ as an internal standard. The **M50^{Pd}** was kept and dried at 100 °C under vacuum and re-used if necessary.



Scheme 1. Preparation of bis-silylated surfactant Si-P123.



Scheme 3. Preparation of polyether functionalised material M50.



Figure 1. ¹³C CP-MAS NMR spectrum of material M50.

Results and Discussion

Preparation and Characterization of Hybrid Material

Bis-silylated triblock copolymer Pluronic P123 was synthesized as depicted in Scheme 1. Addition of 3isocyanatopropyltriethoxysilane to a solution of P123 in the presence of Et₃N afforded qualitatively with 87% yield the corresponding bis-silylated copolymer named **Si-P123**. **Si-P123** was fully characterized by IR, ¹H, ¹³C and ²⁹Si NMR spectroscopies (see Experimental)

Triblock copolymers such as P123 are good candidates to prepare organized hybrid materials, because of their mesostructural ordering property, amphiphilic character and low-cost commercial availability.^[25] In fact, a dilute aqueous acidic (pH = 1.5) solution of P123, gives rise to a stable microemulsion containing surfactant micelles. By using a mixture of P123 and **Si-P123**, it will be possible to form silylated hybrid micelles with a lipophilic core and hydrophilic crown (Scheme 2).

Polyether functionalized mesoporous material was prepared using a one-step synthesis method. Co-condensation of a mixture of **Si-P123**, P123 and tetraethoxysilane was achieved under acidic



Figure 2. Powder XRD patterns of M50. The inset shows the TEM image for the same material.



Figure 3. N₂ adsorption – desorption isotherm of M50.

conditions (Scheme 3). The resulting solid was filtered off and the unsilylated surfactant was removed by extraction with hot ethanol in a soxhlet apparatus, leading to material named **M50** (**M** for material and the followed number to indicate the molar percent of **Si-P123** introduced during the synthesis).

The ²⁹Si CPMAS NMR spectrum of **M50** displayed two signals at -101.8 and -111.0 ppm attributed to the Q³ and Q⁴ substructures respectively. The T substructures are not detectable due to the low molar ratio (0.01) of **Si-P123**/TEOS. Figure 1 represents the ¹³C CPMAS NMR spectrum of **M50** with four signals (75.3, 73.3, 70.5 and 17.4 ppm) assigned to the PEO and PPO units. It is worth noting that, the resonances of the propyl spacers and the carbonyl groups are not detectable because of the high content in PEO and PPE units.

The presence of carbonyl groups in the material was confirmed by FT-IR spectra, which display an absorption band at 1725 cm⁻¹ attributed to the stretching vibration of C=O groups.

The TGA under air for **M50** was realized and the total weight loss corresponding to the decomposition of the organic groups was found to be 39.3%, close to the theoretical value (43.5%).

The symmetry of **M50** was determined from powder X-ray diffraction (XRD) and TEM analyses. The XRD pattern exhibits three low-angle reflections, d_{100} , d_{110} and d_{200} , characteristic of well-ordered SBA-15 type materials (Fig. 2). Further evidence for an



Figure 4. TEM image M50^{Pd} showing Pd nanoparticles.

ordered hexagonal structure was provided by TEM image (see inset, Fig. 2) showing large domains of highly ordered material.

The N₂ adsorption–desorption measurements at 77 K for **M50** showed type IV isotherm with a clear H₁-type hysteresis loop at relative high pressure, characteristic for mesoporous materials (Fig. 3). The BET surface area was found to be 350 m² g⁻¹ with total pore volume of 0.9 cm³ g⁻¹ and pore size distribution around 7 nm.

In order to obtain supported palladium catalysts, impregnation method was used. **M50** was refluxed with a THF solution of $Pd(OAc)_2$ for 24 h and the resulting solid was copiously washed with ethanol–THF to eliminate any non-complexed salt and named **M50^{Pd}**.

From elemental analyses (Pd, Si and C) of **M50^{Pd}**, the Pd/**Si-P123** ratio was found to be 10, confirming the accessibility of the polyether groups. The TEM image of material **M50^{Pd}** shows the presence of Pd nanoparticles (Fig. 4).

The Heck reaction in the presence of **M50^{Pd}** was tested in the substitution reaction between *t*-butyl acrylate and phenyl iodide [eqn (1)], under microwaves, for a short reaction time (30–60 min).^[26] A mixture of PhI, *t*-butyl acrylate, **M50^{Pd}** and Et₃N was heated in DMF or NMP at 100 °C [eqn (1)]. The quantity of Pd evaluated by EDX experiments was kept constant throughout the study, at 1.2 mol%. At the end of the reaction, the mixture was cooled down, filtered, evaporated and analyzed by ¹H NMR using CH₂Br₂ as an internal standard. Integration of the signal corresponding to the H_β of *t*-butylcinamate [eqn (1)] measured against the unique signal of the standard (CH₂Br₂) provided the yield of the product. For the recycling experiment, the **M50^{Pd}** that served in the first experiment was rinsed with CH₂Cl₂, dried at 100 °C under vacuum and used again in the next experiment, adjusting the reaction time to 30–60 min.



M50^{Pd} was evaluated in four cycles of the Heck reaction with two different solvents that showed promising activity (DMF or NMP). These preliminary results are shown in Fig. 5. In DMF, from the first run, the catalytic activity of **M50^{Pd}** was high and 83% of the expected product was obtained. This material could be recycled and an even better yield of 93% was obtained. In the third cycle, the yield decreased, providing 55% of *t*-butylcinammate, but increased in the last run (a 92% yield was obtained). Hence **M50^{Pd}** kept a high activity throughout the different cycles even if irregular results were obtained. Switching to NMP, again a high activity was observed but the catalytic system needed an



Figure 5. Conversion in the M50^{Pd} catalyzed-Heck for different cycles.

induction period: a 40% yield was obtained at the first cycle, followed by 95 and 85% yields in the next two cycles then the activity decreased in the fourth cycle (64%). Anticipating a drop in the activity, the reaction time for the third and fourth cycles was increased from 30 min to 1 h. It is worth noting that these irregularities were reproducible in both cases. Consequently, organic–inorganic hybrid material-based catalysts such as **M50^{Pd}** are promising for performing Pd-catalyzed transformations with a high catalytic activity and capacity for catalyst recycling. The variations in catalytic activities presented herein are most probably due to changes in the morphology and loading of the palladium catalyst. Studies are underway in our laboratory to investigate these parameters and will be reported in due course.

Conclusion

In conclusion, we have prepared a new palladium catalyst supported on mesoporous silica-bearing polyether units. This catalyst is active for the Heck coupling reaction. The reactions proceed in high yields and the catalyst may be recovered almost quantitatively by simple filtration and reused several times with limited leaching of palladium and loss of activity. In our case, this reaction seem to be more appropriate than systems based on organic polymer-stabilized palladium species that have been reported,^[27,28] as well as silica based catalysts.^[29] Finally, based on this recovery process, problems related to catalyst recovery and metal separation from the organic substrates can be resolved. This last feature combined with the air-stability of the catalyst may be of interest for large industrial applications, in particular for pharmaceutical products.

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