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Cross-Linked Thiazolidine Network as Support for Palladium: A New Catalyst for Suzuki and Heck Reactions

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A thiazolidine-based material was used for the first time as support for palladium. The support was prepared by starting from a highly cross-linked thiazolium-based material, obtained by radical oligomerization of a bisvinylthiazolium dibromide salt in the presence of 3-mercaptopropyl-modified silica SBA-15. Palladium was immobilized by treatment with tetrachloropalladate salt. Reduction with sodium borohydride afforded a thiazolidine-based material that acted as ligands for the Pd species. The thiazolidine-based palladium catalyst was fully characterized and, working in only 0.1 mol% amount, displayed good activity in the Suzuki–Miyaura and in the Heck reactions. Several biphenyl and alkene compounds could be prepared in high yields. The catalytic material proved to be fully recoverable and it was representatively used for three times in the Suzuki–Miyaura reaction without showing any decrease in its activity.

Introduction

Carbon–carbon bond forming reactions, such as Suzuki–Miyaura and Mizoroki–Heck reactions, catalyzed by palladium compounds are nowadays of great interest from both academic and industrial points of view.[1] These important and useful transformations are widely employed in synthetic organic chemistry for the synthesis of pharmaceuticals and natural products,[2] but also in the field of materials chemistry for the preparation of conjugated polymers.[3] The rush towards the development of more active, selective, and recyclable catalysts has led to the use of a plethora of different palladium-based catalytic systems.[4] Nevertheless, in order to limit problems related to separation of homogeneous catalysts from reaction crude and, with the aim of costs abatement, in recent years a lot of efforts have been devoted to the preparation and application of recyclable supported palladium catalysts. These catalysts have been immobilized on various supports such as silica, alumina, zeolites, organic polymers, magnetic nanoparticles, and dendrimers.[5] However, although the literature is full of C-, N-, S-, and P-based ligands for the immobilization of Pd^{II} species and palladium nanoparticles, there are very few examples in which these species are stabilized and/or anchored by employing SN ligands.[6] The knowledge of oxygen and moisture stability of Pd^{II} complexes with a thiazolidine derivative obtained from thiamine dates back to 1981,[7] and the first example of a Heck reaction promoted by $Pd(OAc)_2$ immobilized onto a polystyrene resin through a SN ligand has been reported in 1987.[8] However, very recently a 4-amino-5-methyl-3-thio-1,2,4-triazole-functionalized polystyrene resin supported Pd^{II} complex has been successfully employed in the Suzuki, Heck, and copper-free Sonogashira reactions,[9] whilst the complex between palladium and 1-benzyl-4-phenylthiomethyl-1*H*-1,2,3-triazole promoted C–C coupling processes in 0.01 mol% loadings by forming in situ Pd nanoparticles that were stabilized by the ligand.[10] Oxazolidine–thioether and thiazolidine–alcohol palladium complexes were used in the asymmetric palladium-catalyzed allylic alkylation.[11]

These few data indicated that there is still a lot of room to explore the use of SN ligands for the immobilization of Pd nanoparticles.

Recently, we have developed a new concept of heterogeneous materials based on highly cross-linked imidazolium salts supported on silica gel for the immobilization of palladium nanoparticles in high loadings. Such kind of supported ionic-liquid-like phase (SILLPs) resulted to be highly efficient, recoverable, and reusable in the Suzuki–Miyaura and in Heck reactions both under batch[12] and flow conditions.[13] Interestingly, these materials are also able to effectively promote the synthesis of cyclic carbonates,[14] ethers,[15] or even to act as palladium scavengers.[14a, 16] Finally, these SILLPs found application as non-covalent supports for the reversible immobilization of ionic liquid tag-endowed organocatalysts[17] working under a “release and catch” regime.[18]

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Such highly cross-linked imidazolium networks are obtained by radical oligomerization of bis-vinylimidazolium salts on the surface of mercaptopropyl-modified amorphous silica gel or ordered mesoporous silica SBA-15 giving a multilayered ionic-liquid-like material.[12–17] The advantage of such highly loaded SILLP material arise from the possibility that are able to stabilize high amounts of catalytically active Pd species. Indeed, it has been possible to immobilize up to 10 wt% of palladium on such materials.

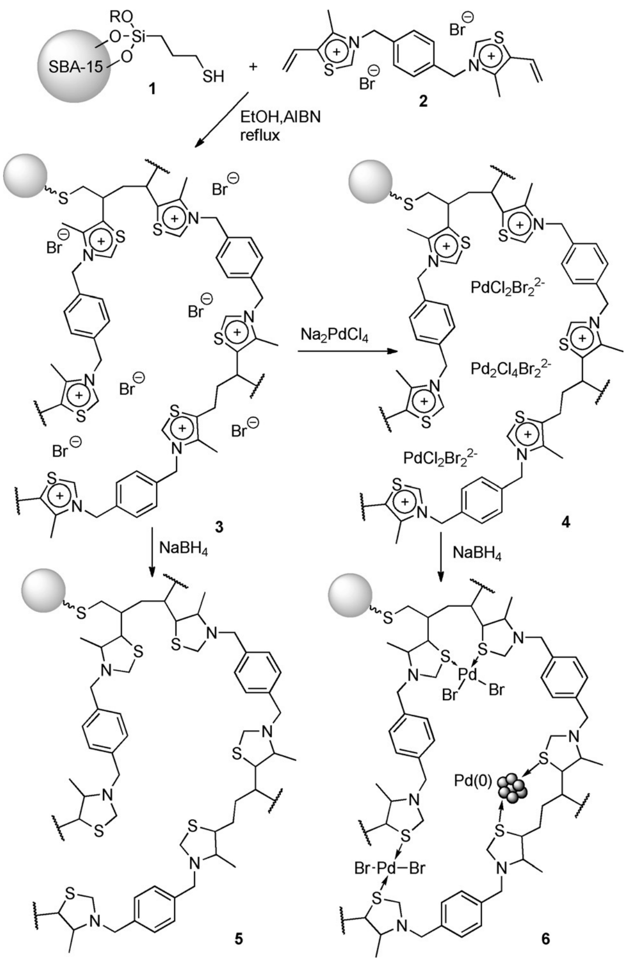
Whereas imidazolium-based ionic liquids as well as imidazolium-based supports have been largely used as homogeneous and heterogeneous supports for Pd-based catalysts, sulfur–nitrogen ligands such as the thiazolidine ring has been very scarcely used as ligands for palladium[7] and thiazolidine-based supports have not been previously reported or used for such scope. Taking advantage of our synthetic methodology for the preparation of highly loaded imidazolium-based silica, we envisaged a new approach for the palladium immobilization based on a highly loaded thiazolidine-functionalized silica support. Herein we describe the synthesis, characterization and uses of a new palladium catalyst immobilized on a cross-linked thiazolidine-modified mesoporous silica gel.

Results and Discussion

The first step was the synthesis of the thiazolium-based SBA-15 material **3** (Scheme 1). This material was prepared by reaction between the mercaptopropyl-modified silica SBA-15 **1** and the bisvinylthiazolium salt **2** (Figure S1 to S3).[15] Support **3** has a specific Brunauer–Emmett–Teller (BET) surface area of 116 $m^2 g^{-1}$ and a cumulative pore volume of 0.14 $cm^3 g^{-1}$ (Figure S4). Transmission electron microscopy investigation (Figure S5) allow evidencing the presence of the typical structure of the SBA-15 solid as well as of the polymeric network. Elemental analysis gave a thiazolium loading of 2.28 $mmol\,g^{-1}$. These data are comparable with those of a previous synthesis of the same material.[15]

In addition, the ^{13}C magic angle spinning (MAS) NMR spectroscopy data of the freshly prepared material was superimposable to that of a previous preparation.[15] These results demonstrate the reproducibility of our synthesis methodology.

The thiazolium-based SBA-15 material **3** was stirred with an aqueous solution of sodium tetrachloropalladate (Na_2PdCl_4). Material **4** was recovered by filtration and no palladium was found in the filtrate. The material **4** was treated with $NaBH_4$ in ethanol and the final Pd loading was determined by atomic absorption spectrometry (AAS) with a graphite furnace on the final material **6**. It is known that the thiazolium ring is reduced to thiazolidine if treated with sodium borohydride in methanol[19] or water.[20] In addition, such treatment causes partial palladium reduction. To confirm the formation of the thiazolidine network, the thiazolium-based material **3** was treated with $NaBH_4$ to give the material **5**. Solid-state ^{13}C MAS NMR spectra of materials **5** and **6** were recorded (Figure 1 b and 1 c). ^{13}C NMR spectrum of material **3** (Figure 1 a) shows the signal at approximately 155 ppm, which is ascribed to C-2 of the thiazolium ring.



Scheme 1. Synthesis of thiazolidine-based materials **5** and **6**.

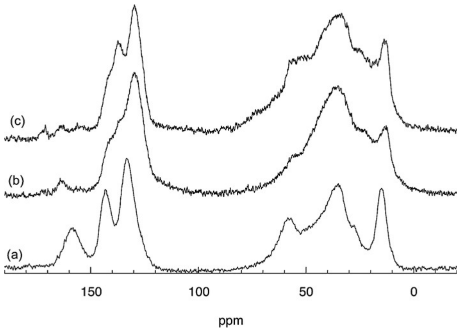


Figure 1. Solid-state ^{13}C NMR spectrum of: a) material **3**; b) material **6**; c) material **5**.

In Figure 1 b the ^{13}C NMR spectrum of material **5** is shown. The disappearance of the signal at 155 ppm and the increase of signals in the aliphatic region could be explained with the formation of the thiazolidine network. An almost identical spectrum is obtained in the case of material **6** (Figure 1 c).

Material **6** was further characterized by TEM and X-ray photoelectron spectroscopy (XPS). TEM analysis does not show traces of ionic liquid polymer as a separate domain. Palladium nanoparticles are not clearly visible (Figure 2 a) or are com-

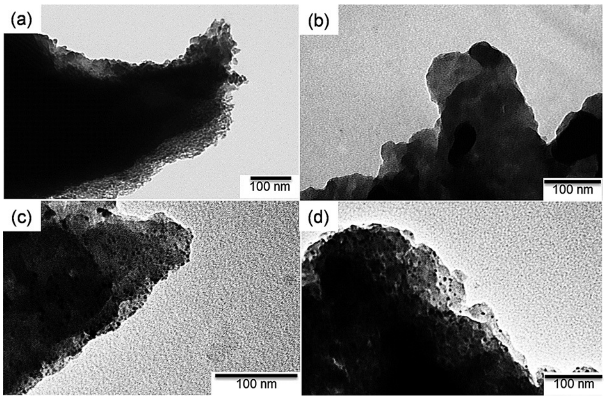


Figure 2. TEM images of: a, b) fresh material **6**; c, d) reused material **6** after 3 cycles.

pletely absent (Figure 2b) suggesting a low percentage of Pd^0 in the sample with the formation of clusters or small nanoparticles with a narrow particle size distribution.

Information on the chemical state and the surface chemical composition of the fresh and used catalyst were obtained by XPS (Table 1 and Figure 3). As expected, the fresh sample exhibited a higher percentage of Pd^{II} (85%; binding energy, BE, 337.0 eV) with respect to metallic Pd (15%; BE 335.4 eV) indicating that the treatment with $NaBH_4$ was not able to completely reduce palladium and confirming the previous observation by electron microscopy investigation. The low amount of Pd^0 found in fresh catalyst could be ascribed to the stabilization of Pd^{II} species by the thiazolidine ligands.

XPS and energy-dispersive X-ray (EDX) analysis of material **6** indicated the presence of bromo and absence of chloro atoms. The absence of chloro atoms could be a consequence of anion exchange process in which the labile tetrachloropalladate has reacted with bromide anions giving mononuclear $PdCl_2Br_2^{2-}$ and/or dinuclear bromide bridged Pd^{II} species $Pd_2X_6^{2-}$ (X = Cl, Br)[21].

In Scheme 1 is reported a tentative picture of the obtained material. Very likely, Pd species can be stabilized through the sulfur atoms of the heterocyclic ligand to give complexes of type PdL_2Br_2.[22] The high-resolution S 2p core-level XPS spectrum of material **6** (Figure S6 in the Supporting Information) shows the presence of a broad peak indicating the presence of different sulfur moieties. Three different doublets (attributable to S $2p_{3/2}$ and S $2p_{1/2}$ components originating from the spin-orbit splitting- effect contributions) can be thus resolved. The peak at 162.1 eV can be ascribed to the presence of C–S→Pd interaction, as previously reported.[23] The other two peaks at 164.6 and 167.3 eV can be assigned to the sulfur of free thiazolidine in its reduced and oxidized form, respectively. The oxidation of sulfur after exposure to air is a known process that may take place in the presence of palladium.[23b]

Table 1. XPS Pd $3d_{5/2}$ binding energies (eV) and Pd^0 (%) of prepared and used catalyst **4**.

Entry	Cat. **6**	Pd $3d_{5/2}$ [eV] $[Pd^{2+}]$[a]	Pd $3d_{5/2}$ [eV] $[Pd^0]$[a]	Pd^0 [%]	Pd/C
1	fresh	337.0	335.4	15	0.02
2	after 1 cycle	337.0	335.2	20	0.02
3	after 3 cycles	337.0	335.1	32	0.02
4[b]	after 3 cycles	336.9	335.1	28	0.02

[a] The reference signal C 1s was fixed at 284.6 eV. [b] Repeated cycles.

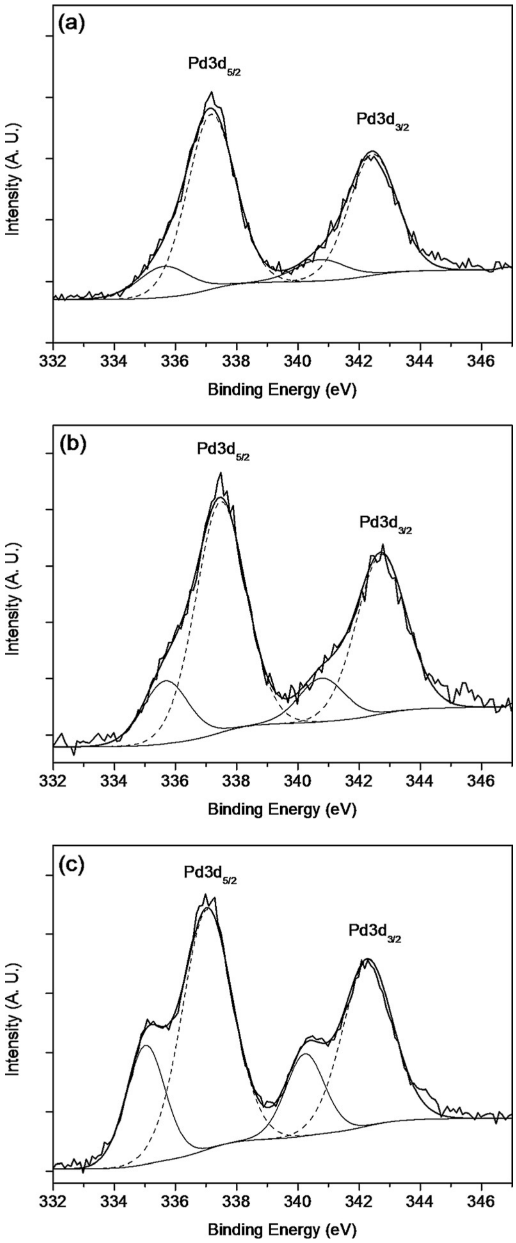
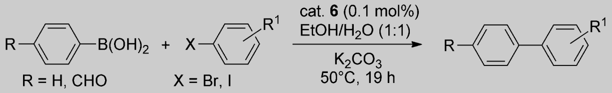
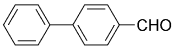
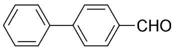
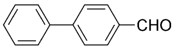
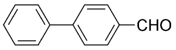
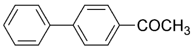
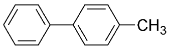
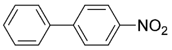
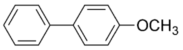
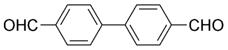
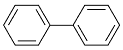
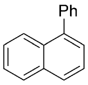
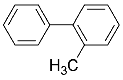
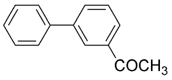
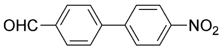
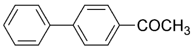
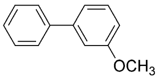
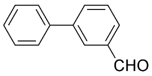
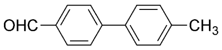
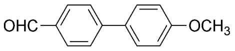
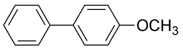
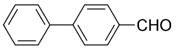
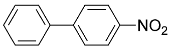


Figure 3. XPS spectra and deconvolutions of: a) material **6**; b) reused material **6** after 1 cycle; c) reused material **6** after 3 cycles.

Catalyst **6** was used in the Suzuki–Miyaura reaction between phenylboronic acid or 4-formylphenylboronic acid and a set of aryl bromides (or iodides) in ethanol/water at 50 °C in the presence of K_2CO_3 as base under an open atmosphere (Table 2). All the reactions were run for 19 h. The ^1H NMR spectra of the products reported in Table 2 can be found in the Supporting Information (Figure S7–S31). Catalyst **6** was used in 0.1 mol%

Table 2. Suzuki–Miyaura reactions between phenylboronic acid and aryl halides in the presence of catalyst **6**.[a]



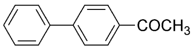
Entry	R	X	Product	Conv. [%][b]	Yield [%][c]	TON [d]
1	H	Br		>99	99	1053
2[e]	H	Br		>99	99	1053
3[f] II cycle	H	Br		>99	98	1043
4[f] III cycle	H	Br		>99	98	1043
5	H	Br		>99	98	1043
6	H	Br		>99	99	1053
7	H	Br		>99	97	1032
8	H	Br		>99	98	1043
9	CHO	Br		98	97	1032
10	H	Br		>99[g]	95	1011
11	H	Br		95[f]	95	1011
12	H	Br		89	88	936
13	H	Br		88	85	904
14	CHO	Br		60	58	617
15[h]	H	I		>99	99	1053
16	H	I		90	90	957
17	H	I		>99	99	1053
18	CHO	I		98	92	979
19	CHO	I		89	88	936
20[i]	H	Br		48	47	500
21[i]	H	Br		77	76	809
22[i]	H	Br		89	87	926

loading. Reaction with 4-bromobenzaldehyde and phenylboronic acid was quantitative (entry 1). This reaction was selected for recycling studies of the catalyst (entries 2–4). Recycling reactions were performed on a larger scale (10 mmol of 4-bromobenzaldehyde) and the catalyst was recovered by filtration. No decrease in its activity was observed. These recycling experiments were duplicated, giving identical results. Catalyst **6** was analyzed by XPS after the first reuse and after the third reuse. As can be clearly observed in Table 1 the materials display the same Pd/C ratio thus proving that no substantial modification of Pd loading is occurring at the surface of the sample. Analysis performed with AAS after the first cycle confirmed that the total Pd loading remains constant within the experimental error. To further support our findings, EDX microanalysis realized with SEM was performed as well. This analysis allowed confirming the previous observation by XPS. The averaged values of Pd/(C+N) of the materials **6** before and after the catalytic cycles were constant and equal to 0.03. The difference in the relative values (Pd/C=0.02 by XPS and Pd/(C+N)=0.03 by EDX) can be ascribed to the different distribution of Pd species at the surface and in the core of the multilayered thiazolidine network (Figure S45–46).

XPS analysis revealed an increased amount of Pd^0 after reuse (Table 1; Figure 3b and 3c) that can be attributed to the in situ reduction likely caused by the solvent under basic conditions.[12b, 13a, 24] Solid state ^{13}C NMR spectrum was also recorded in the case of reused catalyst **6** (after 3 cycles) and no changes were observed (Figure S47).

Interestingly, TEM investigation revealed the presence of metallic nanoparticles on the

Table 2. (Continued)

Entry	R	X	Product	Conv. [%][b]	Yield [%][c]	TON [d]
23[i]	H	Br		85	85	905

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid or 4-formylphenylboronic acid (1.1 mmol), K_2CO_3 (1.2 mmol), EtOH (1.2 mL), H_2O (1.2 mL), catalyst (0.1 mol%, 1 mg). [b] Determined by ^{1}H NMR spectroscopy on isolated reaction mixture. [c] Calculated on isolated products or from the reaction mixture. [d] TON (turnover number calculated as: moles of product/moles of active sites) [e] Reaction on 10 mmol; duplicated experiment. [f] In each cycle the amounts of reagents were scaled in function of the amount of catalyst recovered. Duplicated experiment. [g] Determined by GC. [h] Reaction time: 5 h and 45 min. [i] Reaction performed in ethanol.

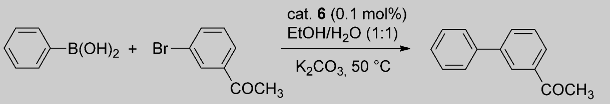
entire sample with an average particle size distribution centered at 3 nm (Figure 1c, 1d and Figure S48). Moreover, no traces of separate domains of silica and polymeric material were found further confirming the stability of the solid in consecutive catalytic cycles.

Excellent conversions were observed in the case of 4-substituted aryl bromides, bromobenzene and 1-bromonaphthalene (Table 2, entries 5–11). High conversions were also observed with 2- and 3-substituted aryl bromides (entries 12, 13) whereas a lower conversion was obtained with 4-formylphenylboronic acid and 4-bromonitrobenzene (entry 14).

As expected, the use of aryl iodides gave also high to excellent conversions (Table 2, entries 15–19). On the other hand, the use of the less reactive aryl chloride 1-chloro-4-nitrobenzene was unsuccessful. A certain conversion (≈6%) was achieved by increasing the amount of catalyst to 1 mol% (Figure S44). As we have previously[13] demonstrated that the Suzuki–Miyaura reaction can be successfully performed under flow condition using ethanol as the sole solvent, we have also shortly investigated the Suzuki–Miyaura reaction in this solvent. Although conversions were not quantitative, the reactions were very clean (entries 20–23).

To investigate if any "release and catch" mechanism[18] is occurring, the reaction between phenylboronic acid and 3-bromoacetophenone in ethanol/water at 50 °C was analyzed in more in details. Three parallel experiments were performed, the first one was stopped and analyzed after 4 h (Table 3, entry 1 and Figure S32), the second one was filtered at 50 °C after 4 h and the filtrate left to react up to 19 h (entry 2 and Figure S33).

Table 3. Suzuki–Miyaura reactions between phenylboronic acid and 3-bromoacetophenone in the presence of catalyst **6**.[a]



Entry	Total reaction time [h]	Procedure	Conv. [%][b]
1	4	no filtration	14
2	19	filtration after 4 h at 50 °C	58
3	19	filtration after 4 h at RT	11

[a] Reaction conditions: 3-bromoacetophenone (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.2 mmol), EtOH (1.2 mL), H_2O (1.2 mL), catalyst (0.1 mol%, 1 mg). [b] Determined by ^{1}H NMR spectroscopy.

The third reaction was filtered after 4 h, but the filtration was performed at room temperature, and the filtrate left to react up 19 h at 50 °C (entry 3, Figure S34 and S49). The reaction filtered after 4 h at 50 °C and left to react gave a higher conversion than both the reaction stopped after 4 h and the reaction filtered after 4 h at room temperature and left to react up to 19 h. It seems that the palladium leaching is operative at 50 °C whereas palladium seems to be recaptured at lower temperature.

Finally, to further explore the versatility of catalyst **6** it was also used in the Heck reaction between aryl iodides and methyl acrylate or styrenes (Table 4 and Figure S35–S43). Yields were high or excellent (entries 1–6), except in the reaction between 2-iodothiophene and methyl acrylate (entry 7). Good conversions were also observed with styrene derivatives (entries 8, 9).

Conclusions

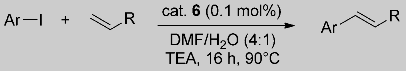
For the first time, a thiazolidine-based mesoporous silica gel was synthesized and used as a new support for palladium immobilization. The synthesis of the support was accomplished by reaction of a highly cross-linked thiazolium-modified mesoporous silica gel, having a high thiazolium loading (2.28 mmol g^{-1}), with sodium borohydride as reducing agent. Indeed, the preparation of a high-loaded thiazolidine-based support allowed the preparation of a high-loaded palladium catalyst (10 wt%). The catalytic material was used in the Suzuki–Miyaura and in the Heck reactions allowing the synthesis of several biphenyl and alkene compounds in high yields working with only 0.1 mol% of catalyst (1 mg of catalyst per mmol of reagent). Recycling (3 times) in the Suzuki–Miyaura reaction showed no decrease in activity. The catalytic material was characterized before and after reuse by solid state ^{13}C NMR spectroscopy, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy, and transmission electron microscopy. Having demonstrated the usefulness of such catalyst under batch condition, our next goal will be the development of an efficient flow approach for Pd-catalyzed C-C coupling reactions using such catalytic material.

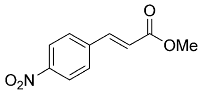
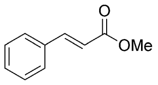
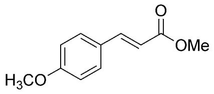
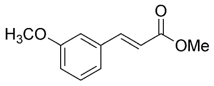
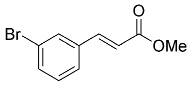
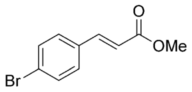
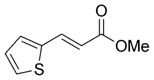
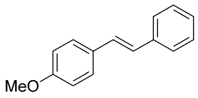
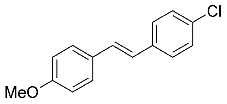
Experimental Section

General methods

Liquid state ^{1}H NMR and ^{13}C NMR spectroscopy were performed with a JEOL 400 spectrometer. ^{29}Si MAS NMR and ^{13}C cross-polarization MAS NMR spectra were recorded with a Bruker 500 spectrometer in the solid state, using a Chemagnetics 3.2 mm probe equipped with thin or standard wall rotors spinning at 12 kHz.

Table 4. Heck reaction between methyl acrylate or styrenes and aryl iodides in the presence of catalyst **6**.[a]



Entry	Ar	R	Product	Yield [%][b]	TON[c]
1	4-NO_2-C_6H_4	CO_2Me		> 99	1053
2	Ph	CO_2Me		85	904
3	4-CH_3O-C_6H_4	CO_2Me		> 99	1053
4	3-CH_3O-C_6H_4	CO_2Me		89	947
5	3-Br-C_6H_4	CO_2Me		91	968
6	4-Br-C_6H_4	CO_2Me		> 99[d]	1053
7	2-thienyl	CO_2Me		48	511
8	4-CH_3O-C_6H_4	Ph		76[e]	809
9[f]	4-CH_3O-C_6H_4	4-Cl-C_6H_4		94[g]	1000

[a] Reaction conditions: acrylate or styrene (1.5 mmol), aryl iodide (1 mmol), triethylamine (2 mmol), catalyst (0.1 mol% 1 mg), 90 °C, 16 h. [b] Calculated on isolated products. [c] TON (turnover number calculated as: moles of product/moles of active sites) [d] Conversion. Mixture (92:8) of monoacrylate/bisacrylate.[12c] [e] Conversion. Mixture (86:14) of *trans*-styrene/*gem*-styrene.[12c] [f] Reaction time: 21 h. [g] Conversion. Mixture (94:6) of *trans*-styrene/*gem*-styrene.[12c]

Combustion chemical analyses (C, H, N) were performed on a Thermo Finnigan- FlashEA 1112 apparatus. TEM images were taken with a PHILIPS TECNAI 10 instrument at 80 kV. Samples were dispersed in ethanol and deposited on a carbon-coated copper grid. EDX measurements were performed with a JEOL JED2200 with an emission current equal to 15 eV. Isothermal nitrogen adsorption was performed with at 77 K with a volumetric adsorption analyzer (Micromeritics Tristar 3000) with a prior sample drying under vacuum at 120 °C. The XPS analyses were performed with a Thermo Scientific K-Alpha Surface Analysis spectrometer, equipped with a monochromatized Al anode (1486.6 eV). The spot size of the X-ray source on the sample was 200 μm, and the analyzer was operated with a pass energy equal to 200 eV for survey spectra, and 50 eV for high-resolution core-level spectra. A flood gun (electrons and Ar ions at very low energy) was used to avoid possible charging effects. Pressure in the chamber was in the range of 10^{-7} mbar. The BE of core levels was calibrated against the C 1s BE set at 284.6 eV. Analyses of the peaks were performed with the software Thermo Avantage, based on nonlinear least-squares fitting program using a weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood. AAS analyses were performed with a PerkinElmer using an electrothermal atomizers (graphite furnace Model HGA 600) and a lamp of palladium (λ = 247.6 nm). All the biphenyl, acrylate, and styrene compounds synthesized are known molecules (see the Supporting Information).

Procedure for the synthesis of 1,4-bis (5-methyl-4-vinyl-thiazolium-1-methylbenzene) bromide

In a two-necked round-bottom flask 1,4-bis-bromomethylbenzene (1.182 g, 4.48 mmol) and chloroform (3 mL) were placed. The solution was heated in an oil bath at 70 °C with magnetic stirring, under argon. A solution of 4-methyl-5-vinyl-thiazole (1 mL, 8.86 mmol, 2 equiv.) in chloroform (2 mL) was added dropwise for 30 min. After 24 h, the reaction mixture was cooled down, filtered, and washed several times with diethyl ether. The solid product was dried overnight in an oven at 60 °C.

1,4-Bis(5-methyl-4-vinyl-thiazolium-1-methylbenzene) bromide: Pale yellow powder, yield: 96 %. M.p. > 250 °C. ^{1}H NMR (400 MHz, D_2O): $\delta = 2.42$ (s, 6H, $-CH_3$), 5.63 (d, 2H, $J = 11$ Hz, *cis* $CH{=}CH_2$), 5.67 (s, 4H, Ar–CH_2–N), 5.89 (d, 2H, $J = 17.2$ Hz, *trans* $CH{=}CH_2$), 6.87 (dd, 2H, $J = 17.4$ and 11.2 Hz, $CH{=}CH_2$), 7.38 (4H, s, Ar–H), 9.67 ppm (s, 2H, S–CH=N). ^{13}C NMR (100 MHz, D_2O): $\delta = 11.2$, 56.3, 121.9, 123.8, 129.2, 132.9, 136.5, 142.3, 155.3 ppm. IR: $\tilde{\nu}_{max} = 2985$, 1103, 1566, 1455, 672 cm^{-1}. Anal. found for $C_{20}H_{22}Br_2N_2S_2$: C, 44.40; H, 4.29; N, 5.08; S, 12.44; calcd. (%): C, 46.70; H, 4.31; N, 5.45; S, 12.47.

Procedure for the synthesis of SBA-15

Mesoporous silica material SBA-15 was prepared starting from tetraethylorthosilicate (TEOS) as the silica source and by using the triblock copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO20PO70EO20, Pluronic P123) as the template. In a general procedure, Pluronic P123 (1.01 g) was dissolved in an acid solution of HCl (0.55 g in 18.35 g of water). The solution was stirred overnight at 35 °C in a 100 mL closed polypropylene bottle. After that, TEOS (2.00 g) was quickly added to this solution and the mixture was stirred at the same temperature for 24 h. The milky suspension was heated to 100 °C for 24 h in a oven. The solid product was filtered and washed with an HCl/H_2O mixture The white solid was calcined at 550 °C for 5 h in air.

Procedure for the synthesis of modified silica SBA-15

In a round-bottom flask SBA-15 (2.0 g), 3-(mercaptopropyl)-trimethoxysilane (0.016 mol) and toluene (15 mL) were placed. The suspension was heated at reflux for 24 h. Then, the suspension was cooled down, filtered, and washed with methanol. The white powder was dried in an oven at 80 °C overnight.

Procedure for the synthesis of material 3

In a two-necked round-bottom flask 3-mercaptopropyl modified SBA-15 (1.0 g, SH loading 0.9 mmol g^{-1}, 0.9 mmol), bisvinylthiazolium salt (3.69 equiv.), ethanol (32.4 mL), and azobisisobutyronitrile were placed. The suspension was degassed by bubbling nitrogen for 30 min. The reaction mixture was heated in an oil bath at 78 °C under nitrogen, and stirred for 20 h. After cooling to RT, the mixture was filtered and the solid washed with methanol in a soxhlet system for 48 h. Then, the obtained material **3** was dried in an oven at 40 °C overnight. Elemental analysis of material **3**: N% (3.2), C% (28.2), H% (3.9), S% (6.9).

Typical procedure for the synthesis of the palladium catalyst 6

In a round-bottom flask were placed $PdCl_2$ (49.8 mg, 0.281 mmol), NaCl (312 mg, 5.342 mmol), and water (6.8 mL). The flask was heated at 80 °C until the $PdCl_2$ was dissolved. This clear orange solution was cooled at RT and added to a suspension of material **3** (250 mg) in water (2.25 mL). The suspension was stirred at RT for 20 h, then filtered under reduced pressure, washed with water and dried overnight under reduced pressure at RT. The material was suspended in anhydrous ethanol (6 mL) and to this suspension a solution of $NaBH_4$ (72 mg, 1.903 mmol, 7 equiv) in anhydrous ethanol (6 mL) was added dropwise. The suspension turned black and was stirred at RT for 6 h, then filtered under reduced pressure, washed with water and ethanol, and dried at RT.

Typical procedure for the Suzuki reaction

In a round-bottom flask, catalyst **6** (0.1 mol%, 1 mg), phenylboronic or 4-formylphenylboronic acid (1.1 mmol), K_2CO_3 (167 mg, 1.2 mmol), the aryl halide (1 mmol), ethanol (1.2 mL), and water (1.2 mL) were placed. The reaction mixture was stirred at 50 °C. After 19 h, the reaction mixture was cooled down, then water was added and the mixture extracted with dichloromethane (3 × 30 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated under reduced pressure and the residue passed through a short silica pad (petroleum ether/ethyl acetate).

Typical procedure for the Heck reaction

To a round-bottom flask, catalyst **6** (0.1 mol%, 1 mg), alkene (1.5 mmol), aryl iodide (1 mmol), triethylamine (2 mmol), and DMF/H_2O (4 mL + 1 mL) were added. The reaction mixture was heated at 90 °C for 16 h. Then, the reaction mixture was cooled at RT, diluted with water and extracted with dichloromethane (3 × 30 mL). The organic phase was dried with Na_2SO_4, evaporated under reduced pressure and the residue passed through a short silica pad (petroleum ether/ethyl acetate).

Recycling procedure for the Suzuki reaction

In a round-bottom flask, catalyst **6** (0.1 mol%, 10 mg), 4-bromobenzaldehyde (10 mmol), phenylboronic acid (11 mmol), K_2CO_3 (12 mmol), ethanol (12 mL), and water (12 mL) were placed. The reaction mixture was stirred at 50 °C for 19 h. Then, it was allowed to cool down, filtered under reduced pressure, and after that extracted and purified as in the typical procedure for the Suzuki reaction. The catalyst was washed with water, dichloromethane, and dried at 40 °C overnight, to be subsequently reused in the next cycles.

General procedure for "hot filtration" and "room-temperature" Suzuki reaction

In a round-bottom flask, catalyst **6** (0.1 mol%, 1 mg), phenylboronic acid (138 mg, 1.1 mmol), K_2CO_3 (167 mg, 1.2 mmol), 3-bromoacetophenone (0.134 mL, 1 mmol), ethanol (1.2 mL), and water (1.2 mL) were placed. The reaction mixture was heated at 50 °C for 4 h to be subsequently filtered (in the case of hot filtration) or cooled at RT and then the catalyst was separated from the reaction mixture by means of a syringe filter. Then, the mixture was heated at 50 °C for 15 h. After that, it was allowed to cool down, water was added, and the mixture extracted with dichloromethane (3 × 30 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with a short plug of silica under vacuum using hexane/ethyl acetate as eluent.

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