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Expanded Heterogeneous Suzuki–Miyaura Coupling Reactions of Aryl and Heteroaryl Chlorides under Mild Conditions


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Abstract: A mesoporous LTA zeolite (MP-LTA)-supported palladium catalyst was developed for the highly efficient Suzuki–Miyaura reaction of aryl and heteroaryl chlorides. The couplings of various aryl chlorides with arylboronic acids in aqueous ethanol were efficiently achieved in the presence of 1.0 mol% of the catalyst. Furthermore, the scope of this catalyst was extended to the coupling of heteroaryl chlorides. Regardless of the substituents, all of the coupling reactions were very clean and highly efficient under mild heating. It shows that our catalyst is one of the most powerful heterogeneous catalysts

for the coupling of a wide range of aryl and heteroaryl chlorides. The catalyst could be repetitively used at least 10 times without a significant loss of its catalytic activity. Compared to mesoporous SBA-15 and MCM-41 materials, the MP-LTA support proved to be very stable and robust to prevent degradation upon reuse.

Keywords: heterogeneous catalysis; immobilization; mesoporous materials; palladium; Suzuki–Miyaura reaction

Introduction

The palladium-catalyzed Suzuki–Miyaura reaction is one of the most powerful and convenient methods for the synthesis of unsymmetrical biaryls.^[1] Over the last decade, studies on the coupling reactions have been focused on the use of aryl chlorides as readily accessible and cheap coupling substrates.^[2] Much progress has been achieved with homogeneous Pd catalysts in this area. One practical limit to performing homogeneously catalyzed reactions is the difficulty of removing the catalyst from the reaction mixture or separating the product continuously. This limit is of significant environmental and economic concern in large-scale organic syntheses. The use of heterogeneous Pd catalysts would be a promising solution to this problem because of their easy separation and recycling.^[3] The known heterogeneous catalytic systems include those that utilize supported Pd complexes,^[4] supported Pd nanoparticles,^[5] unsupported Pd nanoparticles,^[6] and encapsulated Pd complexes.^[7] Although

the heterogeneous catalysts provided good results for Suzuki–Miyaura coupling of aryl iodides and bromides, their catalytic activities were unsatisfactory for aryl chlorides. To date, unactivated aryl chlorides are not feasible substrates for the heterogeneous Suzuki reactions. Successful examples of heterogeneous Suzuki coupling with unactivated chlorides are quite rare.^[4b,d,e] Moreover, the Pd catalysts under the stringent conditions suffer from Pd agglomeration, Pd leaching or a structural damage of the supports. The efficient heterogeneous coupling of unreactive aryl chlorides is still challenging. Previously, a β -oxoiminatophosphanyl Pd complex was found to be an efficient catalyst for the coupling reaction.^[2g] We have anchored a triethoxysilyl-functionalized Pd complex onto an LTA zeolite with hierarchically mesoporous and microporous structure (MP-LTA). Herein, we report the synthesis of MP-LTA zeolite-supported β -oxoiminatophosphanyl palladium complex (Pd@MP-LTA) and its application as a catalyst for the Suzuki–Miyaura reaction of aryl and heteroaryl chlorides.

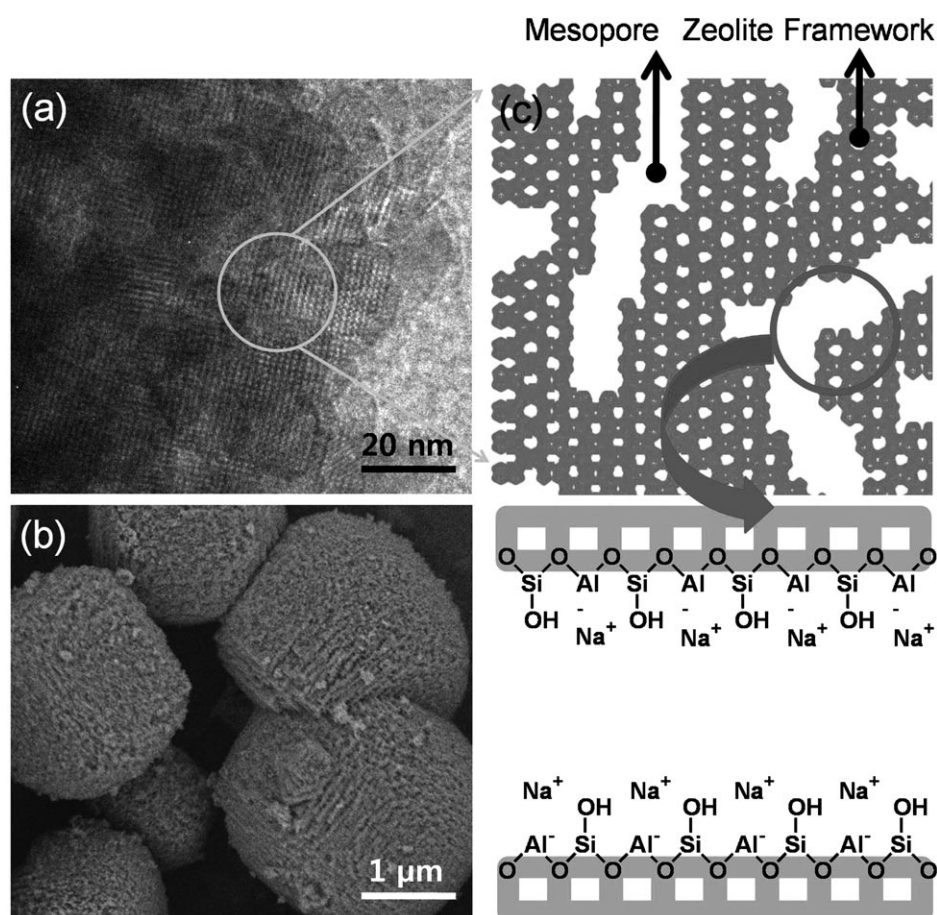


Figure 1. (a) TEM image; (b) SEM image; (c) schematic representation of MP-LTA zeolite structure.

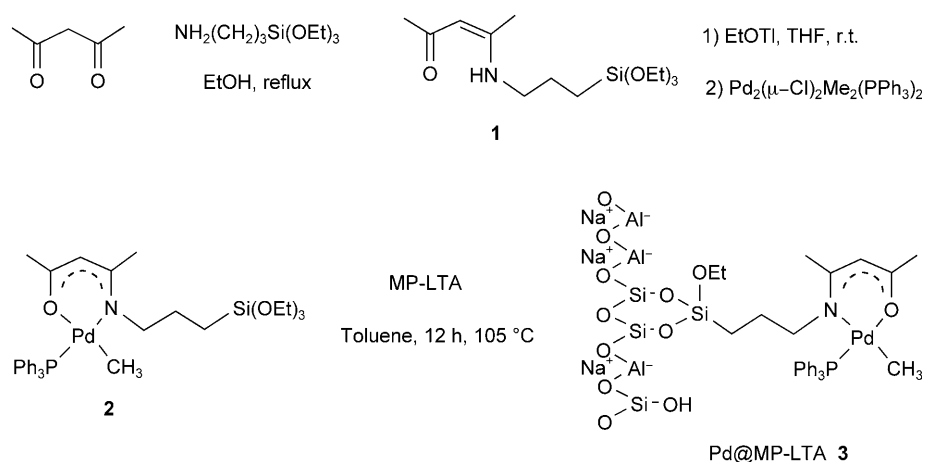
The MP-LTA zeolite (Si/Al=1.0) was obtained according to the synthesis route using an organosilane surfactant as a mesopore-generating agent.^[8] The mesopore walls of the zeolite are made of crystalline microporous zeolite frameworks. The zeolite frameworks possess a plethora of silanol groups on the surface of the mesopore walls (Figure 1). Thus, the mesopore surface can be easily functionalized through condensation of the surface silanols with well known organosilanes. Considering the robustness of the MP-LTA zeolite frameworks, we envisaged that the MP-LTA could be a promising mesoporous silica support with high chemical and hydrothermal stability.

Results and Discussion

Pd@MP-LTA **3** was prepared from 2,4-pentanedione as shown in Scheme 1. Schiff base condensation of 2,4-pentanedione and 3-aminopropyltriethoxysilane gave β -oxoiminopropyltriethoxysilane **1** in quantitative yield. Deprotonation of **1** with EtONa or EtONa, followed by treatment with $\text{Pd}_2(\mu\text{-Cl})_2\text{Me}_2$ (PPh_3)₂,^[9] led to the formation of silylated Pd complex **2**. Subsequent treatment of **2** with MP-LTA zeolite gave

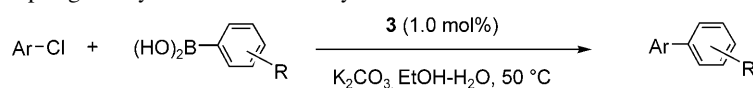
Pd@MP-LTA **3**. Loading amounts of Pd on the mesopore surface can be controlled in this step. Pd@MP-LTA **3** of 0.30 mmol Pd/g was prepared for this study and the value was confirmed by inductively coupled plasma atomic emission spectrometry (ICP-AES). After anchoring the Pd complex, the mesopore diameter and pore volume of **3** were decreased from 10 to 9 nm and from 0.42 to 0.31 mL g⁻¹, respectively. X-ray powder diffraction (XRD) patterns, N₂ adsorption-desorption isotherms, transmission electron microscopic (TEM), and scanning electron microscopic (SEM) images of **3** were very similar to that of the parent MP-LTA, indicating that the immobilization did not affect the pore structure of the zeolites. The detailed experimental and characterization data of **3** are given in the Supporting Information.

We tested the Suzuki–Miyaura coupling of various aryl chlorides with arylboronic acid in the presence of 1.0 mol% of catalyst **3** at 50 °C (Table 1). Outstanding catalytic activity was observed in the coupling of chlorobenzene and activated 1-chloro-4-nitrobenzene, 1-chloro-2-nitrobenzene, and 4-chlorobenzonitrile (entries 1–4). High reactivity was also observed for deactivated aryl chlorides including 4-chlorophenol, 4-chlorotoluene, 4-chloroanisole, 2-chlorotoluene, 2-



Scheme 1. Preparation of MP-LTA-supported β -oxoiminatophosphanyl palladium complex **3**.

Table 1. Suzuki–Miyaura coupling of aryl chlorides with arylboronic acids.^[a]



Entry	Aryl chloride	Arylboronic acid	Time [h]	Yield [%]	Entry	Aryl chloride	Arylboronic acid	Time [h]	Yield [%] ^[b]
1			4	92 (95)	11			5	93 (95)
2			3	95 (98)	12			4.5	92 (96)
3			3	91 (95)	13			4.5	91 (94)
4			3.5	91 (90)	14			5	91
5			4.5	90 (94)	15			5	89
6			4.5	93 (95)	16			5	87 (91)
7			4.5	92 (96)	17			5	85 (89)
8			5	85 (89)	18			5	84 (85)
9			5	91 (94)	19 ^[c]			12	88
10			5	89 (91)	20 ^[c]			12	85

^[a] *Reaction conditions:* aryl chloride (1.0 mmol), arylboronic acid (1.2 mmol), **3** (1.0 mol%), K₂CO₃ (2.0 mmol), EtOH–H₂O (2 mL, 1:1, v/v) and 50 °C.

^[b] Isolated yields (GC yields in parenthesis).

^[c] Reaction temperature: 80 °C.

Table 2. Suzuki–Miyaura coupling of heteroaryl chlorides with arylboronic acids.^[a]

Entry	Heteroaryl chloride	Arylboronic acid	Time [h]	Yield [%] ^[b]	Entry	Heteroaryl chloride	Arylboronic acid	Time [h]	Yield [%] ^[b]
1			3	92 (94)	17 ^[c]			8	82 (83)
2			4	91 (92)	18 ^[c]			8	90 (93)
3			3.5	90 (93)	19			4	90 (91)
4			4	93 (95)	20			5	91 (93)
5			4	91 (93)	21			5	92 (95)
6			4	91 (94)	22			5	88 (91)
7			4	90 (92)	23			5	83 (87)
8			4.5	88 (90)	24			4	90 (92)
9			5	84 (87)	25			4	93 (96)
10			4	93 (95)	26			4.5	91 (94)
11			4.5	92 (90)	27			5	90 (91)
12			5	86 (87)	28			5	88 (90)
13			4	96 (97)	29			5	81 (83)
14 ^[c]			8	90 (92)	30			6	87 (91)
15 ^[c]			8	81 (83)	31			6	90 (92)
16 ^[c]			8	84 (85)	32			6	81 (87)

^[a] Reaction conditions: heteroaryl chlorides (1.0 mmol), arylboronic acids (1.2 mmol), **3** (1.0 mol%), K₂CO₃ (2.0 mmol), EtOH–H₂O (2 mL, 1:1, v/v) and 50 °C.

^[b] Isolated yields (GC yields in parenthesis).

^[c] Reaction temperature: 80 °C.

chloroanisole, 2-chloroaniline and 3-chloroaniline (entries 5–11). 1-Chloronaphthalene and 9-chloroanthracene were efficiently coupled with phenylboronic in excellent yields (entries 12 and 13). Furthermore,

the catalyst system was also efficient for Suzuki coupling reaction of aryl chlorides with different arylboronic acids (entries 14–18). Deactivated 4-chlorotoluene and 2-chlorotoluene reacted with electron-

rich 2- or 4-methylphenylboronic acid, affording the corresponding products with high yields, respectively. It is noteworthy that deactivated and sterically hindered 2-chloro-1,3-dimethylbenzene was coupled in good yield, although a higher temperature and a longer time were required (entries 19 and 20). Regardless of the substituents, all of the coupling reactions were very clean and highly efficient in aqueous ethanol under mild heating. To the best of our knowledge, our catalyst **3** showed the highest catalytic activity reported for the heterogeneous Suzuki coupling of aryl chlorides.

The Suzuki–Miyaura coupling of heteroaryl halides is of particular interest to the pharmaceutical industry since many biologically active compounds are accessed through this methodology.^[10] However, there are only a few successful examples of the Suzuki coupling of heteroaryl chlorides.^[11] Catalyst deactivation has been observed with many of the substrates. Thus, a need exists for the development of efficient catalysts for the coupling of heteroaryl chlorides. We investigated the catalytic behavior of **3** in the coupling of heteroaryl chlorides with arylboronic acids (Table 2). Chloropyridines bearing the halogen in the 2-, 3-, or 4-position underwent the coupling with different arylboronic acids in the presence of 1 mol% of **3** in 5 h, affording the corresponding desired products in excellent yields (entries 1–9). Other heteroaryl chlorides such as 2-chloropyrimidine, 2-chloroquinoline and 2-quinoline-4-carboxylic acid reacted very well (entries 10–13). Typically, the coupling of basic heteroaryl chlorides bearing an unprotected amino group is slowed down due to competitive binding of the amino group to the Pd center of the catalyst. Catalyst deactivation has been noted with this kind of substrates. Interestingly, our catalyst **3** was found to be active for the coupling of unprotected aminochloropyridines (entries 14–18). Besides, chloroimidazoles were converted to the corresponding coupling products in high yields (entries 19–21). It is also noteworthy that the present protocol is applicable to the coupling of 2-chlorobenzoxazole and 2-chlorobenzothiazole (entries 22 and 23). To further extend the scope of our catalytic system, we carried out the coupling of unactivated chlorothiophenes. The reactions of 2- and 3-chlorothiophenes with arylboronic acids proceeded very well in satisfactory yields (entries 24–29). These results came as a surprise since chlorothiophenes in the coupling reaction are challenging substrates due to the strong affinity of the sulfur to the Pd. Furthermore, this catalytic system allowed for the coupling with 3-pyridineboronic acid known as less efficient reagent (entries 30–32). This is the first example of the effective coupling of unreactive heteroaryl chlorides over a heterogeneous Pd catalyst.

The reusability of catalyst **3** is an important factor for the heterogeneous reaction. We examined the re-

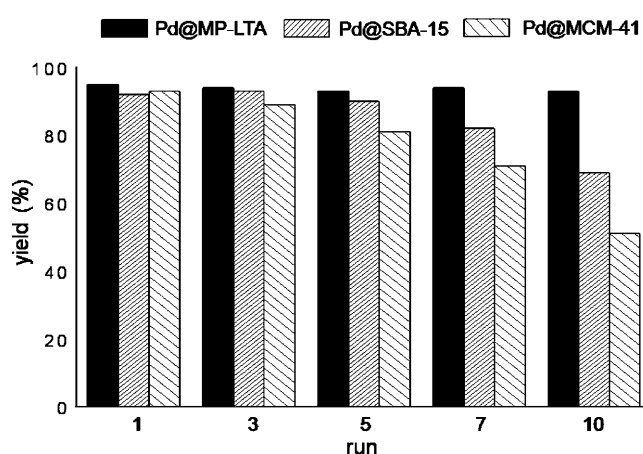


Figure 2. Reusability of the Pd catalysts in Suzuki–Miyaura coupling of 4-chloroanisole with phenylboronic acid.

usability of catalyst **3** in the coupling of 4-chloroanisole with phenylboronic acid. After the reaction, the catalyst was separated from the reaction mixture, and Pd metal in the solution was analyzed by ICP-AES method. The results indicated that only less than 0.0009% Pd of initial added catalyst was leached out from the catalyst surface. In addition, the isolated solution did not exhibit any further reactivity. As shown in Figure 2, the integrity of MP-LTA was indeed demonstrated by the finding that catalyst **3** could be used 10 times without loss of activity. When MCM-41^[12] and SBA-15^[13] were used as supports instead of MP-LTA, the Pd catalysts exhibited significant decreases in catalytic activity during the recycling. The excellent reusability of the Pd@MP-LTA would be attributed to the structural durability of the crystalline MP-LTA support under the basic reaction conditions. The pore size analysis showed that the original mesoporosity of MP-LTA was maintained up to 4 days at 90°C under the basic condition (Figure 3, a), whereas mesoporous SBA-15 and MCM-41 with amorphous frameworks lost completely their mesoporosity in 12 h and 6 h, respectively (Figure 3, b and Figure 3, c). The structural collapse of SBA-15 and MCM-41 might hinder the diffusion of substrates into the metal sites. In addition, the recovered Pd@MP-LTA was very similar to the original in the powder X-ray diffraction pattern (Figure 3, d). The efficiency of the recycled reactions was obviously influenced by the used supports. The TEM analysis visualized that no formation of Pd agglomerated nanoparticles on the external MP-LTA was detectable and also demonstrated that its mesoporosity was still retained after 10 consecutive runs (Figure 4). However, the use of mesoporous SBA-15 and MCM-41 led to the agglomeration of Pd(0) nanoparticles after the repeated reaction. This is probably due to the approach of the Pd complex fragments formed by the collapse of the walls. On the contrary, the mesopore wall of the MP-LTA support with crys-

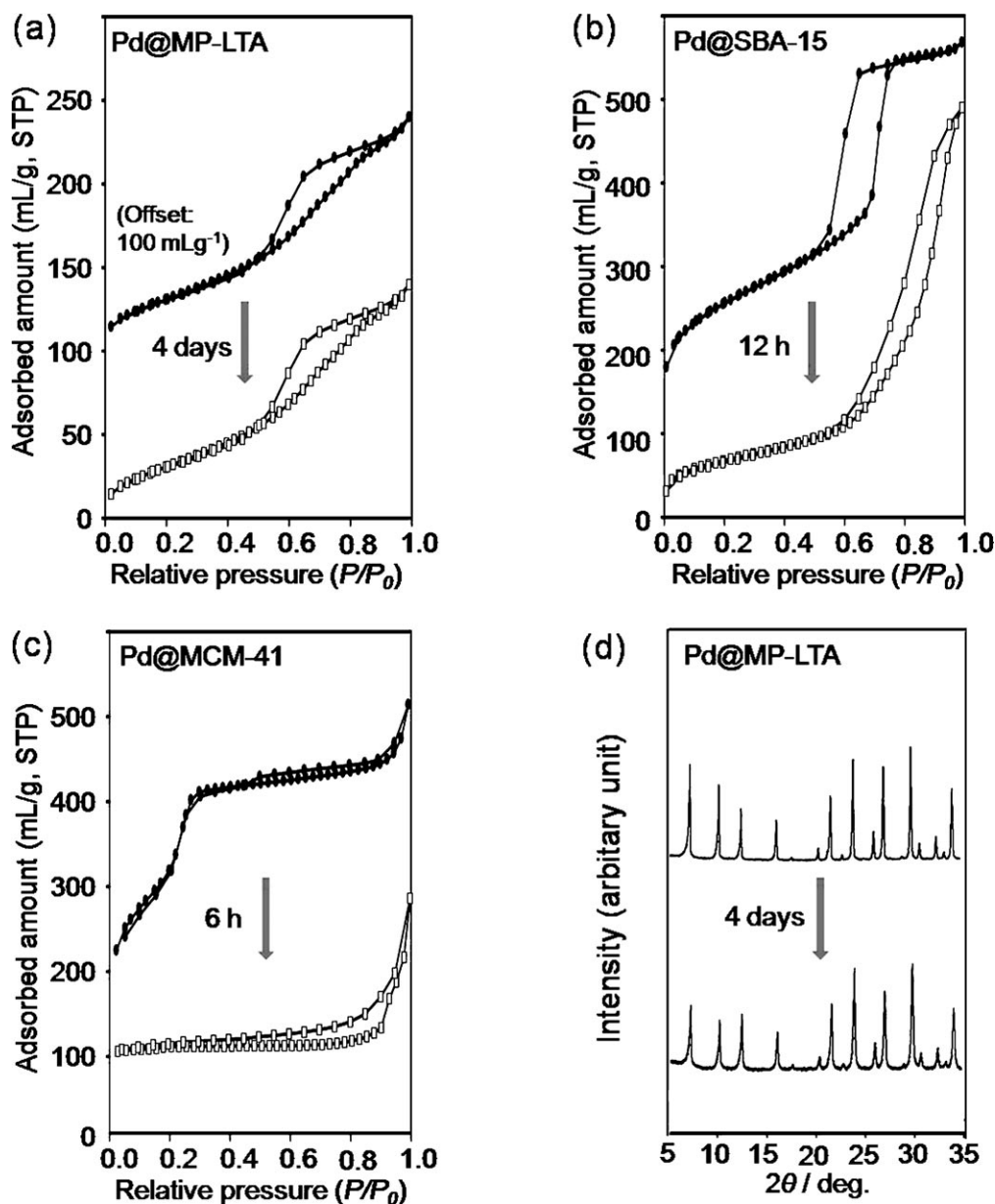


Figure 3. Hydrothermal stability under the basic reaction conditions. (a) N_2 adsorption-desorption isotherms of Pd@MP-LTA; (b) Pd@SBA-15; (c) Pd@MCM-41 and (d) powder X-ray diffraction patterns of Pd@MP-LTA

talline zeolite frameworks is effective for preventing Pd metal aggregation, which results in the high durability of Pd@MP-LTA **3**. Apparently, our catalyst **3** proved to behave as a real heterogeneous catalyst. Along with inherent nature of the free Pd complex, the high activity of **3** is probably due to a high stability of the active Pd species by the zeolite framework.

Conclusions

Pd@MP-LTA **3** exhibited high catalytic activity for the Suzuki–Miyaura coupling reactions and typical

behavior of a heterogeneous catalyst. A wide range of both aryl and heteroaryl chlorides were coupled very well under mild conditions. Unlike SBA-15 and MCM-41, MP-LTA could offer high stability to the active Pd species. The performance of the catalyst was fully retained during the reuse process. These results are very important from a practical point of view. Overall, the scope of the heterogeneous Suzuki–Miyaura reaction was expanded with the MP-LTA-supported Pd complex. Our studies would hopefully stimulate ongoing research in heterogeneous coupling chemistry.

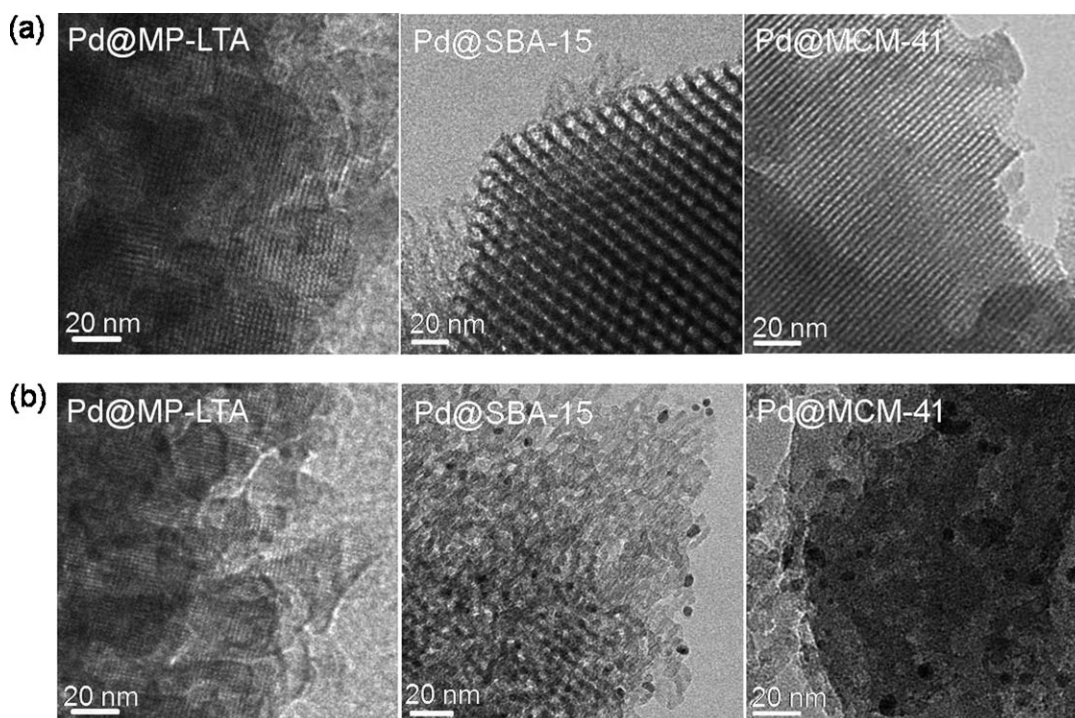


Figure 4. (a) HR-TEM images of Pd catalysts before use; (b) after the 10th use.

Experimental Section

Preparation of Mesoporous-Microporous Hierarchical LTA Zeolite

Organosilane [(CH₃O)₃SiC₃H₆N(CH₃)₂C₁₆H₃₃]Cl (51.45 wt% methanol solution) was mixed with sodium metasilicate (Na₂O₃Si·9H₂O), sodium aluminate (53% Al₂O₃, 43% Na₂O), NaOH and H₂O to obtain the gel composition 100 SiO₂/250 Na₂O/75 Al₂O₃/14600 H₂O/5 organosilane. The synthesis gel was hydrothermally crystallized at 95 °C for 4 h under stirring. The product was filtered and thoroughly washed with distilled water. The product was dried at 100 °C and subsequently calcined in air at 550 °C.

Characterization of the Materials and Compounds

Reagents were used as received from commercial source. All manipulations were conducted under an atmosphere of dry nitrogen. ¹H, ¹³C NMR and ³¹P NMR spectra were recorded on Varian Unity Inova (400 MHz), Bruker AM 400 (400 MHz) and FT AM 300 (300 MHz) NMR spectrometers, respectively. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. ³¹P NMR spectra were referenced to external PPh₃ (0 ppm relative to free PPh₃).

X-ray diffraction (XRD) patterns were recorded with a Rigaku Multiflex diffractometer equipped with CuK α radiation (40 kV, 40 mA). N₂ adsorption-desorption isotherms were measured at liquid nitrogen temperature (77 K) using a Quantachrome Nova 2000 series analyzer. Before adsorption measurements, all samples were degassed for 12 h at 300 °C. Pore size distribution was calculated by the Barrett-Joyner-Halenda method using the adsorption branch. Ele-

mental analyses (EA) were carried out using an EA-110 (Thermo Finnigan, Italia). Analysis of Pd content was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using an OPTIMA 4300 DV (Perkin-Elmer). Scanning electron micrograph (SEM) images were taken at a low electron acceleration voltage (2 kV, Hitachi S-4800), without metal coating. Transmission electron micrograph (TEM) images (JEOL Corp. JEM-210F) were obtained at an operating voltage of 200 kV from the calcined samples after being supported on a porous carbon grid.

General Procedure for the Synthesis of β -Oxoiminopropyltriethoxysilane 1

To a solution of 2,4-pentanedione (1.0 g, 10.0 mmol) in EtOH (20 mL) was added 3-aminopropyltriethoxysilane (2.21 g, 10.0 mmol). The solution was stirred at reflux for 12 h. The solvent was removed under reduced pressure to give β -oxoiminopropyltriethoxysilane **1** as a light yellow liquid; yield: 2.9 g (96%). ¹H NMR (400 MHz, CDCl₃): δ = 10.82 (br s, 1H), 4.99 (s, 1H), 3.82 (q, 6H, *J* = 11.6 Hz), 3.24 (q, 2H, *J* = 12 Hz), 2.00 (s, 3H), 1.92 (s, 3H), 1.75 (t, 2H, *J* = 7.2 Hz), 1.22 (t, 9H, *J* = 6.8 Hz), 0.68 (t, 2H, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 194.29, 162.80, 94.91, 58.34, 45.41, 28.68, 23.82, 18.75, 18.25, 7.60; anal. calcd. for C₁₄H₂₉NO₄Si (MW 303.47): C 55.41, H 9.63, N 4.62; found: C 55.62, H 9.54, N 4.58.

General Procedure for the Synthesis of β -Oxoiminato-propyltriethoxysilanephosphanyl palladium Complex 2

A solution of Ti(OC₂H₅)₄ (0.3 g, 1.2 mmol) in THF (10 mL) was added dropwise at room temperature to a solution of β -

oxoiminopropyltriethoxysilane **1** (0.30 g, 1.0 mmol) in THF (10 mL). After stirring for 2 h at room temperature, a solution of [Pd(PPh₃)MeCl]₂ (0.51 g, 0.6 mmol) in THF (5 mL) was dropwise added to the mixture. After 2 h, the mixture was filtered through celite on a frit. The solvent was removed under reduced pressure and the residue was washed with hexane (30 mL) and extracted with dichloromethane (10 mL). Removal of the solvent gave Pd complex **2** as a light brown crude solid; yield: 0.56 g (82%). ¹H NMR (400 MHz, CDCl₃): δ = 7.79–7.52 (m, 5H), 7.49–7.27 (m, 10H), 4.70 (s, 1H), 3.83 (q, 6H, *J* = 6.8 Hz), 3.45 (m, 2H), 2.00 (s, 3H), 1.75 (m, 2H), 1.52 (s, 3H), 1.22 (m, 6H), 0.63 (t, 2H, *J* = 7.2 Hz), 0.097 (d, 3H, *J* = 2.8 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 176.86, 163.95, 134.74, 134.63, 132.00, 131.91, 131.78, 131.37, 130.90, 129.83, 128.43, 128.30, 128.05, 127.76, 127.66, 97.94, 67.93, 58.43, 58.33, 58.16, 26.14, 25.64, 18.59, 18.39, 18.34, 7.69, –2.21; ³¹P NMR (162 MHz, CDCl₃): δ = 43.88; anal. calcd. For C₃₃H₄₆NO₄PPdSi: C 57.76, H 6.76, N 2.04; found: C 57.74, H 6.53, N 2.10.

Synthesis of MP-LTA-Supported β-Oxoiminatophosphanyl-palladium Complex **3**

Mesoporous-microporous hierarchical LTA zeolite (MP-LTA) (1.0 g) was added to a solution of compound **2** (0.24 g, 0.35 mmol) in toluene (10 mL) and the mixture was refluxed for 12 h. After filtration, the powder was washed several times with dichloromethane and dried under vacuum at 70 °C to give MP-LTA-supported β-oxoiminatophosphanyl-palladium (Pd/MP-LTA) **3**. The product was filtered, washed with CH₂Cl₂ (10 mL) three times, and dried under vacuum at 80 °C. The Pd content of 0.30 mmol g⁻¹ was measured by inductively coupled plasma (ICP) analysis.

General Procedure for the Suzuki–Miyaura Coupling Reaction

The reaction was carried out by using a glass vial equipped with a Teflon screw cap. Aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K₂CO₃ (276 mg, 2.0 mmol) and catalyst **3** (33.3 mg, 0.30 mmol g⁻¹, 1 mol%) were mixed in EtOH–H₂O (2.0 mL, 1:1, v/v). The reaction mixture was stirred at 50 °C and monitored by GC/GC-MS. GC/GC-MS analyses were performed on an Agilent 6890N GC coupled to an Agilent 5975 Network mass selective detector. EtOH solvent was removed under reduced pressure. After diethyl ether (5 mL) and water (2 mL) was added, the mixture was filtered. The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried (MgSO₄) and filtered, and the solvent was removed. The residue was purified by short column chromatography on silica gel to afford the desired product. The filtered catalyst was reused without further purification.

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