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Palladium nanoparticles encapsulated inside the pores of a metal-organic framework as a highly active catalyst for carbon-carbon cross-coupling⁺

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Well dispersed palladium nanoparticles were successfully encapsulated in the cages of a metal–organic framework, MIL-101, by using a "double solvents" method coupled with subsequent reduction with NaBH₄. Such a fabrication method can effectively avoid the aggregation of palladium nanoparticles on the external surfaces of MIL-101. The as-prepared catalyst, Pd@MIL-101, was characterized by transmission electron microscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy, N₂ adsorption and inductively coupled plasma atomic emission spectroscopy. The Pd@MIL-101 composite exhibited high catalytic activity toward the Suzuki–Miyaura and Heck cross-coupling reactions. The catalyst can be readily recovered and reused in at least 5 consecutive cycles without significant loss its catalytic activity.

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Introduction

The palladium-catalyzed carbon-carbon coupling reactions, such as Suzuki-Miyaura and Heck reactions, are of great importance as very versatile routes to construct biaryl units in organic chemistry and industrial processes.1-4 Traditional Suzuki and Heck reactions are performed mostly with homogeneous palladium salts or organometallic complexes with special ligands (such as phosphine complexes). Although homogeneous catalytic systems are known to exhibit better activity than heterogeneous systems, for large scale applications in liquid phase reactions, they bring about concerns of high cost and environmental issues. Conversely, heterogeneous catalysts can be easily separated from the reaction systems and reused. However, Pd nanoparticles (NPs), important kind of heterogeneous catalysts, are prone to aggregate and lose their catalytic activity without the use of a stabilizer.⁵ Therefore, the suitable stabilizers and/or supports for Pd NPs catalysts are generally required. A number of solid materials, such as carbon,6,7 zeolites,8 mesoporous silica9-11 and polymers,12 have been used as catalysts for C-C coupling reactions. However, these materials have one or more limitations in terms of stability, catalytic efficiency, and recyclability. Therefore, it is still attractive to explore efficient heterogeneous Pd catalyst for the coupling reactions.

Currently, metal-organic frameworks (MOFs) have received significant attention in recent years as a novel class of nanoporous materials mainly due to their tunable pore sizes, high specific surface areas, the possibility to functionalize, and designable framework structures modularly built from transition-metal clusters as nodes and organic ligands as struts.13-15 Due to their outstanding features, they have found potential applications in hydrogen storage, drug delivery, gas separation, sensing, and catalysis.¹⁶⁻²¹ MOF materials as host matrices to support Pd NPs for catalyzed C-C coupling reactions have been reported recently.²²⁻²⁹ It is well known that the size and location of supported palladium NPs have an important effect on their catalytic activity. Loading of metal NPs inside the porous matrices of MOF is of current interest.³⁰⁻³³ Various techniques, such as impregnation, chemical vapor deposition (CVD), solution infiltration, and solid grinding, have been adopted to encapsulate metal NPs within MOF pores.34-37 Jiang and co-workers prepared Pd/MIL-101 by impregnation method and subsequent molecular H₂ reduction and which was used as catalyst for the Suzuki coupling reactions.24 The reactions were carried out at 80 °C under an inert atmosphere. In 2011, Cao et al. used amino-functionalized MIL-53(Al)-NH₂ supported Pd NPs as a catalyst for the Suzuki coupling reaction.25 As an extension, they also reported the preparation of Pd NPs supported on amine-functionalized mix-linker MIL-53(Al) materials and their application for Heck reaction.²⁶ In addition, Martín-Matute group followed this idea and immobilized Pd NPs into an amino-functionalized MOF, MIL-101Cr-NH2. Good yields were obtained for a wide scope of substrates under remarkably mild conditions.28 [Pd(C3H5)(C5H5)]@MOF-5 catalyst was prepared by a CVD method. The resulting supported Pd catalyst showed good initial activity for Suzuki reaction in the solvent of dimethylformamide (DMF) with K₂CO₃ as the base.²⁷ However,

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 $[\]dagger$ Electronic supplementary information (ESI) available: EDX data and N_2 sorption isotherms of Pd@MIL-101, size distribution of Pd NPs. See DOI: 10.1039/c4ra10065d



Scheme 1 Schematic representation of immobilization of Pd NPs to a MIL-101 matrix and the C–C coupling reactions catalyzed by Pd@MIL-101.

with these methods, the precursor compounds can actually diffuse out of the pores of MOFs to form the aggregated nanoparticles on the external surfaces of MOFs, which would decrease the catalytic activity and reusability of the catalyst.³⁸ So it is always a down-to-earth question of how to avoid the formation of metal NPs on the external surfaces of MOFs.

Recently, double solvents method (DSM) derived from incipient wetness impregnation techniques has been developed by Xu *et al.*, which could greatly minimize the deposition of metal precursors on the outer surface.³⁹ However, the immobilization of Pd nanoparticles in the pores of MIL-101 and their catalytic performance for different organic transformations are still untouched.

MIL-101 (Cr₃F(H₂O)₂O[(O₂C)C₆H₄(CO₂)]₃·nH₂O, $n \approx 25$) is a Cr-based MOF synthesized by Férey *et al.*,⁴⁰ the interconnected three-dimensional hydrophilic zeotypic cavities accessible through small pore windows could be an appropriate host for nucleation and growth of metal NPs as such systems allow the metal precursors to infiltrate the cavities through the small pore windows and prevent metal nanoparticles from escaping or agglomerating from cavities due to the size limitations to cross the windows.

As a continuation of our effort to develop heterogeneous transitional metal catalysts and new functional materials,⁴¹⁻⁴⁴ herein, the ultrafine Pd nanoparticles were encapsulated in the pores of MIL-101 (Pd@MIL-101) without aggregation on the external surface of the host framework by using the double solvents method for the first time. To investigate the catalytic performance of the as-prepared Pd@MIL-101 catalyst, Suzuki and Heck reactions were selected as the model reactions (Scheme 1). The results demonstrated that the as-obtained catalyst exhibited high catalytic activity toward the Suzuki-Miyaura and Heck cross-coupling reactions.

Experimental section

Materials and methods

All chemicals were commercial and used without further purification. Chromic nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O, 99\%$),

aqueous hydrofluoric acid (HF, 40%), sodium borohydride (NaBH₄, 99%), terephthalic acid (HO₂CC₆H₄CO₂H), palladium chloride (PdCl₂), aryl boronic acid, aryl halides were purchased from Aladdin Reagent Limited Company. Potassium carbonate, *n*-hexane, anhydrous ethanol, DMF, and ether were all obtained from Chengxin Chemical Reagents Company (Baoding, China) and used as received.

The size and morphology of the nanoparticles were observed by transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) at 200 kV. The X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku D/max 2500 X-ray diffractometer using Cu Ka radiation (40 kV, 150 mA) in the range $2\theta = 10^{\circ}$ -80°. X-ray photoelectron spectroscopy was performed with a PHI 1600 spectroscopy using Mg K α X-ray source for excitation. The Pd content was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Thermo Elemental IRIS Intrepid II. The Brunauer-Emmett-Teller (BET) surface areas measurements were performed with N2 adsorption/desorption isotherms at liquid nitrogen temperature (77 K) after dehydration under vacuum at 150 °C for 12 h using a V-Sorb 2800P volumetric adsorption equipment (Jinaipu, China). The pore volume was calculated by a single point method at $P/P_0 = 0.99$.

Catalyst preparation

MIL-101 were synthesized and purified according to the method described by Férey *et al.*⁴⁰ Terephthalic acid (3.76 g), Cr(NO₃)₃·9H₂O (6.0 g), 40% HF (0.75 mL) and de-ionized water (75 mL) were placed in a 100 mL Teflon-liner autoclave and heated at 220 °C for 8 h. After cooling, the mixture was filtered to remove the unreacted crystals of terephthalic acid, and then further purified by solvothermal treatment in ethanol at 80 °C for 24 h. The resulting green solid was soaked in NH₄F (1 mol L⁻¹) solution at 70 °C for 24 h to eliminate the terephthalic acid inside the pores of MIL-101 and immediately filtered, washed with water several times, finally dried overnight at 150 °C under vacuum to obtained activated MIL-101 powder.

For preparing Pd encapsulated by MIL-101, 100 mg of activated MIL-101 powder was suspended in 20 mL of anhydrous *n*-hexane as hydrophobic solvent and the mixture was sonicated for 15 min until it became homogeneous. After stirring for 1 h, 0.16 mL of aqueous PdCl₂ solution (20 mg mL⁻¹) as the hydrophilic solvent was added dropwise over a period of 15 min with constant vigorous stirring. The resulting solution was continuously stirred for 2 h. After filtration, the green powder was dried in air at room temperature. These synthesized samples were further dried at 150 °C under vacuum for 12 h. An overwhelming reduction approach was employed by using 3.5 mL freshly prepared 0.6 mol L⁻¹ NaBH₄ aqueous solution while vigorous stirring, resulting in the generation of catalysts as a dark green suspension. The synthesized samples were collected by centrifuging, and used for the catalytic reactions.

General procedure of Suzuki reactions

A mixture of aryl bromide or iodide (0.5 mmol), phenylboronic acid (0.6 mmol), potassium carbonate (1.5 mmol), 4 mL

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EtOH–H₂O (1 : 1, v/v) and the catalyst Pd@MIL-101 (3 mg, 0.15 mol%) was stirred at room temperature for a desired reaction time. After the reaction was complete, the mixture diluted with 10 mL of H₂O and extracted with ethyl acetate (3 \times 10 mL). The organic layers were combined, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated by vacuum. The pure products were obtained by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent.

General procedure of Heck reactions

Aryl halide (0.5 mmol), vinyl substrate (0.75 mmol), K_2CO_3 (0.75 mmol), TBAB (0.5 mmol) and Pd@MIL-101 (3 mg, 0.15 mol%) was added to DMF (2 mL). The reaction mixture was stirred at 120 °C for a desired time. After the reaction was complete, the solution was centrifuged and washed with ethyl acetate for three times. The organic phase was subsequently washed with brine, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated by vacuum. The pure products were obtained by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent.

Hot filtration test

In the case of the Suzuki reaction, reaction mixture of bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), potassium carbonate (1.5 mmol), EtOH-H₂O (4 mL, 1:1, v/v) and the catalyst Pd@MIL-101 (3 mg, 0.15 mol%) was stirred at room temperature. After 0.5 h, the catalyst was separated by centrifugation, the reaction solution was stirred at ambient temperature for another 2 h, and the progress of the reaction was examined by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent.

Results and discussion

For the DSM, the double solvents, a hydrophilic solvent (water) and a hydrophobic solvent (n-hexane), was used in this paper. The former containing the metal precursor (PdCl₂) with a volume set equal to or less than the pore volume of the MOF could be absorbed within the hydrophilic pores of the MOF. The latter, in a large amount, was used to suspend the adsorbent and facilitate the impregnation process. Because the inner surface area of MIL-101 is much larger than the outer surface area, the small amount of PdCl₂ aqueous solution could go inside the hydrophilic pores by capillary force, which make the deposition of PdCl₂ on the outer surface of the MOF reduce greatly. In contrast, a large amount of solvent containing the metal precursor is used in the conventional single-solvent impregnation process, some of which will be deposited on the outer surfaces of the MOF after drying, generating aggregated MNPs on the outer surfaces.45 At the same time, an overwhelming reduction approach with a high-concentration NaBH₄ solution was carried out for avoiding Pd nanoparticles aggregation on external surfaces of the MOF.

Characterization of the catalysts

The synthesized Pd@MIL-101 catalyst was characterized by transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), N2 adsorption and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The TEM images (Fig. 1a and b) show that the Pd nanoparticles were highly dispersed. The average sizes of the Pd NPs were 2.4 nm (Fig. S1, see ESI[†]), which are small enough to be accommodated in the mesoporous cavities of MIL-101. The corresponding carbon, oxygen, chromium and palladium element mappings were shown in Fig. 1c-f, respectively. Fig. 1f clearly demonstrated the uniform distribution of ultrafine Pd nanoparticles throughout the Pd@MIL-101 composite. The EDX data (Fig. S2,†) further confirm the presence of the Pd in the Pd@MIL-101 composite. The palladium content in Pd@MIL-101 was determined by means of ICP-AES and amounted to 2.7 wt%.

The X-ray powder diffraction patterns of our synthesized samples of MIL-101 (Fig. 2a) matched with those reported in the literature.⁴⁰ Furthermore, no significant diffraction peak characteristic of Pd species is detected from the wide-angle XRD pattern for Pd@MIL-101 (Fig. 2b), which can be ascribed to the encapsulated of Pd nanoparticles into the pores of MIL-101, low Pd loading and small well dispersed palladium nanoparticles. This observation is very similar to the results reported by Zhou *et al.*²²

The XPS spectra (Fig. 3) demonstrate that the Pd species in the sample Pd@MIL-101 was present in the metallic state with the bond energy about 335.5 and 340.98 eV in the Pd $3d_{5/2}$ and $3d_{3/2}$



Fig. 1 (a and b) TEM images of Pd@MIL-101, (c-f) the corresponding carbon (c), oxygen (d), chromium (e), and palladium (f) element mappings, respectively.



core level. The presence of PdO species in Pd@MIL-101 was confirmed by fitted the high energy shoulder on the metallic Pd lines at bond energy of about 336.95 and 342.6 eV.⁴⁶ The production of oxidized Pd species could be due to the oxidation of metallic Pd left in an oxygen-containing environment.^{47,48}

The N₂ physisorption–desorption isotherms of the Pd@MIL-101 were shown in Fig. S3.† The experimental multipoint Brunauer–Emmett–Teller (BET) surface areas and the total pore volume of the MIL-101 and Pd@MIL-101 were calculated to be 3664.6 m² g⁻¹and 1.79 cm³ g⁻¹, 1986.0 m² g⁻¹and 1.0 cm³ g⁻¹, respectively. The great decrease in the amount of N₂ adsorption and the pore volume of Pd@MIL-101 indicated that the pores of the MIL-101 were occupied by the highly dispersed Pd nanoparticles.

The nature of base in Suzuki coupling reaction greatly affects the efficiency of the reaction. In general, the reactivities of different bases for the coupling reactions of aryl iodides and bromides decreased in the order: $OH^- > CO_3^{2-} > AcO^{-.28}$ High concentrations of base can lead to the formation of unreactive boronates (ArB(OH)_3⁻) and thus, the [OH⁻]/[ArB(OH)_2] ratio needs to be controlled.^{49,50} Moreover, MIL-101 was not stable enough under these strongly basic conditions.⁵¹ For this reason, carbonates were preferred because the release of hydroxy anions into the aqueous medium was relative slow. Carbonates, K₂CO₃, Na₂CO₃, and NaHCO₃ were used as the base and the results



Fig. 3 XPS measurement of Pd@MIL-101.

were summarized in Table 1 (entries 4–6), with the amount of catalyst fixed as 0.15 mol%, an excellent yield was obtained when the inorganic base K_2CO_3 was used.

Further experiments shows that 0.15 mol% amount of Pd@MIL-101 was sufficient to guarantee a clean and complete conversion. The reaction does not take place in the absent of catalyst (Table 1, entry 8). The yield of biphenyl increased from 51% to 97% when the amount of catalyst increased from 0.05 mol% to 0.15 mol% (Table 1, entries 4, 9). When the amount of the catalyst was larger than 0.15 mol%, the yield of biphenyl no longer increased greatly (Table 1, entry 10).

With the optimized reaction conditions in hand, the scope of catalytic utility of Pd@MIL-101 in Suzuki reaction was explored with various aryl halides and arylboronic acids. Those reactions were carried out in the presence of K₂CO₃ using EtOH-H₂O (1:1, v/v) as environmentally benign solvents. It is known that the yields of the Suzuki coupling reactions depend on the type of halide element, the positions of the substitutional groups and their electron withdrawing/donating capabilities. As shown in Table 2, excellent yield was achieved in the reactions of aryl iodides with phenylboronic acid (Table 2, entries 1-3). For the less reactive bromobenzene, the coupling reactions could also proceeded well and the reactions could be completed in 1-6 hours at ambient temperature with good to excellent yields (Table 2, entries 4-9). Among them, the electron donating groups on aryl bromides needed relatively long reaction time (6 h). However, when those reactions were carried out at 60 °C, the coupling reaction can be completed within 1.5 h with yields of 95-99% (Table 2, entries 10-13). Unfortunately, this catalytic system was less effective for the reaction of inactive aryl chlorides (Table 2, entries 14, 15) because of the strength of the C-C bond, whose bond dissociation energy was 96 kcal mol⁻¹.⁵²

In order to evaluate the efficiency of the catalyst Pd@MIL-101 for the Suzuki–Miyaura reaction, the present catalytic system was compared with other reported Pd nanoparticles catalysts in terms of the yield of the product, the dosage of catalyst, reaction

 Table 1
 Optimization of the reaction conditions for the Suzuki reaction of bromobenzene with phenylboronic acid^a

Entry	Solvents	Bases	Pd/mol%	Time/h	Yield/%
1	МеОН	K-CO-	0.15	2	15
2	FtOH	K_2CO_3	0.15	2	17
3	H ₂ O	K ₂ CO ₂	0.15	2	24
4	EtOH- $H_2O(1:1)$	K_2CO_3	0.15	2	97
5	EtOH- $H_2O(1:1)$	Na ₂ CO ₃	0.15	2	84
6	EtOH- $H_2O(1:1)$	NaHCO ₃	0.15	2	50
7	EtOH- $H_2O(1:1)$	_	0.15	2	_
8	EtOH- $H_2O(1:1)$	K_2CO_3	_	2	_
9	EtOH- $H_2O(1:1)$	K_2CO_3	0.05	2	51
10	EtOH- $H_2O(1:1)$	K_2CO_3	0.25	2	98
11	EtOH- $H_2O(1:1)$	K_2CO_3	0.15	0.5	41
12	EtOH- $H_2O(1:1)$	K_2CO_3	0.15	1	75
13	EtOH- $H_2O(1:1)$	K_2CO_3	0.15	3	99
14	EtOH $-H_2O(1:1)$	K_2CO_3	0.15	2	43^b

^{*a*} Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), solvents (4 mL), 25 °C. ^{*b*} The catalyst was removed after 0.5 h, the filtrate was stirred for another 2 h.

Table 2 Pd@MIL-101-catalyzed Suzuki coupling reaction

R1	X + (HO) ₂ B	Pd@MIL-101			
Entry	Aryl halides	Time/h	Products	Yield ^a /%	
1		1		95	
2	H3CO-	2		97	
3	H3COC	1		99	
4	⟨Br	2		97	
5	H ₃ COC-	1		99	
6	HO-Br	6	ОН-	91	
7	H ₃ C-	6		92	
8	Br CH ₃	6	H ₃ C	90	
9	H ₃ COBr	6	С-С-ОСН3	95	
10^b	HOBr	1.5	()-он	98	
11^b	H ₃ C-	1.5		96	
12^b	H ₃ CO-	1.5		99	
13^b	Br CH ₃	1.5	H ₃ C	95	
14	СІ	12		Trace	
15	H ₃ C-	12	————————————————————————————————————	Trace	

 a Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), K₂CO₃ (1.5 mmol), EtOH–H₂O (1 : 1) (4 mL), 25 °C. b 60 °C.

temperature and time (Table 3). The data in Table 3 indicated that the as-prepared Pd@MIL-101 can efficiently catalyze the coupling reaction with comparable or higher yield, low catalyst loading and relative short reaction time. Especially the reaction catalyzed by Pd@MIL-101 can be performed efficiently at room temperature without using toxic organic solvent. It has been known that the catalytic activity generally increases with decreasing metal NP size, as smaller particles possess higher surface areas available for reactants. The high catalytic activity of Pd@MIL-101 could be attributed to the well dispersion of Pd nanoparticles in the pores of MIL-101 and the confinement effect. The presence of monodisperse pores in MIL-101 has a confinement effect on the growth and gathering of Pd particles in the cages, which would avoid the aggregation of Pd particles before and after catalysis.

The Heck reaction is also an important method often used for the formation of C-C bonds by coupling aryl halides with activated alkenes. First, the coupling of iodobenzene with styrene was chosen as model reaction. The reactions were carried out with Pd@MIL-101 as a catalyst and DMF as a solvent under air atmosphere (Table 4). It was found that K₂CO₃ worked the best compared with Na₂CO₃, NaHCO₃, KOH and NaOAc. The addition of tetrabutylammonium bromide (TBAB) enhanced the yield of the product, presumably due to the stabilization effect of TBAB for the Pd(0) species.56 The influence of solvent on the catalytic activity was also investigated with the optimized base. The catalytic activity of the catalyst in DMF was higher than that in H₂O, ethylene glycol, and ethanol (Table 4, entries 1, 6-8). For the reaction of iodobenzene with styrene in DMF nearly quantitative conversion was obtained at 120 °C for 2 h. We next tested the effects of the amount of catalyst on the vields of the products. From the results listed in Table 3 (Table 4, entries 1, 9–11), we can see that 0.15 mol% amount of catalyst was sufficient to guarantee a clean and complete conversion. When the amount of the catalyst was reduced to 0.05 mol% under otherwise same conditions, the yield decreased to 49%. Moreover, the reaction can not occur in the absence of Pd catalyst (Table 4, entry 9).

Under the optimized reaction conditions, the scope of the Pd@MIL-101 catalyzed Heck reactions were investigated by employing a variety of substrates. These results are summarized in Table 5. The Heck reactions of aryl iodobenzene with styrene proceeded easily with excellent yield at 120 °C (Table 5, entries 1–3). In addition, various olefin derivatives were applied to this reaction, resulting in the formation of cinnamic esters in yields of 95–99% (Table 5, entries 4–6). Owing to the higher bond energy of the C–Br bonds, aryl bromide compounds are difficult to activate. Therefore, the reactions of bromobenzene with different olefins required relative long reaction time and the yields were ranged in 46–84% (Table 5, entries 7–10).

To verify the heterogeneity of the catalyst, a hot filtration test was performed for the Suzuki–Miyaura reaction of bromobenzene with phenylboronic acid. After 0.5 h, the Pd@MIL-101 catalyst was separated though centrifugation and the filtrate was monitored under identical reaction conditions for another 2 h. It was noticed that no further conversion was detected after the removal of the catalyst (Table 1, entry 14). The inductively coupled plasma atomic emission spectroscopy analysis of the supernatant solution of the reaction mixture thus collected by filtration also confirmed the absence of palladium ions in the liquid phase. These results clearly demonstrate that Pd nanoparticles were not being leached out from the MIL-101 during the cross-coupling reactions, which can be ascribed to the encapsulated of Pd nanoparticles into the pores of MIL-101.

The recyclability of the catalyst was further investigated because the recycling of the heterogeneous catalysts plays an important role in practical applications. The heterogeneous catalyst, Pd@MIL-101, can be separated easily *via* filtration. The Suzuki coupling reaction between bromobenzene and phenylboronic acid and the Heck reaction of iodobenzene with styrene under the optimized reaction conditions were used for

Aryl halide	Catalyst	Reaction conditions solvent/temp./time/Pd loading	Yield/%	Ref.
Bromobenzene	Pd/MIL-53-NH ₂	EtOH-H ₂ O/40 °C/0.5 h/0.5 mol%	94	25
<i>p</i> -Bromoanisoles	Pd@MIL-101-NH ₂	EtOH-H ₂ O/23 °C/0.5 h/3 mol%	95	28
Bromobenzene	Pd@MOF-5	DMF/90 °C/20 h/2 mol%	81	27
Bromobenzene	IRMOF-3-PI-Pd	EtOH-H ₂ O/80 °C/2 h/0.024 mol%	98	53
Bromobenzene	Pd/PMA-MIL-101	DMF/130 °C/24 h/1.3 mol%	50	54
<i>p</i> -Bromoanisoles	MOF-253-PdCl ₂	DMF-EtOH/100 °C/14 h/0.23 mol%	90	55
Bromobenzene	Pd@MIL-101	EtOH–H ₂ O/25 °C/1–6 h/0.15 mol%	97	This study

Table 4 Optimization of the reaction conditions for Heck reaction of iodobenzene with styrene catalyzed by $Pd@MIL-101^a$

Entry	Solvent	Base	Catalyst/mol%	Time/h	Yields/%
1	DMF	K_2CO_3	0.15	2	98
2	DMF	Na_2CO_3	0.15	2	62
3	DMF	NaHCO ₃	0.15	2	37
4	DMF	KOH	0.15	2	55
5	DMF	NaOAc	0.15	2	21
6	H_2O	K_2CO_3	0.15	2	5
7	Ethylene glycol	K ₂ CO ₃	0.15	2	9
8	Ethanol	K_2CO_3	0.15	2	7
9	DMF	K ₂ CO ₃	_	2	_
10	DMF	K_2CO_3	0.05	2	49
11	DMF	K_2CO_3	0.1	2	82

^a Reaction conditions: iodobenzene (0.5 mmol), styrene (0.75 mmol), base (0.75 mmol), TBAB (0.5 mmol), solvent (2 mL).

 Table 5
 Results for the Heck reaction catalyzed by Pd@MIL-101^a

/=

	R_1 $X + =$	$R_2 K_2$	CO ₃ , DMF, 120°C		2
Entry	R ₁	Х	R ₂	Time/h	Yields/%
1	Н	Ι	Ph	2	98
2	4-COCH ₃	Ι	Ph	2	97
3	$4-OCH_3$	Ι	Ph	2	92
4	Н	Ι	CO_2Me	2	95^{b}
5	Н	Ι	CO_2Et	2	99
6	Н	Ι	CO_2Bu	2	97
7	Н	Br	Ph	24	46
8	Н	Br	CO ₂ Me	24	81^b
9	Н	Br	CO_2Et	24	80
10	Н	Br	CO_2Bu	24	84

^{*a*} Reaction conditions: aryl halide (0.5 mmol), Pd(MIL-101 (0.15 mol)), olefin (0.75 mmol), K₂CO₃ (0.75 mmol), TBAB (0.5 mmol), DMF (2 mL), 120 °C. ^{*b*} 2 equiv. of methyl acrylate was used.

reusability experiments. As can be seen from Fig. 4, after being recycled for five successive runs, the catalyst still exhibits an excellent activity. Inductively coupled plasma atomic emission spectroscopy analysis showed that the leaching of Pd into the reaction solution is negligible, which could account for the preservation of the catalytic activity of Pd@MIL-101 composite.



Fig. 4 Reusability of the Pd@MIL-101 catalyst for the Suzuki and Heck reactions.

Conclusions

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In conclusion, we have successfully encapsulated the ultrafine Pd in the pores of MIL-101 by the double solvents method in combination with the overwhelming reduction approach, which could minimize the aggregation of the NPs on the external surface of the host framework. Those well-dispersed Pd NPs show high catalytic activity for the Suzuki and Heck coupling reactions. Moreover, the Pd@MIL-101 catalyst exhibit high stability which can be recycled and reused easily without reduction of catalytic activity. The present study might highlight the development of high performance heterogeneous catalysts by using functionalized cavities of MOFs as hosts for ultrafine metal NPs.

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