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PII: S0040-4020(20)30871-1

DOI: https://doi.org/10.1016/j.tet.2020.131664

Reference: TET 131664

To appear in: *Tetrahedron*

Received Date: 8 July 2020

Revised Date: 3 October 2020

Accepted Date: 6 October 2020

Please cite this article as: Wu S, Zhang Y, Jiang H, Wu L, Ding N, Jiang P, Zhang H, Zhao L, Yin F, Yang Q, Anchoring Pd(OAc)₂ on amide-bonded covalent organic frameworks: an efficient heterogeneous Pd@OC-MA catalyst for Suzuki-Miyaura coupling reactions in water, *Tetrahedron*, https://doi.org/10.1016/j.tet.2020.131664.

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Graphical Abstract

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Tetrahedron journal homepage: www.elsevier.com

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ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

ABSTRACT

A nitrogen-rich of a melamine-based mesoporous COFs material was synthesized and used as a carrier to support $Pd(OAc)_2$. The catalyst Pd@OC-MA revealed an efficient catalytic activity and selectivity for Suzuki-Miyaura coupling reactions in an environmental friendly water medium at room temperature. It has moderate to excellent conversion for inactive chlorinated aromatic hydrocarbons. The catalyst was synthesized simply, high stability, good selectivity and easy to recycle. Excellent catalytic activity of the Pd@OC-MA was observed after five consecutive cycles.

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Keywords: covalent organic frameworks (COFs) palladium catalyst Suzuki-Miyaura coupling reactions

1. Introduction

Covalent organic frameworks (COFs) are rising classes of 2D or 3D porous crystalline polymers, they are linked by covalent bonds.¹ ³ These materials have stable structure and pre-set porosity⁴⁻⁵. Various of COF materials have been synthesized after Yaghi first discovered them in 2005.⁶ In these COFs materials, a variety of two-dimensional (2D) and three-dimensional (3D) COFs have been reported and shown excellent properties in various applications such as gas adsorption and storage,⁷⁻⁸ optoelectronics, ⁹⁻¹⁰ catalysis, ¹¹⁻¹², etc. The COFs materials are comprised of some lightweight elements like C, B, N linked by covalent bonds such as amide linkage,¹³⁻¹⁵ imine linkage¹⁶ into a predictable structural 2D or 3D porous polymer. They are found to be admirable carrier of heterogeneous catalyst owing to their high surface areas, low density, large porosity and excellent stability. Some carriers are unstable when combined with metal particles through physical adsorption.¹⁷ In order to solve these difficulties, novel nitrogen-rich triazine COFs were synthesized with highly stable and the catalyst are more stable due to the coordination between metal particles and nitrogen atoms.¹⁸

The establishment of the carbon–carbon bonds is an extraordinary and significant method in organic synthesis and medical chemistry.¹⁹⁻²³ Transition metal palladium catalyzes cross-reaction of Suzuki–Miyaura, which was provided a general method for the formation of various organic compounds.²⁴⁻²⁶ Due to its excellent functional group tolerance of the catalytic process, it was widely used to prepare asymmetric diaryl derivatives.²⁷⁻²⁸ Palladium catalysts are also diffusely used in the Heck,²⁹ Sonogashira³⁰ and carbonylative³¹ reactions.

In the beginning, homogeneous palladium compounds were used as catalysts. Nevertheless, they have many disadvantages, such as high cost of ligands, difficult to separation, low recyclability and lead to environmental pollution. To resolve these disadvantages, heterogeneous catalysts were developed. In recent years, a variety of carriers were emerged in an endless stream. For example, inorganic carriers (SiO₂, ³²TiO₂, ³³CuO, ³⁴

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Scheme 1. Synthesis of Pd@OC-MA

CeO₂,³⁵ ZrO₂,³⁶), natural carriers (wool,³⁷ palygorskite,³⁸ halloysite³⁹) and organic polymer carriers (chitosan,⁴⁰ SNW1,⁴¹ COFs,⁴² MOF⁴³).

Nowadays, using of water as a solvent has developed rapidly in organic reactions. It is a non-toxic property, cheap, environment friendly solvent, therefore, regarded as an excellent substitute for expensive organic solvent.

Melamine is a chemical material with abundant nitrogen atoms and widely used in the synthesis of porous COFs. In this work, we have reported a novel covalent organic frameworks OC-MA was synthesized by one-step condensation reaction with melamine (MA) and 4,4' - oxybisbenzoyl chloride (OC) as raw materials. Further, OC-MA was used as a carrier to obtain Pd@OC-MA (to see **Scheme 1**). The catalyst has excellent catalytic activity and high stability towards the Suzuki - Miyaura cross-coupling reaction in water, and the catalytic activity did not decrease significantly after five consecutive cycles.

2. Results and Discussion

2.1. Synthesis and characterization of the catalyst Pd@OC-MA

A 100 mL round-bottomed flask was charged with melamine (0.2 mmol, 25.2 mg), 10 mL of THF and fully stirred. Then dropwise added 4,4' - oxybisbenzoyl chloride (0.3 mmol, 89.1 mg) dissolved in THF (10 mL) and Na₂CO₃ (0.3 mmol, 31.8 mg). The mix was stirred at 40 $^{\circ}$ C for 24 h. After the reaction, the solvent was removed by high speed centrifugation. Subsequently, the solid was washed with THF and hot water to get rid of the unreacted reactant. Finally, the product was dried at 70 $^{\circ}$ C for 12 h to get white solid OC-MA in 74% yield.

OC-MA (200 mg) was added to solution of $Pd(OAc)_2$ (20 mg) in CH₃CN (15 mL), followed by agitation at r.t. for 24 hours. After that, a yellow solid was obtained by high-speed centrifugation. And then, the solid was washed with secondary water (3×5mL) and CH₃CN (3×5mL), dried overnight at 70 °C to get light yellow powder Pd@OC-MA. The palladium content in the Pd@OC-MA was 0.816 wt% (0.077 mmolg⁻¹) by ICP-AES.

The prepared covalent organic frameworks OC-MA was confirmed by FT-IR spectrum (Figure 1 (a)). The characteristic absorption peaks of OC-MA at 1594 cm⁻¹ and 1254 cm⁻¹ were put down to the absorption II and III band of amide respectively.

The peak at 3077 cm⁻¹ can vest in C-N coupled vibration and 3409 cm⁻¹ to N-H stretching vibration. Therefore, it can be proved that the COFs was formed. The FT-IR absorption spectrum of the catalyst Pd@OC-MA is similar to the OC-MA, but there are several weak characteristic absorption peaks at 3100 cm⁻¹ ~ 2500 cm⁻¹. The peak at 2986 cm⁻¹ is attributed to the stretching vibration of methyl, asymmetric deformation vibration of methyl group has shifted to a wave number (1420 cm⁻¹) and the band at 2859 cm⁻¹ is attributed to the stretching vibration of methylene. The band at 2669 cm⁻¹ and 2550 cm⁻¹ can be indexed to the -OH in the carboxyl group. The absorption peak showed a slight red shift at 1685 cm⁻¹ because a coordination bond is formed between palladium acetate and C=O. Therefore, it can be proved that palladium acetate was supported on OC-MA successfully and obtained the catalyst Pd@OC-MA.



Figure 1. FT-IR spectra of compounds (a) OC-MA and (b) Pd@OC-MA

The crystal structure and properties of the OC-MA and catalyst Pd@OC-MA were confirmed by the powder X-rays diffraction analysis and the results were shown in Figure 2. The peaks at 17.53, 19.52, 21.50, 23.53 and 27.16 20 could be assigned to the (010), (011), (102), (012) and (110) Bragg peaks of P1/1 respectively. The experiment data is basically consistent with the XRD of the OC-MA using Material Studio simulation. It was shown that OC-MA was triclinic system and the cell parameters was a = 7.4179 Å, b = 6.1916 Å, c = 11.9510 Å, and $\alpha = \beta = 90^{\circ} \gamma = 120^{\circ}$. The structure of the OC-MA was reserved still

3 in

of palladium acetate was so less that it was below the detection limit of the instrument on the power XRD pattern of the catalyst Pd@OC-MA. Therefore, it is needed to use X-ray photoelectron spectroscopy (XPS) to confirmed further the Pd(OAc)₂ anchor on Pd@OC-MA.



Figure 2. Powder XRD pattern and simulated structures of OC-MA and Pd@OC-MA.

The elemental composition of the catalyst Pd@OC-MA and the chemical valence of Pd were further analyzed by XPS spectral analysis (Figure 3). The survey scan for Pd@OC-MA Figure 3 (a). It can be seen from Figure 3 (b) that the binding energy of the N1s in the synthesized OC-MA was changed from 399.67 eV to 399.04 eV after loading Pd(OAc)₂, which was indicated that the coordination bond between Pd (II) and N atoms generated the Pd@OC-MA rather than simple adsorption. There are two peaks at 338.1 eV and 343.5 eV corresponds to Pd3d_{5/2} and Pd3d_{3/2} for the catalyst, therefore, it can be stated that the Pd particles were bivalence³³(Figure 3 (c)).

The morphologies of the OC-MA and catalyst Pd@OC-MA were confirmed by SEM and TEM further (Figure 4). In Figure 4 (a), the OC-MA was shown a porous cross-networking structure, which was confirmed the preparation of the covalent organic frameworks successfully. However, the morphology of the Pd@OC-MA was flower-like structure (Figure 4 b). It was changed from a network structure to a flower-like structure may be the reason for $Pd(OAc)_2$. It can be seen from Figure 4 (C) that some of the sheet-like morphology of the reused catalyst was corroded leading to a reduction in catalytic activity. Figure 4 (d, e, f) shows the TEM at different magnifications of the Pd@OC-MA, and the TEM images clearly showed that the Pd (II) particles were symmetrical distribution on OC-MA. And its partical sizes were mainly distributed in 4-6 nm (Figure 4 g). The average partical size of Pd (II) was obtained by statistical calculation is 5.24 nm. Additionally, the elemental composition of OC-MA and catalyst Pd@OC-MA were confirmed by EDS, shown in Fig. S1 and Fig. S2.



Figure 3. XPS analysis of (a) survey scan for Pd@OC-MA, (b) N 1s comparison chart of OC-MA and Pd@OC-MA (c) Pd 3d for Pd@OC-MA.



Figure 4. SEM images of OC-MA (a), Pd@OC-MA (b), Pd@OC-MA cycle (c), TEM images of Pd@OC-MA (d, e, f) and particles size distribution in (g).

were characterized by the N2 adsorption desorption MA isotherms measurement at 77K. From the Figure 5 (a) we can get it belongs to III model nitrogen adsorption desorption isotherm. The application of the BET accounted in the porosity and specific surface area of the material Pd@OC-MA were found to be $0.03975 \text{ cm}^3\text{g}^{-1}$ and $8.5929 \text{ m}^2\text{g}^{-1}$ respectively (P/P₀=0.994). The pore-size of Pd@OC-MA was calculated by nonlocal density functional theory methods applied to the N₂ adsorption desorption isotherms at Figure 5 (b) and the pore-size is 3.3 nm and it is a mesoporous material.



Figure 5. (a) N2 adsorption (square symbol) / desorption (circle symbol) and (b) pore size distribution of Pd@OC-MA.

The thermostability of the synthesized OC-MA and Pd@OC-MA were performed by TGA under N₂ ambience, the temperature range from room temperature (r.t.) to 800 $^{\circ}$ C and the heating rate was 10 K/min as shown in Figure 6. Both OC-MA and Pd@OC-MA exhibits 4.38 % of weight loss from r.t. to 280 °C, it was attributed to the evaporation of water and solvent molecules entrapped in the synthesized materials. The decomposition of Pd@OC-MA starts at near 300 °C, it can be clearly shown that the catalyst has high thermal stability. And the difference was appeared between 380 °C to the end, which was authorized the Pd(OAc)₂ successful supporting on OC-MA.



Figure 6. TGA of synthesized OC-MA and Pd@OC-MA.

2.2. Catalytic studies of Pd@OC-MA in Suzuki-Miyaura coupling reaction

In succession, we researched the catalytic activity of Pd@OC-MA complex in Suzuki - Miyaura coupling reaction. Water is the best solvent in organic reactions due to its green, cheap and nontoxic properties. Hence, we selected water instead of organic solvent in the optimization of reaction conditions and the consequences were shown in Table 1. Furthermore, in the blank control experiment, no biphenyl product was obtained either without catalyst Pd@OC-MA or only with OC-MA (Table 1, entries 1and 2). However, the biphenyl in 99 % yield was acquired with Pd@OC-MA catalyst in the with Pd@OC-MA catalyst in the coupling reaction (Table 1, entry 3). It is

Suzuki-Miyaura coupling reaction. The effects of miscellaneous contributing factors on the reactivity further. Firstly, the reactivity time was studied in coupling reaction. And the optimal reaction time was 5 h. (Table 1, entries 4-8). Secondly, the reaction was investigated with different bases such as NaHCO₃, NaOAc, TEA, Cs₂CO₃, Na₂CO₃, NaOH (Table 1, entries 3, 8-12). Among them only NaHCO₃ and NaOH have the highest yield and other bases have a middle yield. NaOH has a strong alkalinity to corrode the catalyst, which is disadvantage to the recyclability of catalyst Pd@OC-MA. So NaHCO₃ was the optimum base. Finally, the amount of catalyst was optimized in the reactivity (Table 1, entries 3, 13, 14): by using 1 mg, 2 mg and 3 mg of Pd@OC-MA (Pd 0.816 wt%), the yield of biphenyl were 24 %, 82 % and 99 % severally. In summary, optimal of the reaction conditions were bromobenzene (0.1 mmol), benzene boricacid (0.15 mmol), NaHCO₃ (0.15 mmol), Pd@OC-MA (3

Table 1. Optimization of Suzuki - Miyaura coupling reaction conditions

mg), water as solvent in r.t. for 5 h.

Br	B(OH) ₂				
\bigcirc	+	Pd@OC-MA		\bigcirc	\bigcirc
Entry	Catalyst	Solvent	Base	Time (h)	Yield %
1	-	H ₂ O	NaHCO ₃	5	-
2	OC-MA	H_2O	NaHCO ₃	5	-
3	Pd@OC-MA	H_2O	NaHCO ₃	5	99
4	Pd@OC-MA	H_2O	NaHCO ₃	1	34
5	Pd@OC-MA	H_2O	NaHCO ₃	2	51
6	Pd@OC-MA	H_2O	NaHCO ₃	3	76
7	Pd@OC-MA	H_2O	NaHCO ₃	4	87
8	Pd@OC-MA	H_2O	NaOAc	5	88
9	Pd@OC-MA	H_2O	TEA	5	78
10	Pd@OC-MA	H_2O	Cs_2CO_3	5	90
11	Pd@OC-MA	H_2O	Na ₂ CO ₃	5	93
12	Pd@OC-MA	H_2O	NaOH	5	100
13 ^b	Pd@OC-MA	H_2O	NaHCO ₃	5	24
14 ^c	Pd@OC-MA	H_2O	NaHCO ₃	5	82
15	Pd(OAc) ₂	H_2O	NaHCO ₃	5	100

^aReaction condition: bromobenzene (0.1 mmol), benzene boricacid (0.15 mmol), base (0.15 mmol), H₂O (3 mL), catalyst (3 mg), ^bcatalyst (1 mg), catalyst (2 mg)

With the optimal coupling reaction conditions, the reactivity was investigated with different substituted aryl halides (X= Br, Cl) with different substituted boric acid and the results were shown in Table 2. It's worth noting that the electron character has no obvious affect on the conversions of the brominated aromatic hydrocarbon coupling reaction (Table 2, entries 1-8). These results were indicated that Pd@OC-MA was a high-efficiency catalyst for Suzuki cross-coupling reactions. Nevertheless, the ortho-substituted bromoaryl and phenyl boronicacid were reacted hardly in the reactivity (Table 2, entry 19). The result shows that the steric-hindrance effect has a significant effect on the C-C coupling reaction. Chlorinated aromatic hydrocarbons are less active than brominated aromatics, because they are not conducive to the oxidative addition of palladium, which was leaded to a low



Table 2. Suzuki-Miyaura coupling reaction catalyzed by Pd@OC-MA with various substituents



B(OH)₂



84

90

63

65

364

390

272

281

377

428

294

238



Me

2.3. Thermal filtration experiment of catalysts Pd@OC-MA

Generally speaking, thermal filtration experiment can be judged whether the catalysis was concluded from the Pd@OC-MA or from the leached palladium. It was carried out using bromobenzene and phenylboronic acid as reactants in the Suzuki reaction (Figure 7). The reactivity was conducted under the optimal conditions for 3 h and it had a conversion of 76 %; the catalyst Pd@OC-MA was separated from the reaction mixture and further stirred under the preceding conditions for 2 h. There is no change in the conversion of the reaction mixture by GC analysis. It can be seen that Pd@OC-MA catalyst plays a catalytic role in the reaction rather than the leached Pd in the solution.



Figure 7. The influence of reaction time on the conversion of bromobenzene in Suzuki reactions and thermal filtration experiment for Pd@OC-MA.

14

Journal Pre-proo

The active-life and recyclability of catalysts are obvious chanracteristics of heterogeneous catalysts. Hence, the recyclability of the Pd@OC-MA was studied under the optimal conditions for the reactions and the results were shown in the Figure 8. (a). After the reaction, the catalyst Pd@OC-MA was separated by high-speed centrifugation and then washed with water (3 \times 10 mL) and CH₃COOC₂H₅ (3 \times 10 mL) and the reclaimed catalyst was dried at 60°C for 8 hrs. Under the same reaction conditions, the catalyst was continuously recycled for five times and the catalytic activity of the catalyst was not significantly reduced (in 99%, 99%, 98%, 98%, 98% yield). XPS analysis was again used to detect the reused catalyst Pd@OC-MA. In the Figure 8. (b), there are two different valences of Pd, with the peaks at 335.5 eV (Pd $3d_{5/2}$), 341.2 eV (Pd $3d_{3/2}$) that can be confirmed the existence of Pd (0) in the reused Pd@OC-MA catalyst.³¹ It was shown that a small amount of Pd (II) was reduced to Pd (0) during the coupling reactions.



Figure 8. (a) the recyclability of the Pd@OC-MA, (b) XPS of Pd3d in reused Pd@OC-MA.

3. Conclusions

In summary, we have obtained a melamine-based mesoporous COFs material OC-MA for anchoring Pd(OAc)₂. The heterogeneous catalyst Pd@OC-MA has a high-efficiency recyclable for Suzuki - Miyaura cross-coupling reaction, NaHCO₃ as base and H₂O as solvent, to obtain the product in 99 % yield. With a low catalyst loading, Pd@OC-MA also has moderate to excellent conversion for inactive chlorinated aromatic hydrocarbons in eco-friendly water. The catalytic activity of the heterogeneous catalyst Pd@OC-MA did not decrease significantly after five consecutive cycles. The catalyst Pd@OC-MA has stable chemical properties, simple synthesis process, low cost of raw materials, easy separation and recycling and has potential applications in industrial production.

4. Experimental section

4.1. Materials and methods

If not specified, all chemicals and reactants can be used directly without further processing. The chemical reagents were analytically pure. The FT-IR spectra analysis was obtained on a spectrometer. Powder JASCO FT/IR-660 Plus X-rav diffractometer was obtained on a Rigaku using CuK α (λ =1.5404 Å) source with a scan rate of 0.5° min⁻¹. The micromorphology of OC-MA and Pd@OC-MA were surveyed by SEM (ULTRA Plus, Zaiss) and TEM(TECNAI G²F₂₀STWIN D2278, FEI). Elemental analysis of the catalyst Pd@OC-MA was performed on a scanning electron microscope using an energy dispersive x-ray spectrometer (EDX). The N₂ adsorption-desorption isotherms was measured on a BEL sorp-Max (BEL, Japan) at 77 K. The specific surface area and pore size of the catalyst were calculated by using the BET method. The thermal stability of the Pd@OC-

thermal gravimeter S-1000, Japan) under nitrogen protection, and the heating rate from r.t. to 800 °C was 10 K/min. All NMR spectra were recorded on MERCURY (400 MHz for NMR) spectrometers; chemical shifts are expressed in ppm (δ units) relative to TMS signal as internal reference in CDCl₃. XPS measurement of the OC-MA and Pd@OC-MA were conducted by the ESCALAB 250 Xi Mg X-ray resource (Thermo Scientific).

4.2. General procedure for Pd@OC-MA catalysted Suzuki-Miyaura coupling reactions

In a representative experiment, Pd@OC-MA catalyst (3 mg) was added to mixture of bromobenzene (0.1 mmol), arylboronic acid (0.15 mmol), NaHCO₃ (0.15 mmol) in H₂O (3 mL), and the reaction mixture stirred violently at r.t. for 5 h. After the reaction, it was extracted with CH₃COOC₂H₅ and monitored by TLC analysis. The catalyst was detached by high speed centrifugation and then washed with H₂O (3×3 mL) and CH₃COOC₂H₅ (3×3 mL) and dried at 60 °C for 8 h for the next run. Furthermore, the organic components were concentrated on a rotary evaporator to give the desired biaryl group. The homologous product was obtained by flash chromatography. The product was analyzed by NMR.

4.3. Characterization

4.3.1 Biphenyl (3a, 3i), ¹H NMR (400 MHz, CDCl₃): δ = 7.51-7.48 (m, 4H), 7.35-7.32 (m, 4H), 7.26-7.22 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 141.32, 128.83, 127.33, 127.25 ppm.

4.3.2 3-nitro-1,1'-biphenyl (3b, 3m), ¹H NMR (400 MHz, CDCl₃): δ = 7.55-7.50 (m, 2H), 7.45-7.32 (m, 6H), 7.15-7.00 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 143.6, 140.0, 130.3, 130.2, 128.9, 127.9, 127.1, 122.8, 114.2, 114.0 ppm.

4.3.3 4-methoxy-1,1'-biphenyl (3c, 3k), ¹H NMR (400 MHz, CDCl₃): $\delta = 7.70-7.63$ (m, 4H), 7.55-7.43 (m, 5H), 3.80 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 140.62$, 138.07, 137.80, 128.97, 127.60, 127.35, 127.05, 126.95, 15.95 ppm.

4.3.4 4-methylbiphenyl (3d, 3j), ¹H NMR (400 MHz, CDCl₃): δ = 7.62-7.60 (m, 2H), 7.53-7.44 (m, 4H), 7.36-7.26 (m, 3H), 2.42 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 141.17, 138.37, 137.01, 129.48, 128.71, 127.00, 126.97, 126.97, 21.10 ppm.

4.3.5 4-chlorobiphenyl (3e), ¹H NMR (400 MHz, CDCl₃): δ = 7.57-7.52 (m, 4H), 7.47-7.42 (m, 4H), 7.39-7.36 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 139.99, 139.66, 133.37, 128.90, 128.87, 128.38, 127.57, 126.97 ppm.

4.3.6 4-nitrobiphenyl (3f, 3l), ¹H NMR (400 MHz, CDCl₃): $\delta = 8.43$ (s, 1H), 8.19-8.18 (m, 1H), 7.91-7.90 (m, 1H), 7.62-7.58 (m, 3H), 7.51-7.48 (m, 2H), 7.45-7.42 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 142.81$, 138.59, 132.98, 129.70, 129.15, 128.54, 127.11, 121.99 ppm.

4.3.7 4-bromobiphenyl (3g, 3q), ¹H NMR (400 MHz, CDCl₃): δ = 7.58-7.56 (m, 4H), 7.47-7.44 (m, 4H), 7.39-7.36 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 139.94, 139.63, 133.32, 128.78, 128.87, 128.34, 127.51, 126.98 ppm.

4.3.8 3-methylbiphenyl (3h, 3n), ¹H NMR (400 MHz, CDCl₃): δ = 7.66-7.65 (m, 2H), 7.51-7.46 (m, 4H), 7.41-7.38 (m, 2H), 7.24-7.22 (m, 1H), 2.49 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 141.41, 141.29, 138.35, 128.73, 128.71, 128.04, 128.02, 127.22, 127.20, 124.32, 21.59 ppm.

4. Journal P 7.57-7.55 (m, 2H), 7.45-7.26 (m, 6H), 7.04-7.00 (m, 4H) ppm. 13 C NMR (100 MHz, CDCl₃): δ = 164.47, 162.03, 143.56, 139.99 (d, J = 2.0 MHz), 128.93, 127.89, 127.15, 122.82, 122.79, 114.17, 113.97 ppm.

4.3.10 4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (3p), ¹H NMR (400 MHz, CDCl₃): $\delta = 10.03$ (m, 1H), 7.93-7.91 (m, 2H), 7.72-7.70 (m, 2H), 7.60-7.58 (m, 2H), 7.02-6.99 (m, 2H), 3.86-3.84 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 191.83$, 160.10, 146.74, 134.66, 132.02, 130.28, 128.47, 127.02, 114.46, 55.37 ppm.

4.3.11 4-chloro-4'-nitro-1,1'-biphenyl (3r), ¹H NMR (400 MHz, CDCl₃): δ = 7.48-7.47 (m, 2H), 7.47-7.46 (m, 2H), 7.41-7.40 (m, 2H), 7.40-7.39 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ =138.40, 133.73, 129.02, 128.19, 128.18 ppm.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21962017, 31760608 and 21968032), the Fundamental Research Funds for the Central Universities (31920200002, 31920190016, 31920200042, 31920200086,), the project of cultivating higher education teaching achievements in Gansu Province (No. 2019GSJXCGPY-10), Graduate Research Innovation Project (No. Yxm 2019137) and the Northwest Minzu University's Double First-class and Characteristic Development Guide Special Funds-Chemistry Key Disciplines in Gansu Province (No. 11080316). We also thank Key laboratory for Utility of Environmental Friendly Composite Materials and Biomass in University of Gansu Province (Northwest Minzu University), for financial support.

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A stable heterogeneous palladium catalysts, the porous COFs anchored Pd complex, was synthesized by a simple technique.

Pd@OC-MA complex has been developed an efficient and stable catalyst for Suzuki -Miyaura coupling reactions in an environmental friendly water medium at room temperature.

The catalyst shows outstanding stability and reusability, it can be separated simply, effectively and reused five times without any activity decrease.

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Declaration of interests

 \checkmark The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: