

Pd@UiO-66: An Efficient Catalyst for Suzuki–Miyaura Coupling Reaction at Mild Condition

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Abstract In this paper, the palladium nanoparticles were successfully encapsulated in metal–organic framework material, UiO-66, by a facile approach. Based on the microwave-assisted method, the pores of UiO-66 were activated and the metal precursors were reduced at the same time in the presence of reducing agent. The obtained Pd@UiO-66 was characterized via transmission electron microscopy, powder X-ray diffraction, N₂ adsorption and X-ray photoelectron spectroscopy. The Pd@UiO-66 exhibited efficient catalytic activity for the Suzuki–Miyaura coupling reactions at mild condition.

Graphical Abstract The palladium nanoparticles were successfully encapsulated in metal–organic framework material, UiO-66, by a facile approach. Based on the microwave-assisted method, the pores of UiO-66 were activated and the metal precursors were reduced at the same time in the presence of reducing agent. The obtained Pd@UiO-66 exhibited efficient catalytic activity for the Suzuki–Miyaura coupling reactions at mild condition.



Keywords Microwave · Palladium nanoparticle · Metalorganic frameworks · Suzuki–Miyaura coupling reaction

1 Introduction

Palladium-catalyzed Suzuki–Miyaura coupling reaction is one of the most powerful methods to constructing biaryl units in organic synthesis [1–4]. Based on palladium, homogeneous catalytic system has played a significant role in organometallic catalysis [5]. However, homogeneous catalyst suffers from instability, non-reusability, difficulty to separate from the reaction system. Hence, to develop Pd

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catalyst with excellent recyclability and reusability has the great significance in sustainability development and protecting the environment. In order to achieve this task, heterogeneous catalytic system has been employed in recent years. A number of materials have been used to support the Pd nanoparticles (NPs), such as silica, zeolites, carbon or covalent organic polymers, for the carbon–carbon coupling reactions. Nevertheless, above materials have some limitations such as low stability and catalytic efficiency. Therefore, it is essential to explore an efficient heterogeneous palladium catalytic system for the coupling reaction.

Metal-organic frameworks (MOFs) have emerged as a novel class of functional materials due to their high surface areas, tunable pore sizes, and thermal stability. Owing to these outstanding properties, MOFs have been employed in gas storage [6, 7], catalysis [8, 9], adsorption [10, 11], super-capacitor [12], and drug delivery [13]. In recent years, the employment of MOFs as the supports for Pd NPs has attracted considerable interest [8, 14-17]. Gao et al. [18] used immersion method to prepare Pd@MOF-5 and applied to catalyze coupling reactions. Meike [19] and his co-workers synthesized MIL-53-NH₂ (Al) by a two-step post-synthetic method and the obtained Pd-containing MOFs exhibited high conversion and selectivity in carboncarbon coupling reactions. Pd@MIL-101 was prepared by us using a "double solvents" method, this method could effectively avoid the aggregation of palladium nanoparticles on the external surfaces of MIL-101. So the catalyst could be readily recovered and reused in at least 5 consecutive cycles without significant loss its catalytic activity in Suzuki-Miyaura and Heck cross-coupling reactions [20].

UiO-66, a Zr-based MOF, has outstanding physical and chemical properties, such as large specific area and pore size as well as good chemical resistance to water and organic solvents, which make UiO-66 become a highly desirable and most promising material for catalytic applications [21-24]. Recently, Pd@UiO-66 was fabricated by chemical vapor infiltration of (allyl)Pd(Cp) followed by UV light irradiation, which was used as shape-selective hydrogenation catalyst [25]. Tangestaninejad et al. prepared a heterogeneous catalyst, Pd@UiO-66-NH₂, using a direct anionic exchange method followed by chemical reduction with sodium acetate in methanol. Pd@UiO-66-NH₂ was applied for catalyzing the Suzukie-Miyaura cross-coupling reaction [16]. Bifunctional Zr-MOF catalyst containing palladium nanoclusters, Pd@UiO-66-NH₂, has been developed and exhibited high catalytic activity and selectivity in a one-pot tandem oxidation-acetalization reaction [26]. The molecular formulas of UiO-66 has been demonstrated of $Zr_6O_4(OH)_4(CO_2)_{12}$, and it has the highest coordination in MOFs of 12-coordination and the metal atoms was packed in them. The highly thermal stability could be attributed to the highly symmetrical inorganic metal units and the strong interaction force between the Zr_6 -octahedron with the oxygen atoms. The Zr-based MOF has been synthesized by Lillerud and his co-workers via a conventional solvothermal method [27]. However, the traditional heating methods for the preparation of UiO-66 always need many hours or even several days in the synthesis process, which is not desirable for industrial applications.

Microwave-assisted synthesis as a relatively novel method has found lots of applications in various chemical transformations, including the synthesis of nanoporous materials. The fabrication of MOFs under microwave irradiation not only largely reduce the reaction time, but also can control the size and shape of the crystals [28]. Recently, the microwave-assisted technique has been widely applied as an alternative method in the synthesis of organic-inorganic hybrid materials including MOFs [29-32]. Recently, UiO-66 was synthesized efficiently with a high yield in the presence of an additive (benzoic acid and acetic acid) using microwave irradiation. The result indicated that the microwave irradiation could not only shorten the reaction time, but also improve the surface area of UiO-66. At the same time, the product using microwave irradiation has shown excellent adsorption ability for dyes [33].

Herein, we successfully synthesized UiO-66 by a microwave-assisted method and which was employed as a support for Pd nanoparticles. To evaluate the performance of the obtained catalyst, Pd@UiO-66, Suzuki–Miyaura cross-coupling reaction was selected as the model reaction. The results demonstrated that Pd@UiO-66 can catalyze the Suzuki coupling reaction efficiently even at mild condition.

2 Experiment

2.1 Materials

All chemicals were commercial and used without further purification. Zirconium chloride (ZrCl₄, 96 %), 1,4-benzenedicarboxylate (BDC, 99 %), palladium chloride (PdCl₂), aryl halides, arylboronic acids were obtained from Aladdin Reagent Limited Company. Sodium borohydride (NaBH₄, 99 %), potassium carbonate (K₂CO₃), *N*,*N*dimethylformamide (DMF), anhydrous ethanol (EtOH) were acquired from Chengxin Chemical Reagent Company (Baoding, China).

The X-ray diffraction (XRD) patterns of UiO-66 and Pd@UiO-66 were recorded by Dandong TD-3500 X-ray diffractometer at 40 kV and 150 mA with Cu K α

irradiation. The transmission electron microscopy (TEM) images were observed by FEI Tecnai f20 at 200 kV and the samples were dispersed under the ultrasonic. The image of X-ray photoelectron spectroscopy (XPS) was obtained by Thermo ESCALAB 250Xi using a monochromatic Al K α source at 1486.6 eV. The Brunauer–Emmett–Teller (BET) surface areas of the samples were measured using V-Sorb 2800 at 77 K and dealt at 100 °C for 4 h in vacuum before the nitrogen adsorption and desorption. The catalyst was synthesized by XH-100B at 700 W. The Pd content of the solution after reaction was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Thermo Elemental IRIS Intrepid II.

2.2 Synthesis of UiO-66 and Pd@UiO-66

The UiO-66 was prepared according to the procedure reported by Michael [34]. $ZrCl_4$ (500 mg, 2.16 mmol) was dispersed in HCl (4 mL)/DMF (20 mL) to give a clear solution under ultrasonic. Then, 1,4-benzenedicarboxylate (BDC) (492 mg, 3 mmol) dispersed in 40 mL DMF was added into the above solution. Finally, the mixed solution was placed into the microwave oven and irradiated at 100 °C for 2 h. After centrifugation, the obtained UiO-66 was washed two times with water and dried in vacuum at 150 °C overnight.

UiO-66 (100 mg) was dispersed in water (5 mL) and then the H_2PdCl_4 (3.334 mL, 1 mg/mL) was added to it. Then the mixture was stirred for 24 h at room temperature and the solid was separated by centrifugation to get rid of the unnecessary metal ions from the solution. The obtained solid was redispersed in water and NaBH₄ (7.5 mg) was added in it under stirring. Then, the mixture was placed into the microwave oven and irradiated at 30 °C for 20 min. Finally, the product, Pd@UiO-66, was centrifuged, washed with deionized water and dried in vacuum at 60 °C overnight (Fig. 1).

2.3 General Procedure for Suzuki–Miyaura Reaction

Typically, aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), alkali (1.5 mmol), EtOH-H₂O (4 mL, 1:1,

v/v) and Pd@UiO-66 (2 mg, 0.075 mol%) were added to a round-bottom flask. The mixture was stirred at room temperature for the appropriate time in air. After that, the reaction mixture was diluted with 10 mL of H₂O and extract with ethyl acetate (3×10 mL). Then, the organic layer was combined, dried over anhydrous MgSO₄ and filtered. Solvent was removed under vacuum, and the reaction products were purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent.

In the recyclability experiment, the reaction of bromobezene and phenylboronic acid was chosen as a model reaction. A 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 Pd@UiO-66 (2 mg, 0.075 mol%) was stirred at room temperature for 30 min, then the catalyst was separated by centrifugation and dryed in vacuum at 60 °C. The conditions of the recycling reactions were same as describe above, except of using the recovered catalyst.

2.3.1 Hot Filtration Test

In the hot filtration test, a 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@UiO-66 (2 mg, 0.075 mol%) was stirred at room temperature. After 15 min, the catalyst was separated by centrifugation, the reaction solution was stirred still for 30 min, and the progress of the reaction was examined by flash chromatography on silica gel with petroleum ether/ ethyl acetate as the eluent.

3 Results and Discussion

3.1 Characterization of the Catalyst

The TEM images of Pd@UiO-66 were shown in Fig. 2, the Pd nanoparticles were dispersed over the UiO-66 uniformly. It can be seen that the Pd nanoparticles were obtained with a narrow particle size about 5 nm. Energy dispersive X-ray spectroscopy (EDX) was shown in Fig. 3,





Fig. 2 a and b TEM images of fresh Pd@UiO-66, c and d reused catalyst

which further confirm the existence of the Pd. The palladium concentration in Pd@UiO-66 was determined by means of ICP-AES and amounted to 2.5 wt%.

XRD patterns of UiO-66 and Pd@UiO-66 were shown in Fig. 4. It can be seen that the samples of UiO-66 have the sharp peaks, which are matched with the previous report [35], which indicated that the sample of UiO-66 has the excellent crystallinity. As shown in Fig. 4, the diffraction peaks of Pd@UiO-66 are similar to those of UiO-66, indicating that Pd@UiO-66 exhibit no loss of crystallinity upon metal coordination. Moreover, Fig. 4 has not shown the diffraction peak characteristic of Pd NPs, which can be ascribed to the low amount of Pd NPs, the encapsulated of Pd nanoparticles into the pores of UiO-66, low Pd loading and well dispersed Pd NPs. The result is consistent with the results reported in the document [36]. To further confirm the presence of Pd nanoparticles in the sample, we performed XPS analysis for Pd@UiO-66. In Fig. 5a, the peaks of C, O, Zr, and Pd could be clearly seen, nevertheless, Pd expresses weak peak relatively, it is



Fig. 3 The EDX pattern of Pd@UiO-66

possible that the low content Pd was introduced in. After the deconvolution, the Pd 3d spectrum is exhibited in Fig. 5b, the characteristic peaks of Pd $3d_{3/2}$ and Pd $3d_{5/2}$



Fig. 4 XRD patterns for UiO-66, fresh Pd@UiO-66 and reused Pd@UiO-66 $% \mathcal{M}_{\mathrm{C}}$

are showed at 340.88 and 335.42 eV, respectively, which demonstrated that the Pd species in the Pd@UiO-66 was present in the metallic state.



Fig. 6 N2 adsorption of UiO-66 andPd@UiO-66

 N_2 adsorption experiments of UiO-66 and Pd@UiO-66 are tested at 77 K, the results are shown in Fig. 6. The BET surface areas of UiO-66 and Pd@UiO-66 are 1129.8 and 895.9 m²/g, respectively. And 0.6346 and 0.4864 cm³/g are



Fig. 5 XPS images of Pd@UiO-66 (a and b) and the reused catalyst (c and d)

Table 1Optimization ofinfluence factors for the Suzuki–Miyaura reaction ofbromobenzene withphenylboronic acid

Entry	Catalyst	Solvents	Bases	Pd (mol%)	Time (min)	Yield (%)
1	Pd@UiO-66	EtOH-H ₂ O(1:1)	K ₂ CO ₃	0.1	40	95
2	Pd@UiO-66	EtOH- $H_2O(1:1)$	K ₂ CO ₃	0.075	40	94
3	Pd@UiO-66	EtOH- $H_2O(1:1)$	K ₂ CO ₃	0.05	40	73
4	Pd@UiO-66	EtOH- $H_2O(1:1)$	K ₂ CO ₃	0.075	10	30
5	Pd@UiO-66	EtOH- $H_2O(1:1)$	K ₂ CO ₃	0.075	20	50
6	Pd@UiO-66	EtOH- $H_2O(1:1)$	K ₂ CO ₃	0.075	30	93
7	Pd@UiO-66	EtOH- $H_2O(1:1)$	K ₂ CO ₃	0.075	60	95
8	Pd@UiO-66	EtOH- $H_2O(1:1)$	-	0.075	30	-
9	Pd@UiO-66	EtOH- $H_2O(1:1)$	Na ₂ CO ₃	0.075	30	74
10	Pd@UiO-66	EtOH- $H_2O(1:1)$	Et ₃ N	0.075	30	14
11	Pd@UiO-66	EtOH- $H_2O(1:1)$	NaAc	0.075	30	18
12	Pd@UiO-66	EtOH	K ₂ CO ₃	0.075	30	15
13	Pd@UiO-66	H ₂ O	K ₂ CO ₃	0.075	30	15
14	Pd@UiO-66	EtOH- $H_2O(3:1)$	K ₂ CO ₃	0.075	30	37
15	Pd@UiO-66	EtOH- $H_2O(1:3)$	K ₂ CO ₃	0.075	30	58
16	Pd@UiO-66	DMF	K ₂ CO ₃	0.075	30	2
17	UiO-66	EtOH- $H_2O(1:1)$	K ₂ CO ₃	0.075	30	-
18	Pd@UiO-66	EtOH- $H_2O(1:1)$	K ₂ CO ₃	0.075	15	39
19	Pd@UiO-66	EtOH- $H_2O(1:1)$	K ₂ CO ₃	0.075	30	42 ^a

Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), solvent (4 mL), 30 $^{\circ}$ C

^a The catalyst was removed after 15 min, the filtrate was stirred still for 30 min

the total pore volume of UiO-66 and Pd@UiO-66, respectively. The decreasing of BET and pore volume indicate that the interspace of UiO-66 was occupied by Pd nanoparticles.

3.2 Suzuki–Miyaura Reactions Catalyzed by the Prepared Catalyst

To investigate the catalytic activity of Pd@UiO-66, Suzuki–Miyaura cross-coupling reaction was selected as the model reaction. In the initial experiment of Suzuki– Miyaura reaction, the coupling reaction of phenyl bromide and phenylboronic acid was chosen. The results indicated that Pd@UiO-66 exhibited high catalytic activity for the coupling reaction at mild condition (30 °C). Different reaction conditions that effect the reaction efficiency, such as molar ratio of reactant, reaction time, types of base and solvent, were investigated in detail. The results were shown in Table 1.

In the initial experiments, the reaction time was set at 40 min, the yields of biphenyl increased from 73 to 95 % when the dosage of Pd@UiO-66 was adjusted from 0.05 to 0.1 mol% (Table 1, entries 1–3). 0.075 mol% amount of Pd@UiO-66 was sufficient to guarantee complete conversion. The reaction does not take place in the absent of catalyst, which indicated that the catalyst play a key role for the coupling reaction.

Further experiments showed that the yield of the product increased from 30 to 93 % (Table 1, entries 4–6) with increasing the reaction time from 10 min to 30 min. When the reaction time was larger than 30 min, the yield of biphenyl no longer increased greatly (Table 1, entries 2, 7).

The type of base used in Suzuki coupling reaction greatly affects the reaction efficiency. Some typical bases including Et₃N, NaAc, Na₂CO₃ and K₂CO₃ were investigated (Table 1, entries 6, 8–11). The results showed that good yield was obtained when K₂CO₃ was used as the base. The yield of the product using K₂CO₃ as the base was higher than that using Na₂CO₃, which is probably related to the sizes of the metal cations. Potassium ion with a relatively larger size has a weaker ion-pairing interaction than sodium, which would lead to its higher solubility in the solvent and higher basicity [17]. The type of reaction media were also investigated, the excellent yield was obtained with EtOH–H₂O (4 mL, 1:1, v/v) as the solvent (entries 6, 12–16).

The catalytic activity of Pd@UiO-66 for Suzuki reactions was investigated with various aryl halides and arylboronic acids. Those reactions were conducted in the presence of K_2CO_3 using EtOH-H₂O (1:1, v/v) as environmental friendly solvent. It is well known that the yields of the coupling reactions depend on the type of halide element, the positions of the substitutional groups and their electron withdrawing/donating capabilities. As can be seen from Table 2, good yields were obtained in the reactions of

Entry	Ary halides	Arylboronic acids	Time/h	Products	Yield/%
1		B(OH)2	0.5		96
2	⟨Br	B(OH)2	1		95
3	CH ₃ Br	B(OH)2	1.5		88
4	H ₃ C-	B(OH)2	1.5	CH3	92
5	O ₂ N-Br	B(OH)2	1		93
6	⟨Br	H ₃ C B(OH) ₂	1	CH ₃	96
7	CH ₃ Br	H ₃ C B(OH) ₂	1.5	CH ₃ CH ₃	97
8	H ₃ CBr	H ₃ C B(OH) ₂	1.5	H ₃ C	99
9	O ₂ NBr	H ₃ C B(OH) ₂	1		99
10	⟨Br	CH ₃ B(OH) ₂	1		78
11	O ₂ NBr	CH ₃ B(OH) ₂	1		96
12	СІ	B(OH)2	6		29

Table 2 Pd@UiO-66-catalyzed Suzuki coupling reactions

Reaction conditions: Aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), alkali (1.5 mmol), EtOH-H₂O (1:1, 4 mL) and Pd@UiO-66 (0.075 mol%), 30 °C

aryl iodides and less reactive bromobenzene with phenylboronic acid (Table 2, entries 1–11) at ambient temperature. For most of the substrates, the reaction could be completed in 0.5–1.5 h with moderate or excellent yields, with the substrates having either electron-donating groups or electron-withdrawing groups. It is worth to noted that 2-methyl bromobenzene (Table 2, entry 3) and 2-methyl arylboronic acid (Table 2, entries 10, 11), which were influenced by steric hindrance, the coupling reactions could also proceeded well. Unfortunately, for the reaction of inactive aryl chlorides (Table 2, entry 12), the yield is only 29 % even when the reaction time was 6 h because of the C–Cl bond is more powerful than C–Br and C–I bond.

To confirm the heterogeneity of the catalyst, a hot filtration experiment was performed with the reaction of bromobenzene and phenylboronic acid. After 15 min, the catalyst was separated by centrifugation and the reaction solution was stirred still for 30 min. The result indicated that there was no further conversion after the removal of the catalyst (Table 1, entries 18, 19). The absence of palladium ions in the solution after reaction was also confirmed by the inductively coupled plasma atomic emission spectroscopy analysis.

To evaluate the efficiency of the catalyst for Suzuki coupling reaction, TOF and yield has been calculated for comparison with that of other reported Pd catalyst. The data in Table 3 showed that the Pd@UiO-66 using microwave assisted exhibited efficiently catalytic activity at mild condition without using toxic organic solvent.

The recyclability of Pd@UiO-66 was studied because the recycling of the heterogeneous catalyst plays a key role in practical applications. The heterogeneous catalyst, Pd@UiO-66, can be separated easily via filtration. The Suzuki coupling reaction between bromobenzene and

Catalyst	Dosage (mol%)	T/°C	Recycling times	Yield (%)	TOF/h^{-1}	Refs
Pd@MOF-253	0.23	100	5	90–94	29.8-43.5	[17]
Pd@UiO-66-NH ₂	0.25	60	5	90	623.3-699.2	[16]
Pd@MIL-101-NH ₂	3	23	10	84–99	63.3-66.7	[37]
Pd@H ₂ P-Bph-COF	0.5	110	5	97–99	129.5-131.3	[38]
Pd@Graphene	0.3	80 (MWI)	10	100	108000	[39]
Pd@Fe ₃ O ₄ -Graphene	0.3	80 (MWI)	10	100	111000	[40]
Pd@Uio-66(MW)	0.075	30	5	95	1266.7	This study

Table 3 Suzuki coupling reaction of bromobenzene with phenylboronoic acid by different catalysts



Fig. 7 Recyclability of Pd@UiO-66 for Suzuki reaction

phenylboronic acid under the optimized reaction conditions were used for reusability experiments. As can be seen from Fig. 7, after being recycled for five successive runs, although the catalyst still exhibits good activity, but the yields of the product decreased slightly. In order to research the deactivation mechanism of the catalyst, TEM, XPS, XRD, and BET analysis were provided for the reused catalyst. As shown in the XPS (Fig. 5c, d), no changes in the oxidation states of Pd can be observed in the recycled catalyst. In the TEM images (Fig. 2c, d), the size of Pd nanoparticles in the reused catalyst increased and has a certain degree aggregation. The surface area of the resued catalyst decreased from 638.6 to 560.6 m²/g. The XRD characteristic peaks intensity of the reused Pd@UiO-66 decreased (Fig. 4), which could be ascribed to the partial destruction of the structure of UiO-66.

4 Conclusions

In conclusion, Pd@UiO-66 was successfully fabricated by a microwave-assisted method and which exhibited high catalytic activity for the Suzuki–Miyaura reactions at mild conditions. The catalyst can be recycled and reused easily without significant loss of its catalytic activity. The present study might highlight the development of high performance heterogeneous catalysts by using microwave-assisted method.

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