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Preparation anchored Pd nanoparticles on glyoxal modified metal- organic framework for Sonogashira coupling reactions

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Abstract

UIO-66-NH₂-Gl@Pd nanocatalyst was successfully synthesized during post-synthetic modification (PSM) method and its application was investigated in the Sonogashira coupling reactions. Initially, UIO-66-NH₂ was synthesized and identified. This metal organic framework (MOF) was modified with glyoxal, then, palladium nanoparticles (NPs) were supported on the modified framework through PSM. This nanocatalyst was identified via Fourier-transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (¹HNMR) spectroscopy, N₂ gas adsorption-desorption, thermo gravimetric analyses (TGA), energy dispersive X-ray mapping spectroscopy (EDX-MAP), field emission scanning electron microscopy (FE-SEM), and X-ray diffraction (XRD). ¹HNMR analysis showed that around 30 % of the amine functional groups of nanoporous UIO-66-NH₂ were modified with glyoxal. The formation of Pd NPs supported on MOF was confirmed by transmission electron microscopy (TEM) and EDX-MAP. As well, according to the inductive couple plasma atomic emission spectroscopy (ICP), around 2.98 w% of Pd NPs was present in the modified MOF. Eventually, the nanocatalyst provided the excellent catalytic activity in the Sonogashira coupling reaction. Also, the nanocatalyst has the capability to be easily recycled up to 4 times, while its catalytic activity was maintained during the activity.

Keywords: Metal-organic frameworks; Nanocatalyst; UIO-66-NH₂; Post-synthetic modification; Sonogashira coupling

1. Introduction

Metal-organic frameworks (MOFs) are a new class of porous materials, which are formed from metal ions or metal clusters as nodes and organic ligands as linkers [1]. MOFs have received much attention because of their special properties such as ultrahigh porosity, tunable cavity sizes, various topologies and high surface area as well as the possibility of functionalization with different modifier [2-4]. MOFs have been studied for the various applications, including gas storage [5-7], separation [8, 9], catalysis [10, 11], and drug delivery [12-14]. In recent years, numerous studies have also been focused on investigation of MOFs as active heterogeneous catalysts in a variety of reactions such as alkene oxidation [15-17], aldol condensations [18], hydrogenation [19], epoxide ring opening [20], the Knoevenagel condensation reaction [21], acetalization [22] and isomerization [23]. An attractive feature of MOFs is the possibility of post-synthetic modification (PSM) [24]. PSM can be performed via modification of metallic nodes and/or organic ligands by active functional groups, without displeasing influences on the MOFs stableness [25]. PSM is particularly attractive for production of catalyst materials. There are many reports for the catalytic properties of MOFs prepared using PSM strategy. For instance, Alinezhad et.al reported anchoring of Ni onto surface of MOFs through post-synthesis modification for cross coupling reaction [26]. In the other research, Zhang et.al prepared Ru/UiO-66 catalyst for the reduction of nitroarenes, alcohol oxidation and Knoevenagel condensation [27]. Luan et.al also prepared UIO-66-Sal-CuCl₂ catalyst and considered its application in the selective aerobic oxidation of alcohols [28]. The palladium catalyzed cross coupling reactions is one of the most powerful tools in organic synthesis. The Sonogashira coupling reaction between sp²-hybridized carbon atoms of aryl and vinyl halides with sphybridized carbon atoms of terminal acetylenes has been developed for synthesizing conjugated alkynes. These alkynes are important class of compounds that can be found in wide range of natural products and other bioactive materials [29, 30].

Although homogenous palladium catalysts have remarkable properties such as high activity and selectivity, they inherently suffer from difficulty of reusing and separation from the products

[31]. For instance, Pd-phosphan complex that has been frequently used under homogeneous condition is unstable during reactions losing its high activity as catalyst. Because palladium nanoparticles (NPs) as heterogeneous catalyst commonly lose their catalytic activity under aggregation, they are not economical [32-35]. It is obvious from the given cases that the development of a new catalytic system based on the benefits of both systems of homogeneous and heterogeneous is a significant issue in the novel catalyst researches.

MOFs are suitable support for catalytic reagents. Anchoring Pd NPs to modified MOF can be adjusted to prevent their aggregation. In addition to their high activity, they will have the capability of easy separation. One of the significant features of MOFs is their thermal and chemical stability. Due to the high chemical and thermal stability of UIO-66-NH₂, it remains unchanged during PSM. Some researchers synthesized and identified UiO-66-NH₂ and offered special property through a PSM procedure [36]. UiO-66-NH₂ is made of $[Zr_6O_4 (OH)_4 (CO_2)_{12}]$ clusters linked with 2-aminoterephthalic acid [37]. Moreover, UiO-66-NH₂ has high porosity [23] and the amine groups on MOF can react with other functional groups to obtain appropriate chelating ligands.

Due to exceptional thermal, chemical, and mechanical stability as well as large specific surface of UIO-66-NH₂ area, in this project, nonporous MOF was prepared using organic ligand of 2-amino-1, 4-benzenedicarboxilic acid (NH₂-BDC) and zirconium (IV) chloride. Then, during the process of PSM, MOF was modified by glyoxal due to the formation of N, N-chelating ligand which is suitable for is coordination of the metal ions. Then Pd (II) ions were anchored onto the surface of modified nanoporous UIO-66-NH₂ and then reduced Pd⁰ NPs. Finally, we studied the application of the catalyst in coupling reactions for synthesis of organic materials.

2. Experimental

2.1. Materials

Zirconium (IV) chloride, 2-aminoterephthalicacid, palladium (II) chloride (PdCl₂), glyoxal, aryl halides derivatives and terminal acetylenes and solvents as N, N-dimethyl formamide (DMF), dichloromethane (DCM), hexane and methanol were purchased from Sigma-Aldrich and used without further purification.

2.2. Analysis methods

X-ray diffraction (XRD) was performed by a BRUKER D8-Focus Bragg–Brentano X-ray powder diffractometer supplied with a Cu sealed tube ($\lambda = 1.54178$ nm) at 40 kV and 40 mA. Thermo gravimetric analyses (TGA) were performed using a TGA-STA504 (BAHR). Fourier transform infrared (FTIR) spectroscopy was conducted on a TENSOR BRUKER 27 spectrometer. ¹H NMR spectra were measured on a BRUKER ULTRASHIELD 400 AVANCE III NMR (400 MHz) spectrometer. The surface area, pore volume and pore size distribution of the support and the catalyst were determined by N₂ adsorption–desorption using BELSORP mini II instrument. Morphologies and structures of the obtained products were characterized on a MIRA 3, TESCAN field emission-scanning electron microscope (FE-SEM). Transmission electron microscopy (TEM) was carried out on a JEOL Tecnai-G². The actual loading of Pd NPs was determined by inductively coupled plasma - optical emission spectrometry (ICP- OES) analysis on the SPECTRO ARCOS, GERMANY.

2.3. Synthesis of UIO-66-NH₂

The UIO-66-NH₂ crystals were constructed based on the literature approach [38]. Zirconium (IV) chloride (ZrCl₄) (0.54 mmol, 0.126 g) was added to a mixture of DMF (5 mL) and HCl (37%, 1 mL), and then dispersed with ultrasound for 15 minutes until ZrCl₄ was entirely dissolved. Another mixture of 2-aminoterephthalic acid (NH₂-H₂BDC) (0.75 mmol, 0.136 g) and DMF (10 mL) was also dispersed with ultrasound for 15 minutes, and then two mixtures were dispersed again for further 10 min. The final mixture was heated at 80 °C for 24 h. After naturally cooling to room temperature, the solid crystal powder was washed with fresh DMF for thrice. The solid powder was soaked in water (15 mL) for 1 day. After, it was soaked in methanol (3×15 mL) for 3×24 hours. Eventually, it was activated at 100 °C under vacuum. FTIR (KBr, cm⁻¹): 3550, 3350 (br, v _{asym NH2}, v _{sym NH2}), 1570 (v _{asym COO}), 1504 and 1432 (v _{C=C}), 1385 (v _{sym COO}), 1256 (v _{C-N (aromatic)}), 964, 769, 666. ¹H NMR analysis: ¹H NMR (400 MHz, NaOD- D₂O) δ 7.62 (1 H, d), 7.135 (0.96 H, s), 7.568 (1 H, d) ppm.

2.4. Synthesis of UIO-66-NH₂-Gl

Freshly prepared UIO-66-NH₂ (100 mg) was dispersed in 10 mL of CH₃CN under ultrasonic irradiation. To this suspension to 0.75 equiv. of glyoxal (110 mg, 40% w/w aq. solution) was added drop by drop and mixture was stirred at room temperature for 24 hours. Then solution was

decanted and the crystals were washed with CH₃CN (3×5 mL) by centrifuging and dried in vacuum at 70 °C. FTIR (KBr, cm⁻¹): 3450 (br, v_{NH2}), 1625 ($v_{C=N}$), 1570 ($v_{C=O}$), 1505 and 1425 ($v_{C=C}$), 1383 ($v_{sym \ COO}$), 1270 ($v_{C-N \ (aromatic)}$), 968, 765, 670. ¹H NMR analysis: ¹H NMR (400 MHz, NaOD- D₂O) δ 7.59 (0.61 H, d), 7. 53 (2.13 H, d), 7. 10 (1.80 H, s), 7.02 (2.17 H, d), 6. 96 (0.61 H, d), 6.87 (0.57 H, s) ppm.

2.5. Synthesis of UIO-66-NH₂-Gl@Pd

To prepare UIO-66-NH₂-Gl@Pd, 0.1 g of vacuum-dried UIO-66-NH₂-Gl was firstly dispersed in 10 mL DCM at room temperature. To this suspension, PdCl₂ (10 mg) was added and the mixture was stirred at room temperature for 20 h. Then, by the addition of NaBH₄ (10 mL, 0.04 M), the Pd (II) was rapidly reduced to Pd and the resulting mixture was stirred for 3 h. The product was obtained by centrifuging, washed with methanol (3×10 mL) and dried in vacuum to obtain green-gray powder product. FTIR (KBr, cm⁻¹): 3391 (br, v_{NH2}), 1620 ($v_{C=N}$), 1566 ($v_{C=O}$)

2.6. Sonogashira coupling reactions

A mixture of aryl halide (1 mmol), terminal alkynes (1.2 mmol), K_2CO_3 (652 mg, 2.0 mmol) and UIO-66-NH₂-Gl@Pd NPs (15 mg, 0.05 mol %) in H₂O: EtOH (1:1, *v*: *v*) was stirred under reflux. The progress of the reaction was checked by thin-layer chromatography (TLC). At the end of the reaction, the mixture was cooled gradually to environmental temperature. Then ethyl acetate (15 mL) was added, and the organic phase was separated. The mixture was purified by column chromatography over deactivated silica gel using pure n-hexane as eluent to furnish a crude product. Products were simply detected by ¹H and ¹³C NMR.

3. Results and discussion

3.1. PSM of UIO-66-NH₂

UIO-66-NH₂ is a nanoporous MOF which its organic ligands is adorned with pendant amine $(-NH_2)$ groups. The available NH₂ groups, not all of them, were modified with glyoxal by PSM through a simple imine condensation reaction. By modifying the UIO-66-NH₂ with glyoxal, suitable sites were created to support Pd NPs. The post- synthetic functionalization route for UIO-66-NH₂ preparation is shown in scheme 1.



Scheme 1. PSM procedure for UIO-66-NH₂

3.2. Spectroscopic studies

The FTIR spectra of UiO-66-NH₂, UIO-66-NH₂-Gl and UIO-66-NH₂-Gl@Pd are shown in Fig.1. In the UiO-66-NH₂ spectrum, the appearance of absorption band at 3550, 3350 and 1257 cm⁻¹ indicate the existence of the asymmetric and symmetric N–H stretching vibrations and C–N stretching vibration of aromatic amines. Furthermore, the absorption peaks at 1570 and 1385 cm⁻¹ are correlated to the asymmetric and symmetric O-C-O stretching vibrations and peaks at 1504 and 1435 cm⁻¹ are corresponded to C=C group of the terephthalate linker. In the FTIR spectra of UiO-66-NH₂-Gl, the absorption peak at 1625 cm⁻¹ is due to the formation of azomethine group (C=N). In the FTIR spectrum of UiO-66-NH₂-Gl@Pd, the change in absorption peaks of the azomethine group to lower frequencies and lack of clearness of its peak confirms connection of the Pd NPs to azomethine nitrogen.

Fig. 1

The ¹HNMR spectra upon digestion of the UiO-66-NH₂ and UiO-66-Gl in NaOD and D₂O show the successful modification of a few amines groups in the UIO-66-NH₂ (Fig. 2). The ¹H NMR spectrum of UIO-66-NH₂ shows three resonance signals at 7.062, 7.135, and 7.568 ppm. These peaks are ascribed to the 2-amino-1, 4-benzenedicarboxilic acid ligand. In the ¹H NMR spectrum of UIO-66-NH₂-Gl, in addition to the existing previous signals, several new signals (at 7.59, 6.96, and 6.87 ppm, corresponding to imine and aromatic ring CH protons) appear which can describe the successful modification of approximately 30% of the NH₂ functional groups in the UIO-66-NH₂.

Fig. 2

3.3. XRD studies

UiO-66-NH₂, UiO-66-NH₂-Gl and the UiO-66-NH₂-Gl@Pd nanocatalyst were characterized by XRD analysis (Fig. 3). The main diffraction peaks of UiO-66-NH₂ appear at $2\theta = 7.73$, 8.88 and 26.04° which are in accordance to the previous articles [39]. As can be seen, the characteristic peaks do not show any shift after modification with glyoxal and loading of Pd NPs, which means the lattice structure of UiO-66-NH₂ was well preserved. However the peak strength is obviously weakened due to the interaction between MOF and Pd NPs.

Fig. 3

3.4. Morphological characterization

FESSEM images of UIO-66-NH₂ and UIO-66-NH₂-Gl nanoporous sample at different magnifications show that the nanoparticles are aggregated together and have an irregular shape (Fig. 4a, b, c, d). The images reveal that the average diameter is less than 100 nm. It seems that after modification of UIO-66-NH₂, the morphology of sample is somewhat reserved. TEM images indicate the nanoparticles distribution in the form of small black spots on the surface of UIO-66-NH₂-Gl. As well, no obvious aggregation was observed (Fig. 4e, f and g). Additionally, the size distribution of Pd NPs was determined based on TEM images so the average size is about 10 nm (Fig. 4f).

Fig. 4

3.5. Elemental analysis

Fig. 5 describes the elemental analysis of the UiO-66-NH₂-Gl and UiO-66-NH₂-Gl@Pd obtained using EDX and elemental mapping. From the elements listed for UiO-66-NH₂-Gl@Pd, the corresponding EDX analysis confirm the presence of elements C, O, Cl and, Zr in the UiO-66-

NH₂-Gl and as well as the presence of Pd in UiO-66-NH₂-Gl@Pd as shown in EDX. Also, from mapping analysis, the distribution of elements is relatively homogeneous.

Fig. 5

The existence of Pd NPs in the synthesized UIO-66-NH₂-Gl@Pd was also checked using ICP analysis, and the amount of Pd in the catalyst was measured about 2.98 wt. %.

3.6. N₂ adsorption/desorption characterization

The specific surface area and porosity of UIO-66-NH₂ and its modified samples were obtained using Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively (Fig. 6). According to the results indicated in Table 1, the BET surface area and micropore volume of UiO-66-NH₂ were calculated to be 1124 m^2g^{-1} and 0.479 cm^2g^{-1} , respectively, which is almost according to the previous reports. From comparing the results of surface area between UIO-66-NH₂, UiO-66-NH₂-Gl and UiO-66-NH₂-Gl-Pd to 863 and 524 m^2g^{-1} , respectively, which is due to increasing in the extra volume of Gl groups and Pd NPs to MOF and/or partial destruction of the MOF structure via modifications in harsh conditions which confirms the modification of UIO-66-NH₂.

Fig. 6

3.7. Thermal measurements

Thermogravimetric method was used to survey the thermal stability of MOFs. According to the TGA curves (Fig. 7), weight losses take place in a few steps. The first step weight loss of the UIO-66-NH₂ in ~ 100 °C relates to the removal of water molecules from pores. The next step of weight loss in around 225 °C is assigned to the removal of remaining DMF molecules from the framework cavities. At the end, the final weight loss starts at 490 °C and continues to 585 °C which relates to the decomposition of organic structure and the collapse of the framework. The same weight-loss profile is observed for UIO-66-NH₂-Gl and UIO-66-NH₂-Gl@Pd but with higher disintegration temperature. It is due to the presence of grafted glyoxal onto the framework.

Fig. 7

3.8. Catalytic activity studies

UIO-66-NH₂-Gl@Pd was considered as nanocatalyst for the Sonogashira coupling reaction. The reaction conditions were optimized using the model reaction of phenyl acetylene with iodobenzene in the presence of factors such as solvent, base types, temperature and the amount of catalyst. Primarily, this reaction was tested in various single and mixed solvents (entries 1-4) and then, different bases such as K_2CO_3 , KOH, NEt₃, and pyridine (entries 3, 5-7) were examined. The amount of catalyst and the temperature of reaction were also optimized (entries 2, 8-11) and the best results were obtained with 15 mg of the catalyst in the mixture of solvents H_2O /ethanol and K_2CO_3 at temperature 70°C (Table 2).

In the Sonogashira coupling reaction, the catalytic activities of UIO-66-NH₂-Gl@Pd nanocatalyst for different aryl halides and terminal acetylenes were investigated at 70 °C in air using suitable mixed solvents (H₂O/ Ethanol) and base (K₂CO₃). The results are shown in Table 3. The comparison of the percentage of products (Table 3, entries 1-10) shows that the reactivity as following order: iodobenze > bromobenzene > cholorobenzene in the coupling reactions. Finally, in the reactions between terminal acetylene and aryl halides, the reactivity of aryl halides with electron-withdrawing and electron-donating substituents was studied. The aryl halides with electron- poor substituents, such as $-NO_2$, (Table 3, entries 4, 6 and 10) exhibited a higher activity, while that with electron- rich groups, such as -Me (Table 3, entries 3, 5, 8 and 11) and - OMe (Table 3, entries 2 and 9), exhibited slightly less activity. It was also seen that much less-reactive aryl chloride (Table 3, entry 7) give corresponding coupling products with 30% yield. The percentage of products related to phenylacetylene is higher than that of terminal acetylene aliphatic.

3.9. Catalyst reusability

An important in the case of porous solid catalysts is the reusability. According to this point, UIO-66-NH₂-Gl@Pd nanocatalyst was investigated for the recoverability and reusability in the Sonogashira coupling reaction among terminal acetylene and aryl halides. At the end of the

reactions, catalyst was isolated by centrifuging and washed with ethylacetate (2- 4 mL). Then it was dried at 60 °C for 12 h in vacuum condition. The recovered UIO-66-NH₂-Gl@Pd could be reused directly for the further reactions. Catalytic activity was retained after 4 times recovery and reuse nearly. (Table 4).

The Pd leaching from UIO-66-NH₂-Gl@Pd nanocatalyst into reaction solution was investigated by ICP analysis. The results show the heterogeneity of catalytic processes and partial leaching of Pd from the catalyst. The results also confirmed the high stability, strong attachment of Pd NPs onto the modified MOF. The ICP analyses on the catalyst before the reaction and after the fourth run showed the presence of 2.98 and 2.49 wt. % Pd in the catalyst, respectively. Therefore, it can be concluded that the amount of Pd leaching was partial. The XRD pattern and TEM images of the recycled catalyst are shown in Fig. 3 and Fig. 8, respectively. A comparison between the TEM images of the catalyst before and after four runs indicates the presence of Pd NPs on the surface of the recycled catalyst.

Table 5 shows the merit of this catalytic method, and the performance of UIO-66-NH₂-Gl@Pd in the Sonogashira coupling reactions between iodobenzene and phenylacetylene is compared with some other catalysts. The catalysts with higher TOF are generally more active and efficient in shorter reaction times and low amount of them are enough to complete the reaction. Although the number of recycled UIO-66-NH₂-Gl@Pd nanocatalysts is lower than other catalysts, a prominent issue that makes this nanocatalyst has better performance than the other catalysts, is higher activity of the catalyst in term of TOF. The other highlights of UIO-66-NH₂-Gl@Pd nanocatalysts are: a) facile synthesis of catalyst, b) higher catalytic activity with lower Pd content (0.05 mol %), c) wide substrate scope, d) heterogeneous nature, and e) reusability.

The mechanism pathways for the Sonogashira coupling reaction using UiO-66-NH₂-Gl@Pd nanocatalyst are shown in scheme 2. Oxidative addition of arylhalides to Pd generates intermediate Pd (II) species (a). Intermediate (b) causes the subsequent transmetalation of an alkynyle from palladium to palladium, followed by reductive elimination from intermediate (c) to afford unsymmetrical acetylene.



Scheme 2. A plausible mechanism for the Sonogashira coupling reaction using UiO-66-NH₂-Gl@Pd nanocatalyst

Conclusion

In this work, the efficient UIO-66-NH₂-GI@Pd nanocatalyst was successively synthesized by glyoxal condensing to UIO-66-NH₂, and introducing Pd NPs onto the modified MOF during the PSM process. The nanocatalyst was characterized by FTIR, NMR, ICP, XRD, SEM, TEM, TGA, BET and EDX-MAP techniques. UIO-66-NH₂-Gl@Pd nanocatalyst was used for the carbon-carbon bond formation by the Sonogashira coupling reaction. The performance of nanocatalyst in catalyzing the reaction of terminal acetylenes and aryl halides is efficient. Mild conditions operation, good tolerance for air and moisture, high activity due to high surface area and porosity are some of the assets that can be highlighted for UIO-66-NH₂-Gl@Pd nanocatalyst. Along with these advantages, using low amount of the nanocatalyst for the 4th cycle make the nanocatalyst as candidate for efficient Sonogashira reactions.

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	UiO-66-NH ₂	UiO-66-NH ₂ -Gl	UiO-66-NH ₂ -Gl@Pd
BET specific surface area (m ² g ⁻¹)	1124	863	524
BJH average pore volume (cm ² g ⁻¹)	0.479	0.382	0.246

Table 1. Surface area and porosity of the UIO-66-NH2, UiO-66-NH2-Gl, and UiO-66-NH2-Gl@Pd

Table 2. Optimization of reaction conditions for the Sonogashira coupling reaction between phenyl acetylene and iodobenzene using UiO-66-NH₂-Gl@Pd as catalyst



Entry	Solvent	Base	Catalyst amount (mol %)	Temperature °C	Yield %
1	H ₂ O	K ₂ CO ₃	0.05	70	65
2	Ethanol	K ₂ CO ₃	0.05	70	60
3	H ₂ O/ Ethanol	K ₂ CO ₃	0.05	70	95
4	Hexane	K ₂ CO ₃	0.05	70	40
5	H ₂ O/ Ethanol	КОН	0.05	70	75
6	H ₂ O/ Ethanol	NEt ₃	0.05	70	75
7	H ₂ O/ Ethanol	Pyridine	0.05	70	70
8	H ₂ O/ Ethanol	K ₂ CO ₃	0.03	70	60
9	H ₂ O/ Ethanol	K ₂ CO ₃	0.1	70	95
10	H ₂ O/ Ethanol	K ₂ CO ₃	None	70	-
11	H ₂ O/ Ethanol	K ₂ CO ₃	0.05	r.t	20

General reaction conditions: phenyl acetylene (1.2 mmol) and iodo benzene (1 mmol) were mixed together with bases (2 mmol) and catalyst in various amounts in 1 mL solvent under atmosphere. (Reaction time was 0.5 h)

Table 3. C-C cross coupling reaction of aryl halides with terminal acetylene.^a

$$R^{1} \longrightarrow H + \bigvee_{R^{2}}^{X} \xrightarrow{UiO-66-NH_{2}-GI@Pd} R^{1} \longrightarrow R^{2}$$

Entry	R ¹	R ²	X	Product	Time (h)	Yield (%) ^b	TON	TOF (h ⁻¹)
1	Ph	Н	Ι	Ph-=	0.5	95	1900	3800
2	Ph	OCH ₃	Ι		2	87	1740	870
3	Ph	CH ₃	Ι	PhCH3	2	87	1740	870
4	Ph	NO ₂	I	Ph	0.5	97	1940	3880
5	Ph	CH ₃	Br	PhCH3	3	80	1600	533.3
6	Ph	NO ₂	Br	Ph	2	87	1740	870
7	Ph	СНО	Cl	РһСно	3	30	600	200
8	CH ₃ -(CH ₂) ₅ -	CH ₃	Ι	C ₆ H ₁₃	4	80	1600	400

9	CH ₃ -(CH ₂) ₅ -	OCH ₃	Ι	C ₆ H ₁₃	5	80	1600	320
10	CH ₃ -(CH ₂) ₅ -	NO ₂	Br	C ₆ H ₁₃	5	75	1500	300
11	CH ₃ -(CH ₂) ₅ -	CH ₃	Br	C ₆ H ₁₃	5	70	1400	280

^a Reaction conditions: Aryl iodids (1 mmol), terminal acetylenes (1.2 mmol), K₂CO₃ (2 mmol), UIO-66-NH₂-Gl@Pd nano catalyst (0.015 g, 0.05 mol%) were mixed in H₂O/EtOH (1 mL) at 70 °C. ^b Isolated yield.

Table 4. Re	ecyclability	study of	UIO-66-NH ₂ -	Gl@Pd	nano catalyst	a
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Run	1	2	3	4
Time (h)	0.5	1.5	3	3
Yields (%) ^b	95	92 ^c	90°	90°

^a UIO-66-NH₂-Gl@Pd (0.015 g, 0.05 mol%), phenyl acetylene (1.2 mmol), iodobenzene (1mmol), K₂CO₃ (2 mmol) and H₂O/EtOH (1 mL) at 70 °C were stirred under air.

^b Isolated yield.

^c Recovered and used

Table 5. Catalytic activity of UIO-66-NH₂-Gl@Pd in comparison to some reported catalysts in the Sonogashira coupling reaction between iodobenzene and phenylacetylene.

Entry	Catalyst	Conditions	Time	Yield	TOF	reuses	Ref.
			(h)	(%)			
1	PS-Pd(II)-furfural (1 mol%)	Et_3N , DMF, 90 °C	8	100	12.5	5	[40]
2	PdCo NPs/ 3DG (4 mol %)	H ₂ O (3mL), 80 °C	8	94	2.93	7	[41]
3	PdCu@GQD@Fe ₃ O ₄ (Pd 0.3	DABCO, Toluene or	24	99	13.75	10	[42]
	mol %, Cu 0.35 mol %)	DMA, 60 °C					
4	CS-MMT/Pd (0.3 mol %)	DMSO/CH ₃ COOK,	5	94	62.66	4	[43]
		110 °C					
5	Pd–Au/C [2 mol%]	K ₃ PO ₄ , iPrOH/H ₂ O,	20	73	1.82	5	[44]

		80 °C					
6	Fe ₃ O ₄ @SiO ₂ @Pd (II)-Slp.	H ₂ O/DMF [2/1],	1	96	480	8	[45]
	Comp. (0.2 mol %)	K ₂ CO ₃ ,90 °C					
7	pramipexole– MWCNTs/Pd (0.1 mol %)	DMF, ET_3N , 96 °C	2	96	480	6	[46]
8	NHC- Palladium complex (1 mol %)	DMSO, K_3PO_4 , 100 °C	1	81	81	4	[47]
9	Nano Pd@Fe ₃ O ₄ (1 mol %)	DMF, Piperidine, 110°C	24	83	3.46	6	[48]
10	SiO ₂ @Fe ₃ O ₄ -Pd (1 mol %)	DMF, K ₂ CO ₃ , 100°C	6	95	15.83	8	[49]
11	UiO-66-NH2-Gl@Pd (0.05	H ₂ O, Ethanole, 70 °C	0.5	95	3800	4	This
	mol %)						work
12	UiO-66-NH ₂	H ₂ O, Ethanole, 70 °C	8	30	-	-	This
							work

Figure captions

Figure 1. FTIR spectra of UIO-66-NH₂, UIO-66-NH₂-Gl and UIO-66-NH₂-Gl@Pd

Figure 2. ¹H NMR spectra of digested UIO-66-NH₂ and UIO-66-NH₂-Gl samples using NaOD in D₂O (1 M)

Figure 3. XRD patterns of UIO -66-NH₂, UIO -66-NH₂-Gl, UIO-66-NH₂-Gl@Pd NPs and recovered UIO-66-NH₂-Gl@Pd after four times

Figure 4. FESEM of UIO-66-NH₂ (a, b), UIO-66-NH₂-Gl (c, d) and TEM of UIO-66-NH₂-Gl@Pd (e, f, g)

Figure 5. EDX spectra (inset is the EDX mapping) of the UIO-66NH₂-Gl and UIO-66-NH₂-Gl@Pd samples

Figure 6. N2 adsorption-desorption isotherm of UIO-66-NH2, UiO-66-NH2-Gl, and UiO-66-NH2-Gl@Pd

Figure 7. TGA profiles of UIO-66-NH₂, UIO-66-NH₂-Gl, and UIO-66-NH₂-Gl@Pd samples

Figure 8. TEM pictures of the recovered UIO-66-NH2-Gl@Pd nanoparticles after four reaction cycles



Fig.1. FTIR spectra of UIO-66-NH₂, UIO-66-NH₂-Gl and UIO-66-NH₂-Gl@Pd

Johngreek



Fig.2. ¹H NMR spectra of digested UIO-66-NH₂ and UIO-66-NH₂-Gl samples using NaOD in D₂O (1 M)



Fig.3. XRD patterns of UIO -66-NH₂, UIO -66-NH₂-Gl, UIO-66-NH₂-Gl@Pd NPs and recovered of UIO-66-NH₂-



Gl@Pd after four times

Fig.4. FESEM images of UIO-66-NH $_2$ (a, b), UIO-66-NH $_2$ -Gl (c, d) and TEM of UIO-66-NH $_2$ -Gl@Pd (e, f, g)

ounderegion



Fig.5. EDX mapping spectra of UIO-66NH2-Gl and UIO-66-NH2-Gl@Pd samples

Fig.6. N2 adsorption-desorption isotherms of UIO-66-NH2, UiO-66-NH2-Gl, and UiO-66-NH2-Gl@Pd



Fig.7. TGA profiles of UIO-66-NH₂, UIO-66-NH₂-Gl, and UIO-66-NH₂-Gl@Pd samples



Fig.8. TEM pictures of the recovered UIO-66-NH2-Gl@Pd nanoparticles after four reaction cycles

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Highlights

- > A strategy for development of catalyst with high performance is well-defined.
- > Metal organic frameworks is used as support.
- ▶ UIO-66-NH₂-Gl@Pd was synthesized using to PSM method.
- > UIO-66-NH₂-Gl@Pd exhibited high catalytic performance in the Sonogashira coupling reactions.

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Declaration of interests

 \boxtimes 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:

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