Received: 25 May 2018 | Revised: 8 July 2018 | Accepted: 9 July 2018
DOI: 10.1002/aoc.4539

FULL PAPER

WILEY Applied Organometallic Chemistry

Stepwise post-modification immobilization of palladium Schiff-base complex on to the OMS-Cu (BDC) metal–organic framework for Mizoroki-Heck cross-coupling reaction

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Palladium ions were successfully immobilized within the pores of open metal site (OMS) metal organic frameworks (MOFs) with Schiff-base (2-Py-SI) grafted in OMS-Cu (BDC) using the hydrothermal method. This Schiff-base complex on the Cu (BDC) greatly increased catalytic activity and acted as an efficient stabilizer of Pd ions. The hydrothermal method was a more efficient method for generating small metal ions in the MOF structures. The results revealed that the Pd^{II}@Cu (BDC)/2-Py-SI is a promising catalyst for the Mizoroki-Heck coupling reaction. The proposed catalyst has better recyclability and can be reused several times without apparent loss of activity.

KEYWORDS
metal organic frameworks, Mizoroki-Heck reaction, open metal site MOF, Pd^{II}@Cu (BDC)/2-Py-SI

1 | INTRODUCTION

Hybrid porous coordination polymers as metal organic frameworks (MOFs) have emerged as an important class of nanoporous solid material owing to their high porosity, surface area and tenability.[1] Compared with conventionally used micro−/meso-porous inorganic metal oxides, MOFs have the potential for flexible rational and functionalization of the pores.[2] MOFs are also the ideal platform for post-synthetic modification chemistry to achieve multi-purpose materials. A wide range of metal groups can be incorporated into the ligand structure or post-synthetically constructed in the pores of the MOF.[3] Among them, MOFs with open metal sites (OMS-MOFs) are promising candidates for adsorption/storage, separation gases and catalysis purposes.[2]

In recent years, application of MOFs as heterogeneous catalysts has attracted interest, especially in the use of OMS-MOFs as scaffolds for the grafting of metal (Pd, Au, Pt and Ru) nanoparticles.[4] Indeed, metal@MOFs have been used as catalysts in diverse reactions, such as cross-coupling,[5] C-H activation[6] and nitro reduction.[7] The treatment of MOFs supports after metal loading with reducing agents such as $NaBH_4$ and $LiAlH_4$ has been avoided in order to maintain the framework rigidity and crystallinity of the support. Also, utilization of these nanoparticles@MOFs as catalysts to be performed in acidic–basic aqueous medium has been avoided.[8]

The Mizoroki-Heck cross-coupling reaction is one of the most commonly employed transformations for C-C bond formation in modern organic synthesis[9] and, because of the availability of reagents and the broad functional group tolerance of this transformation, it has found extensive use in synthetic organic chemistry.[10] Several Pd supports on MOFs are currently reported for the catalysis of the Mizoroki-Heck cross-coupling reaction.[11–14] A number of solid materials as supports have broadly been investigated for the immobilization of palladium, such as carbon nanotube,[15] carbon nanofibers,[16] *N*-doped carbon,[17] grapheme,[18] PMO,[19] MCM-41,[20] SBA-15,[21] magnetic Fe_3O_4,[22] metal oxides[23] and polymers.[14,24] Among the nanoporous and high-surface-area solid supports, MOFs can also be considered as suitable hybrid material for immobilization of Pd ions.[25]

Recently, we have reported on the catalytic application of OMS-MOFs of copper coordinated to carboxylate acids belonging to terephthalic acid (BDC = benzene 1,4-dicarboxylate) and 1,3,5-benzene tricarboxylate.[26] Herein, we have demonstrated Cu (BDC) as an efficient OMS MOF toward the direct grafting of Schiff-base [pyridyl salicylimine (2-Py-SI)] and complexation of that with Pd ions. The synthesized Pd^{II}@Cu (BDC)/2-Py-SI MOF was then applied to the Mizoroki-Heck reaction as a heterogeneous and recyclable green catalyst.

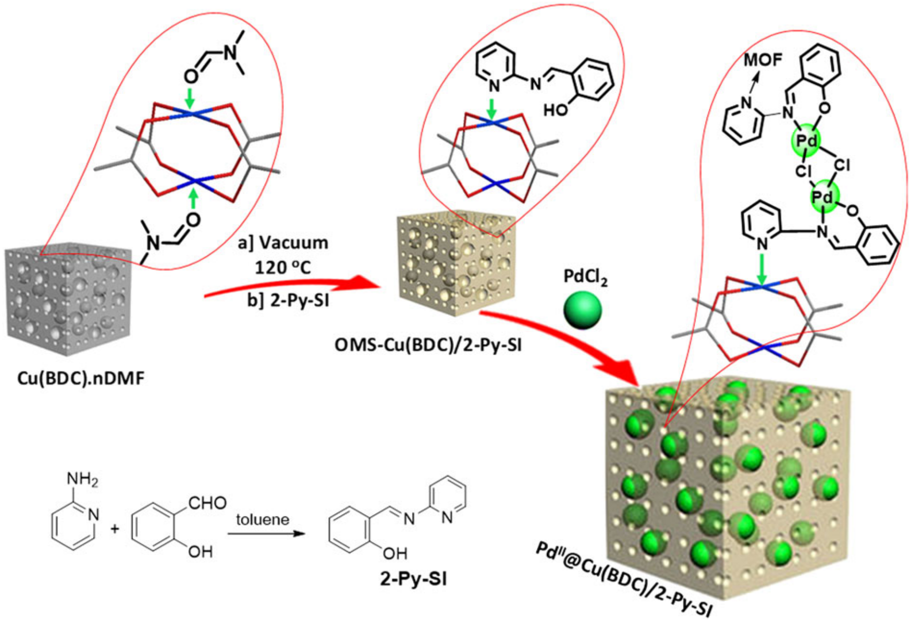
2 | RESULTS AND DISCUSSION

The structure of Cu (BDC) is constituted of a cluster of two copper (II) atoms with a paddle-wheel shape that has a square planar coordination,[27] in which the BDC linker acts as a planar ligand connecting the diatomic copper cluster that defines the nanocage.[11] Dimeric copper (II) cubic clusters of Cu (BDC) possess terminal DMF molecules, and their lability allows their replacement by other groups after vacuum treatment at 393 K, without changes in the structure. Arnanz *et al.* have recently reported synthesis of a pyridine-coordinated Cu-BTC MOF to immobilization of the Pd catalyst for the Sonoghashira/click reaction.[27] Ferey's group prepared a Pd@MIL-101 pre-catalyst for the Heck coupling reaction.[28] Herein, in our current method, the Cu (BDC)·nDMF was prepared by using copper nitrate and terephthalic acid as organic linkers in solvothermal conditions, which was then activated at 393 K under vacuum to obtain OMS Cu (BDC) solid [OMS-Cu (BDC)]. This OMS-MOF reacted with as-synthesized 2-pyridyl-salicylimine (2-Py-SI) moiety in ultra-dried toluene for coordination of 2-Py-SI Schiff-base to unsaturated metal/cluster site of activated Cu (BDC). Then, $PdCl_2$ was added to the Cu (BDC)/2-Py-SI to produce Pd^{II}@Cu (BDC)/2-Py-SI (Scheme 1).

The crystallinity and purity of as-synthesized Cu (BDC) in DMF and Pd^{II}@Cu (BDC)/2-Py-SI were checked by powder X-ray diffraction (PXRD) measurement (Figure 1). The results demonstrate that the peak positions were well matched with those of the simulated diffraction pattern.[29] A comparison of the PXRD patterns of Pd^{II}@Cu (BDC)/2-Py-SI with Cu (BDC) revealed a shift for the main peak (220) to smaller 2θ angles, although other main diffraction peaks are in agreement with the pristine Cu (BDC)·nDMF.

Figure 2 shows the Fourier-transform infrared (FT-IR) spectra of synthesized Cu (BDC)·nDMF, Cu (BDC)/2-Py-SI and Pd^{II}@Cu (BDC)/2-Py-SI. The FT-IR spectrum of the Cu (BDC)·nDMF compared with the samples after Schiff-base ligand and Pd grafting. As for Cu (BDC)·nDMF, the strong peaks at 1396 cm^{-1} symmetric and 1623 cm^{-1} asymmetric vibration correspond to carboxylate presence in the MOF.[26,27,30] The bonds at 1507 cm^{-1} and 2971 cm^{-1} are assigned to C=C in the aromatic ring of BDC, and the aliphatic C-H of coordinated DMF and C-H of aromatic rings of BDC. A new peak that appears at 3357 cm^{-1} in Cu (BDC)/2-Py-SI and Pd^{II}@Cu (BDC)/2-Py-SI shows the frequencies of the O-H group of the 2-Py-SI ligand in MOFs, and also demonstrates the grafting of the 2-Py-SI ligand onto copper (II) CUSs in the cages of the Cu (BDC). The FT-IR of Pd^{II}@Cu (BDC)/2-Py-SI demonstrate that the structure did not change considerably after attachment of the Pd (II) ions onto the Cu (BDC) pore cage.

Scanning electron microscopic (SEM) images of the Cu (BDC)·nDMF and Pd^{II}@Cu (BDC)/2-Py-SI are shown in Figure 3. The SEM images of Cu (BDC) and the modified MOFs sample with the Pd/Py-SI complex revealed the presence of cubic assembled layered microcrystals



SCHEME 1 Post-modification immobilization of Pd ions onto the OMS-Cu (BDC)

150 mm (~0.15 µm) thick (layered thickness; Figure 3c is extracted from Figure 3a by Digimizer image zooming and scale calculator). The SEM micrograph of the Pd^{II}@Cu (BDC)/2-Py-SI shows its stability of structure and even morphology after multi-step post-modifications.

Elemental EDX analysis was performed for the MOFs solids. Figure 4 shows the SEM–EDX spectra of synthesized OMS-Cu (BDC), Cu (BDC)/2-Py-SI and Pd^{II}@Cu (BDC)/2-Py-SI. Based on this analysis, copper, carbon and oxygen atoms exist in the structure of OMS-Cu (BDC), which indicate purity and perfect activation of Cu-MOF solids. C, Pd, Cl and N atoms in Pd^{II}@Cu (BDC)/2-Py-SI demonstrate that palladium ions were successfully coordinated onto the Schiff-base (2-Py-SI) decorated OMS-Cu (BDC) pore cage. The wt% of Pd in the Pd^{II}@Cu (BDC)/2-Py-SI structure was calculated using atomic absorption spectroscopy (AAS), and according to this the wt% of Pd was 0.78%.

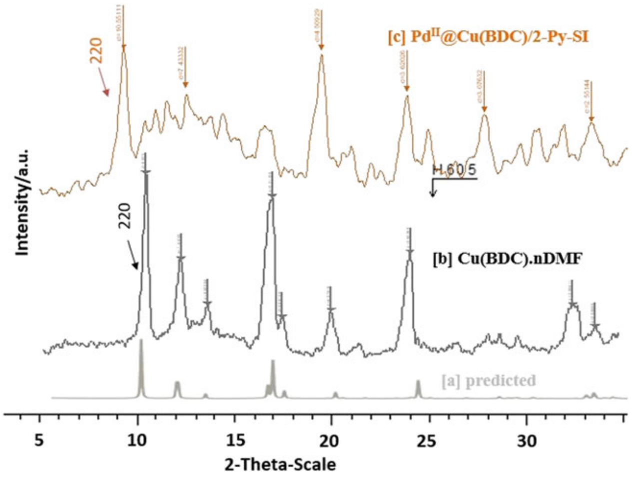


FIGURE 1 Powder X-ray diffraction (PXRD) patterns of as-synthesized Cu (BDC)·nDMF and Pd^{II}@Cu (BDC)/2-Py-SI

The thermal stability of Cu (BDC)·nDMF and Pd^{II}@Cu (BDC)/2-Py-SI was evaluated by thermogravimetric analysis (TGA). In Cu (BDC)·nDMF, the initial weight loss at 200 °C can be attributed to loss of moisture, remained coordinated DMF that continues up to 260 °C. For Pd^{II}@Cu (BDC)/2-Py-SI, a sharp decrease in weight was observed from 280 °C onward, which could be attributed to loss of loosely bound ligand. The weight loss from 260 °C to 400 °C may be due to decomposition of organic BDC linker and collapsing of MOF structure (Figure 5).

After sufficient characterization of the Pd^{II}@Cu (BDC)/2-Py-SI, the catalytic activity of this bifunctional Pd/Cu-MOF was examined for C-C coupling reaction, namely the Mizoroki-Heck reaction. The Mizoroki-Heck coupling reaction of aryl halides and alkenes was examined using different amounts of catalyst, base and solvent at a temperature range of 25–120 °C (Table 1).

To optimize the reaction conditions, when the reaction was carried out in the absence of catalyst there was no product even after 24 hr (Table 1, entry 1). The best yield and selectivity was obtained when the reaction was carried out in the presence of 0.25 mol% of catalyst in solvent DMF and bases K_2CO_3 at reflux conditions (Table 1, entry 3). In the next step, the effect of polar and nonpolar solvent, such as DMF, DMF/H_2O, MeOH, DCM and toluene, on the reaction progress was

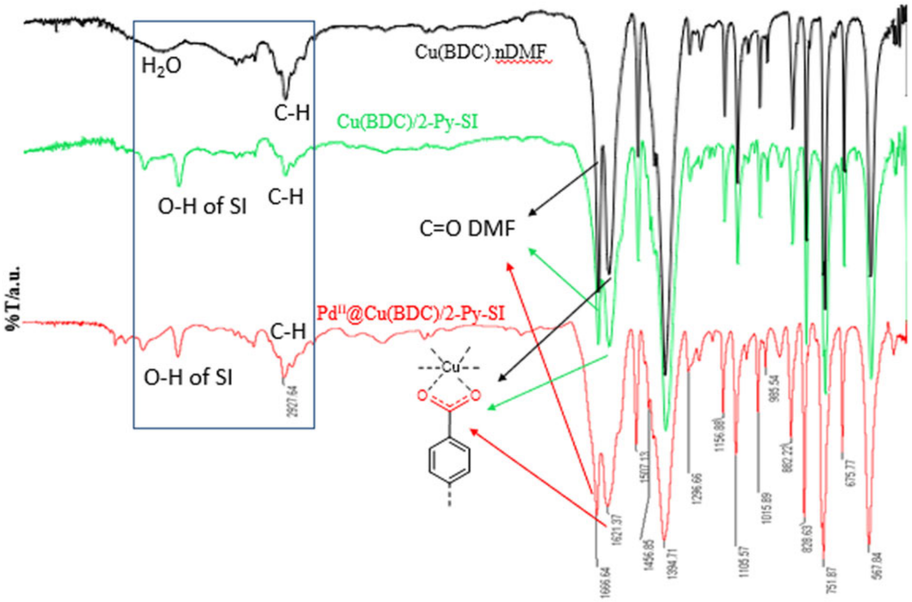


FIGURE 2 Fourier-transform infrared (FT-IR) spectrum of Cu (BDC)·nDMF (black), Cu-BDC/2-Py-SI (green) and Pd^{II}@Cu (BDC)/2-Py-SI (red)

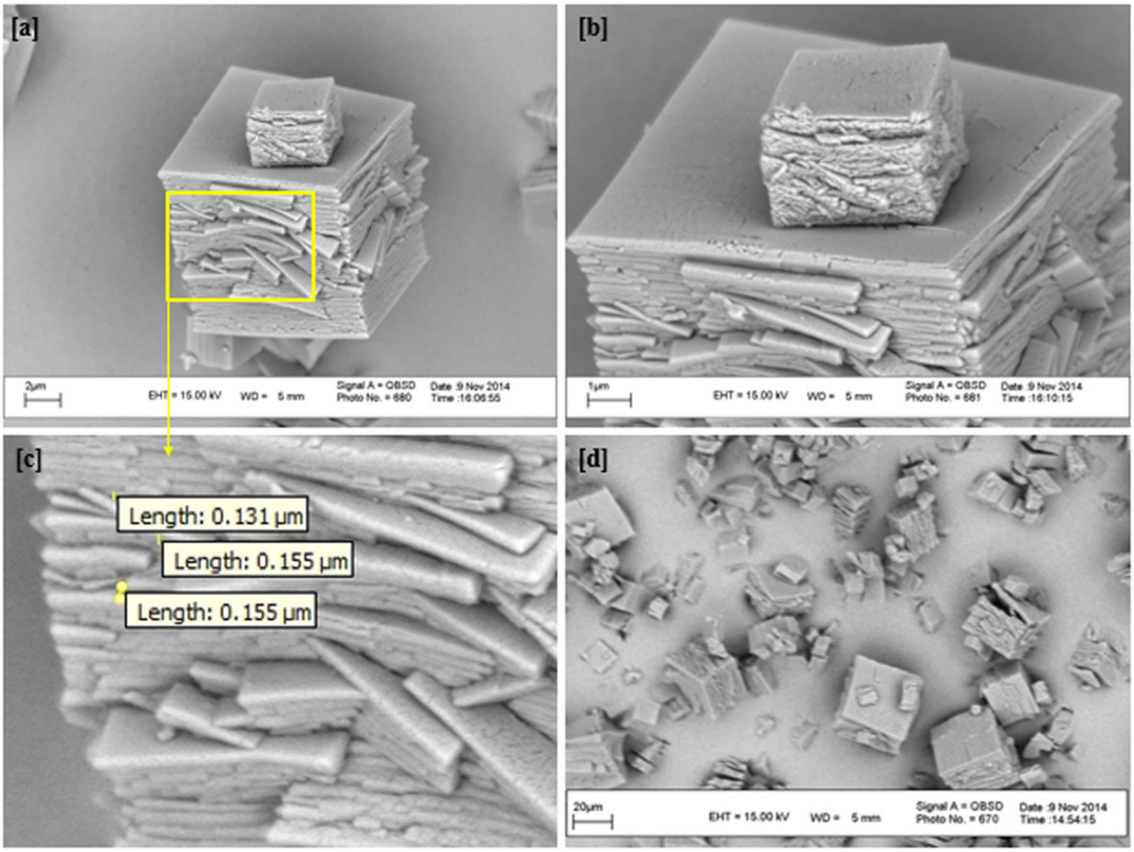


FIGURE 3 (a–c) Scanning electron microscopy (SEM) images of Cu (BDC)·nDMF, and (d) Pd^{II}@Cu (BDC)/2-Py-SI

also monitored (Table 1, entries 3, 5–9). The best results were obtained in solvent DMF. We then investigated the effects of the base on the progress reaction in the optimized condition. Different bases, including NaOAc, Na_2CO_3, Et_3N, KOH and K_2CO_3, were studied on the reaction progress, among them K_2CO_3 was suitable from the viewpoint of yield and selectivity (Table 1, entries 3, 10–13).

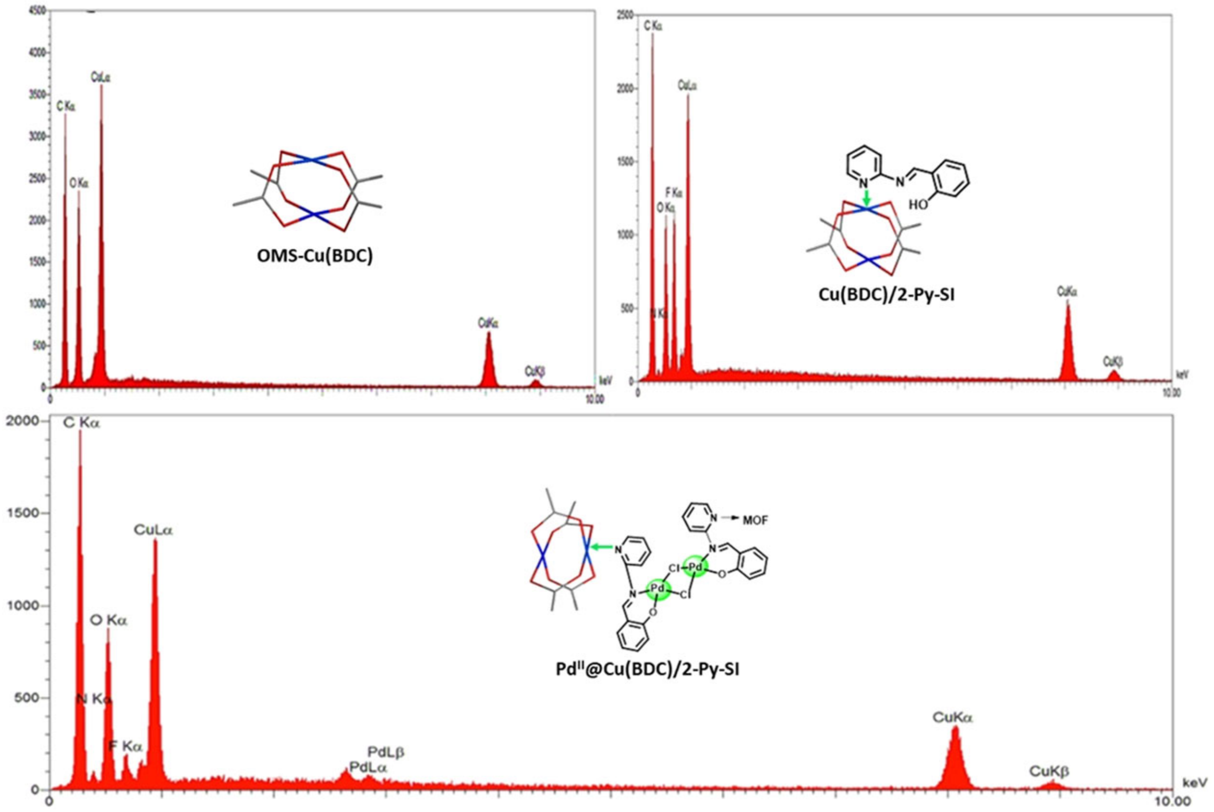


FIGURE 4 EDAX image of OMS-Cu (BDC), Cu (BDC)/2-Py-SI and Pd^{II}@Cu (BDC)/2-Py-SI

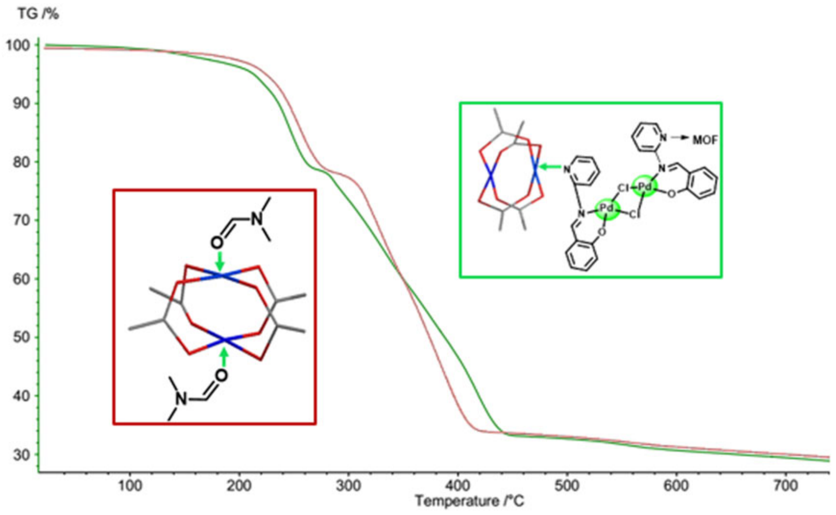
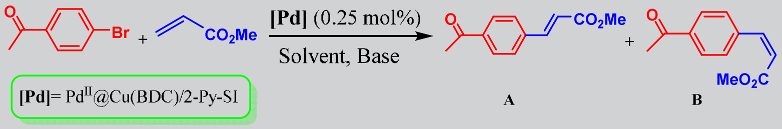


FIGURE 5 Thermogravimetric analysis (TGA) of Cu (BDC)·nDMF (brown) and Pd^{II}@Cu (BDC)/2-Py-SI (green)

After examination of various conditions on the reaction progress, we explored the general applicability of the catalyst with aryl halides and alkenes containing electron-withdrawing or -donating substituents, and the results are presented in Table 2. Indeed, aryl iodides compared with aryl bromides show a high activity and short reaction time in the Heck coupling reaction. As shown in Table 2, all the derivatives, electron withdrawing or donating, were in good to excellent yields. This may be due to the higher activity of the catalyst the reaction progress of each derivative.

A comparison of the efficiency and catalytic performance of Pd^{II}@Cu (BDC)/2-Py-SI with several heterogeneous catalysts and composite materials for the Heck coupling reaction is presented in Table 3. It turned out that Pd/Cu-MOF gave better results than the other material catalysts listed in Table 3 in terms of selectivity and yield. The advantages of our method

TABLE 1 Optimization of reaction conditions in the Heck coupling reaction in the presence of Pd^{II}@Cu (BDC)/2-Py-SI[a]



Entry	Catalyst (mol%)	Solvent	Base	*T* (°C)	*t* (hr)	Conversion (%)[b]	Selectivity (%)[c]
1	–	DMF	K_2CO_3	120	24	–	–
2	0.2	DMF	K_2CO_3	120	18	70	90
3	**0.25**	**DMF**	**K_2CO_3**	**120**	**16**	**98**	**99**
4	0.3	DMF	K_2CO_3	120	16	97	99
5	0.25	H_2O	K_2CO_3	120	16	80	90
6	0.25	MeOH	K_2CO_3	120	16	57	88
7	0.25	EtOH	K_2CO_3	120	16	40	98
8	0.25	DMF/H_2O	K_2CO_3	120	16	90	98
9	0.25	Toluene	K_2CO_3	120	16	45	97
10	0.25	DMF	NaOAc	120	16	60	80
11	0.25	DMF	Na_2CO_3	120	16	50	85
12	0.25	DMF	Et_3N	120	16	60	90
13	0.25	DMF	KOH	120	16	90	98
14	0.25	DMF	K_2CO_3	100	18	85	98
15	0.25	DMF	K_2CO_3	25	24	35	97

[a] Reaction conditions: 4-bromoacetophenone (1 mmol), methyl acrylate (1.2 mmol), K_2CO_3 (2 mmol).

[b] Isolated yield.

[c] Selectivity to *trans*-alkene.

are high selectivity, mild conditions, and good to excellent yields.

We investigated the recyclability and recovery of the Pd^{II}@Cu (BDC)/2-Py-SI in the Heck reaction between 4-bromoacetophenone and ethyl acrylate in the optimized condition. After completion of the reaction, the catalyst was easily and rapidly separated from the mixture reaction by simply centrifuging, and then reused for the next runs. As shown in Figure 6, this catalyst could be recycled over six runs without any significant loss of its catalytic activity, but after the seventh run the yields decreased to 44%, and in this case the XRD pattern fully changed and showed that the MOF structure was destroyed.

3 | EXPERIMENTAL

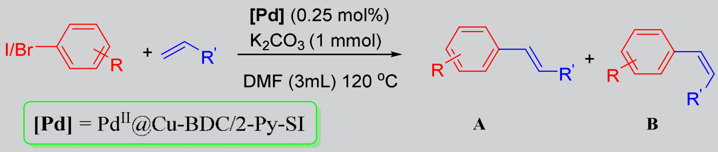
3.1 | Chemicals and apparatus

All reagents were obtained commercially from Sigma-Aldrich, Merck (Germany) and Fluka (Switzerland), and were used without further purification. The crystalline phases of the MOF material were recognized by XRD measurements (Philips-PW 1800 diffractometer). The palladium content of the MOFs was measured by AAS of the solution phase. Thin-layer chromatography (mesh 60) was used to monitor the reaction completion.

3.2 | Synthesis of Cu (BDC)·nDMF and its activation [OMS-Cu (BDC)]

The MOFs of Cu (BDC)·nDMF were synthesized under hydrothermal conditions according to the reported literature.[27,30] In a typical preparation, equimolar quantities of Cu $(NO_3)_2 \cdot 3H_2O$ (7.5 mmol, 1.812 g) and terephthalic acid (7.5 mmol, 1.245 g) in 150 ml DMF were used. This solution was placed in a Teflon-lined autoclave in an oven at 110 °C for 36 hr. Then, the Teflon-lined autoclave cooled slowly at a rate of 1 °C min^{-1} to room temperature. The blue precipitate was collected by centrifugation and washed once with DMF. To remove residual unreacted ions and H_2BDC, the as-synthesized Cu (BDC)·nDMF was purified with hot methanol and DCM for 4 hr, and then it was filtered and dried at 60 °C overnight. The Cu (BDC)·nDMF was activated at 393 K under vacuum to obtain the OMS-Cu (BDC) solid. The Cu (BDC) MOF was then characterized using a variety of different techniques.

TABLE 2 Heck reaction of different aryl halides with alkenes over Pd^{II}@Cu (BDC)/2-Py-SI catalyst



Entry	I/Br	R	R'	*t* (hr)	Conversion (%)[a]	Selectivity (%)[b]
1	Br	H	$-CO_2Me$	18	98	99
2	Br	H	$-CO_2Et$	18	97	98
3	Br	H	$-CO_2Bt$	18	93	98
4	Br	4-COMe	$-CO_2Me$	18	92	88
5	Br	4-COMe	$-CO_2Et$	18	90	90
6	Br	4-COMe	$-CO_2Bt$	18	83	92
7	Br	H	-Ph	18	95	85
8	I	$3-NO_2$	$-CO_2Et$	4	98	99
9	I	$3-NO_2$	-CN	4	98	99
10	I	4-Me	$-CO_2Me$	3	> 99	99
11	I	4-OMe	-CN	3	> 99	99
12	I	4-Me	-Ph	3	> 99	90
13	I	4-OMe	-Ph	3	> 99	99

[a] Isolated yield.

[b] Selectivity to *trans*-alkene.

TABLE 3 Comparison of the effect of Pd/Cu-MOF with other catalysts for the Heck coupling reaction

Entry	Catalyst	Reaction conditions	Yield (%)	Ref.
1	$Fe_3O_4@SiO_2$/Schiff base/Pd^{II}	K_2CO_3, DMF, 110 °C	97	[31]
2	Pd-isatin Schiff base-γ-Fe_2O_3	Et_3N, solvent-free, 100 °C	95	[32]
3	Fe_3O_4@MCM-41@Pd(0)-P2C	K_2CO_3, PEG, 120 °C	96	[20]
4	Pd (II) doped UiO-67	K_2CO_3, DMF, TBAB, 100 °C	97	[11]
5	SiO_2@ Fe_3O_4-Pd	K_2CO_3, DMF,100 °C	95	[33]
6	Pd/ED-MIL-101	Et_3N, DMF, 120 °C	98	[13]
7	Pd(0)@TpPa-1	K_2CO_3,CuI, Ph_3P, 105 °C	95	[8]
8	Fe_3O_4/DAG/Pd	Et_3N, DMF, 120 °C	96	[34]
9	Pd $(OAc)_2$@MNP	Et_3N, DMF, 120 °C	97	[35]
10	$(PdCl_2/bpy)_{10}$ multilayers	Na_2CO_3, DMF, 140 °C	95	[36]
11	Pd (II)-NHC	DMAc, KF, 140 °C	98	[37]
12	Pd^{II}@Cu (BDC)/2-Py-SI	K_2CO_3, DMF,120 °C	> 98	This work

3.3 | Preparation of Cu (BDC)/2-Py-SI

One gram of Cu (BDC)·nDMF was activated at 393 K under vacuum to obtain a dark-violet solid. A solution of 2-aminopyridine (1 mmol) or salicylaldehyde (1 mmol) was reacted under solvent-free conditions and added to a suspension in dry toluene (15 ml), and the mixture was heated at 90 °C for 12 hr. The Cu (BDC)/2-Py-SI was separated by centrifugation, washed with CH_2Cl_2 and dried at 373 K overnight.

3.4 | Preparation of Pd^{II}@Cu (BDC)/2-Py-SI

A solution of $PdCl_2$ (0.1 mmol) in a mixture with dry toluene and DMF (1:1, 5 ml) was added to a suspension of

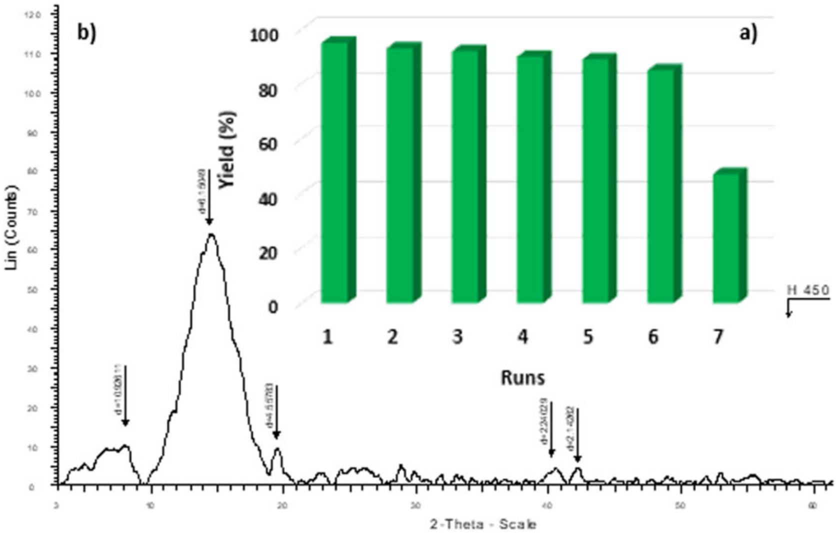


FIGURE 6 Recyclability of Pd^{II}@Cu (BDC)/2-Py-SI in (a) the Heck reaction and (b) its X-ray diffraction (XRD) analysis after the seventh run

400 mg of Cu-BDC/Py-SI in 20 ml CH_2Cl_2. The mixture was heated at reflux for 6 hr, and then cooled to room temperature. Then the Pd^{II}@Cu (BDC)/2-Py-SI was filtered, washed with DMF and CH_2Cl_2, and dried at 60 °C under vacuum. The wt% of palladium ions in Pd^{II}@Cu (BDC)/2-Py-SI was calculated using AAS, which gave a value of 0.78%. The surface area of OMS-Cu (BDC) decreased from 340 $cm^3\ g^{-1}$ to 210 $cm^3\ g^{-1}$ after loading Pd.

3.5 | General procedure for Heck coupling reaction

For the catalyst test, Pd@Cu (BDC)/2-Py-SI (0.25 mol%) was added under stirring to a round-bottomed flask containing aryl halide (1 mmol), alkene (1.2 mmol), K_2CO_3 (2 mmol) in 3 ml of DMF. The mixture was then stirred for a certain time at 120 °C. After completion of the reaction, the product was extracted from the reaction mixture with $CHCl_3$ and DI water, then the solvent evaporated and the residue purified by column chromatography. All products were characterized by comparison of their physical and ^1H and ^{13}C spectra with those already reported.

4 | CONCLUSION

The presence of copper (II) OMSs in Cu (BDC) has been found to provide an intrinsic chelating property with electron-rich functional groups, leading to the formation of the thermally stable pyridyl-salicylimine grafted on the surface MOF. This feature offers a powerful way to selectively functionalize the OMS in Cu (BDC). This methodology has been used to prepare a Pd-pyridyl-salicylimine grafted Cu (BDC) catalyst that exhibits good to excellent activation for the Heck coupling reaction. The Pd^{II}@Cu (BDC)/2-Py-SI catalyst was found to be an efficient, selective, recyclable and heterogeneous catalyst for the Heck reaction. This catalyst could be separated from the reaction mixture by common filtration, and could be reused in the next run a without a significant loss of catalytic activity.

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How to cite this article: Alamgholiloo H, Rostamnia S, Hassankhani A, et al. Stepwise post-modification immobilization of palladium Schiff-base complex on to the OMS-Cu (BDC) metal–organic framework for Mizoroki-Heck cross-coupling reaction. *Appl Organometal Chem*. 2018; e4539. https://doi.org/10.1002/aoc.4539