

Journal Pre-proofs

Designing a Bifunctional Metal-Organic Framework by Tandem Post-Synthetic Modifications; an Efficient and Recyclable Catalyst for Suzuki-Miyaura Cross-Coupling Reaction

Behrang Salahshournia, Hosein Hamadi, Valiollah Nobakht

PII: S0277-5387(20)30406-X
DOI: <https://doi.org/10.1016/j.poly.2020.114749>
Reference: POLY 114749

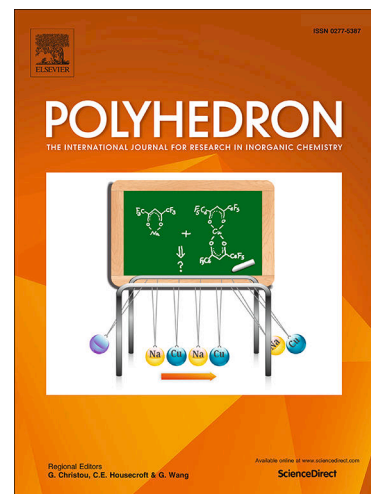
To appear in: *Polyhedron*

Received Date: 9 April 2020
Revised Date: 4 August 2020
Accepted Date: 12 August 2020

Please cite this article as: B. Salahshournia, H. Hamadi, V. Nobakht, Designing a Bifunctional Metal-Organic Framework by Tandem Post-Synthetic Modifications; an Efficient and Recyclable Catalyst for Suzuki-Miyaura Cross-Coupling Reaction, *Polyhedron* (2020), doi: <https://doi.org/10.1016/j.poly.2020.114749>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier Ltd.



Designing a Bifunctional Metal-Organic Framework by Tandem Post-Synthetic Modifications; an Efficient and Recyclable Catalyst for Suzuki-Miyaura Cross-Coupling Reaction

Behrang Salahshournia, Hosein Hamadi*, Valiollah Nobakht

Department of Chemistry, Faculty of Sciences, Shahid Chamran University of Ahvaz, Ahvaz, Iran.

Fax: +98 613 3331042 E-mail: h.hammadi@scu.ac.ir

Abstract

A new Cu/Pd bimetallic Cu-MOF-[Pd] was synthesized through covalent, dative and inorganic post-synthetic modifications. In order to achieve the Cu-MOF-[Pd], Zn-MOF (TMU-17-NH₂) was initially selected and fabricated by grafting of salicylaldehyde *via* Schiff-base formation followed by complex formation with Pd(II). Then, the as-synthesis MOF, Zn-MOF-[Pd], was subjected as 3D-template to obtain Cu-MOF-[Pd] by transmetalation process. The Cu-MOF-[Pd] was characterized by FT-IR spectroscopy, atomic absorption spectroscopy (AAS), field emission scanning electron microscopy (FE-SEM), powder X-ray diffraction (PXRD), energy dispersive X-ray spectroscopy (EDS), and EDS mapping techniques. The feasibility of using Cu-MOF-[Pd] as a highly active recoverable catalyst was confirmed in the Suzuki-Miyaura cross-coupling reaction in a mixed water/ethanol solvent. The results show

that this novel nano-composite could serve as an efficient bimetallic heterogeneous catalyst and reuse at least for 5 times without loss in activity.

Keyword: Metal-organic frameworks, Post-synthetic modification, Heterogeneous catalysis, Suzuki–Miyaura cross-coupling

Introduction

Among a myriad of heterogeneous catalysts metal-organic frameworks (MOFs), as a new class of porous materials, have attracted a great deal of attention for their extraordinary sophisticated properties. In particular, owing to diversity in metal centers and functional groups, high surface area and tunable porosity, MOFs have been implemented as versatile heterogeneous catalysts, considering as promising candidates for overcoming homogeneous catalysts' difficulties. [1-9]

Recently, mounting interest has been expressed for decoration of MOFs by various metals furnishing novel catalysis properties. The catalytic activity of MOFs can be contributed by both metal centers and organic linkers.[10-15] Particularly, the organic linkers have been used as scaffolds which distinct catalytic complexes, bio-molecules, and homogeneous catalysts immobilized or encapsulated.[16-17] In this regard, the metal-binding onto active surface of MOFs can be achieved via direct and post-

synthetic approaches.^[18-19] In the direct method, the functional metals are introduced with predesigned organic linkers bearing metal-binding sites.^[20-22]

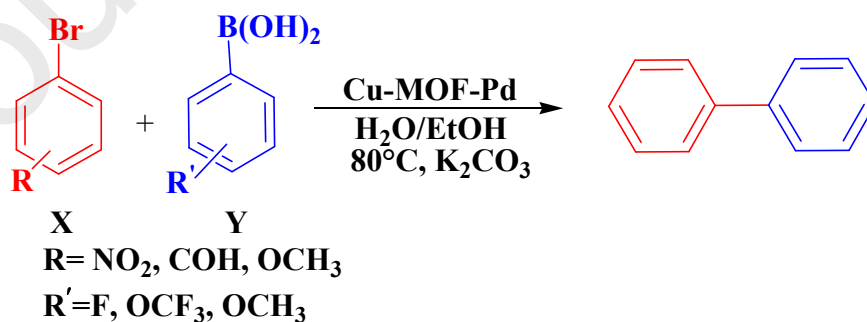
In the post-synthetic modification (PSM), as a general concept, MOF structure can change following synthesis. The main PSMs consist of covalent PSM, dative PSM and inorganic PSM.^[23-24] In this context, the most interesting applications of PSM in catalysis fields are related to MOFs possessing uncoordinated amine groups. The free NH₂ groups can effortlessly undergo chemical modification to produce appropriate chelating ligands *via* Schiff-base formation. Thus the new metal catalytic sites can be anchored in the framework through complex formation.^[25-27]

In view of catalysis, a broad consideration has been paid to organometallic Pd complexes for synthesis of biaryl compounds in Suzuki-Miyaura coupling reaction with different homogenous or heterogeneous palladium catalytic systems.^[28-32] In this regard, palladium decorated MOFs were successfully applied as robust, efficient and recoverable heterogeneous catalysts in C-C bond formation *via* coupling reactions.^[22, 33-37] Further consideration in this area allows us to explore a new Pd decorated MOF as a heterogeneous system toward Suzuki–Miyaura cross-coupling reaction in entirely phosphine-free and leaching free condition.

On the other hand, bimetallic or multimetallic catalysts in comparison to monometallic catalysts may show an increased selectivity, superior performance and substantial resistance to deactivation.^[38-39] Copper and copper based alternatives are particularly

attractive, being orders of magnitude cheaper and also less harmful to the environment than any noble metal,^[40-41] so numerous Cu/Pd bimetallic catalysts have been developed and exhibited unique properties which are different from those of their monometallic Cu or Pd.^[42-44]

Recently, we have reported the synthesis and characterization of a new Cu-MOF via post-synthetic metalation of a Zn-MOF (TMU-17-NH₂).^[41] Following our ongoing research on the development of valuable synthetic protocols,^[16, 19, 41, 45] herein we report engineering of a new Cu/Pd bimetallic heterogonous catalyst through tandem post-synthetic reactions. The catalytic performance of the post-functionalized catalyst was investigated in synthesis of biaryl compounds *via* Suzuki-Miyaura coupling reaction (Scheme 1). Our approach is directed by three imperatives; (i) heterogenization of palladium catalyst; (ii) enhancing the catalytic activity by Cu sites on the MOF and (iii) boosting catalyst performance in a coupling catalyzed reaction.



Scheme 1. Suzuki–Miyaura cross-coupling Reactions Catalyzed by Cu-MOF-[Pd]

Experimental

Materials and Measurements

All chemicals were purchased from commercial sources and used without further purification. The infrared spectra (4000-400 cm^{-1}) were recorded as KBr discs with a BOMEN MB102 FT-IR spectrometer. Powder X-ray diffraction patterns were recorded on a Philips X'Pert Pro diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$) in the 2θ range $5-50^\circ$. The simulated powder XRD pattern based on single crystal data was prepared using Mercury software. The melting points of the products were determined with thermo scientific Type 9200 melting point apparatus. FE-SEM images were recorded using TE-SCAN scanning electron microscope operating at an acceleration voltage 20 kV. NMR spectra were obtained with a Bruker 250 MHz Avance in DMSO-d_6 . An Analytik Jena (Germany) flame AAS instrument was used for determining the amount of Pd. Investigations by means of scanning electron microscopy were carried out by applying an EDS detector. The measurements were conducted using a Rontec scanning electron microscope (Bruker, Germany)

Synthetic procedures

Preparation of $[\text{Zn}(\text{NH}_2\text{-BDC})(4\text{-bpdb})] \cdot 2\text{DMF}$ (Zn-MOF)

As reported by Morsali et. al,^[46] the high quality single crystals were prepared by solvothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.297 g, 1 mmol), 4-bpdb (0.210 g, 1mmol), and $\text{H}_2\text{BDC-NH}_2$ (0.181 g, 1 mmol) at 80 °C in 15 ml DMF.

Preparation of Zn-MOF-Sc

Covalent PSM was applied to prepare Zn-MOF-Sc. hence a mixture of Zn-MOF (200 mg) with a solution of salicylaldehyde (244 mg, 0.2 mmol) in ethanol (15 mL) was refluxed in a round bottom flask in an oil bath for 3 days. The mixture was cooled to the room temperature and the yellow precipitate was separated by centrifugation. The Zn-MOF-Sc was washed several times with ethanol, diethyl ether (2×5 ml), and dried in air.

Preparation of the Zn-MOF-[Pd]

Coordination or dative PSM was applied to prepare bimetallic Zn-MOF-[Pd]. Hence, 0.1 g of PdCl_2 was refluxed in 25 mL of acetonitrile until complete dissolution of PdCl_2 salt. Then 50 mg of Zn-MOF-Sc (50 mg) was added to the solution and consequently five drops of triethyl amine was added to the mixture and refluxed for 24 h. Next, the mixture was cooled to room temperature; the precipitate was centrifuged, washed several times with ethanol and diethyl ether (2×5 ml) and dried in air. After that, it was dried overnight in an oven at 80 °C.

Preparation of the Cu-MOF-[Pd]

Cu-MOF-[Pd] was prepared by transmetalation process. Thus, the as-synthesized Zn-MOF-[Pd] (50 mg) was thoroughly soaked in DMF solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 M) at room temperature for 7 days to afford the transmetalated Cu-MOF-[Pd]. The Cu(II) solutions were refreshed every two days. Then, the solution was filtered and the Cu-exchanged product was washed with DMF and kept in fresh DMF for 3 days. Prior to use as catalyst, the Cu-MOF-[Pd] was activated by washing with ethanol and ether and then dried under vacuum at 80 °C for 5 hours.

General procedure for the Suzuki–Miyaura cross-coupling reaction

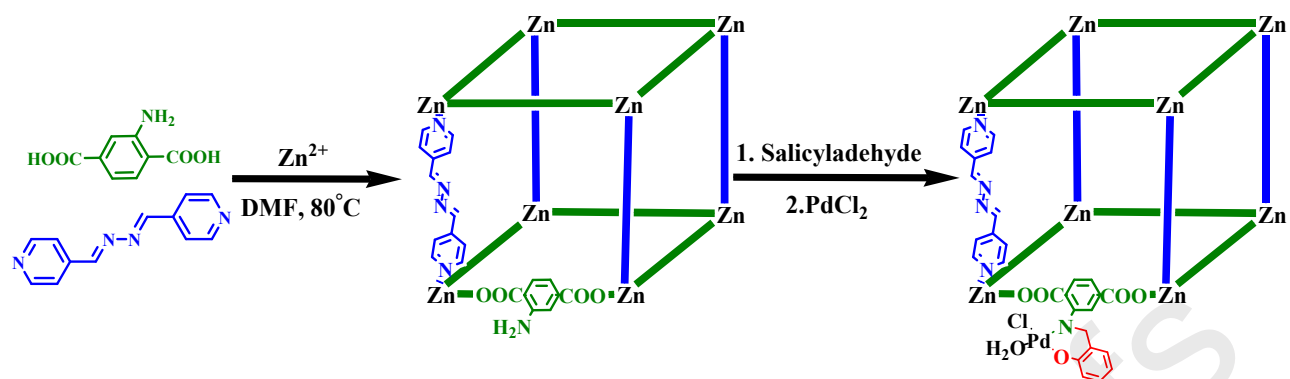
The activated Cu-MOF-[Pd] (10 mg), as catalyst, was added to a solution of aryl halide (1 mmol), phenylboronic acid (1.2 mmol, 0.15 g) and K_2CO_3 (1.5 mmol, 0.21 g) in 4 mL H_2O -EtOH (1:1, v/v). The reaction mixture was stirred at 80 °C for the required time, progressing of the reaction was monitored by TLC simultaneously. After completion of the reaction, the reaction mixture was cooled to room temperature, centrifuged for separation of the catalyst and subsequently dichloromethane (3×10 ml) was added to the reaction vessel. The organic layer was isolated dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product

was purified by column chromatography (n-hexane/ethyl acetate) and the pure desired product obtained by evaporating the solvent.

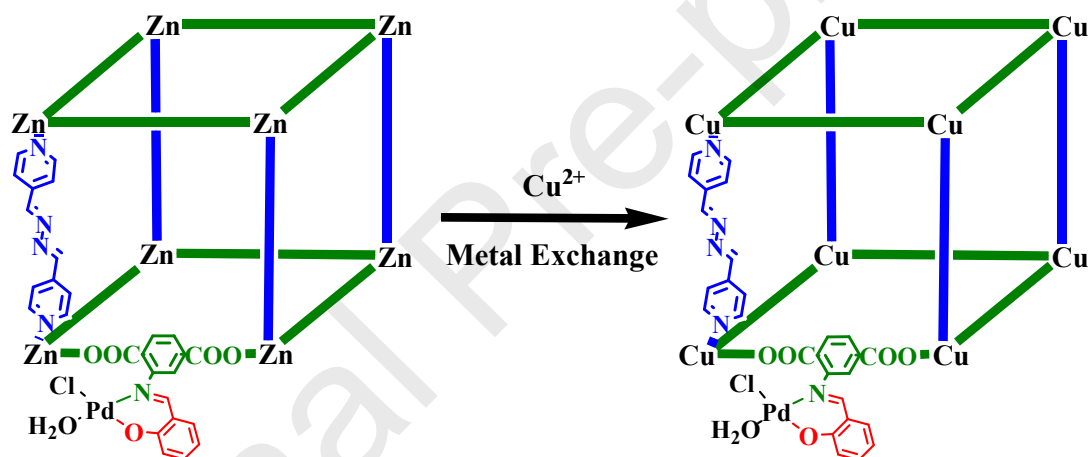
Result and discussion

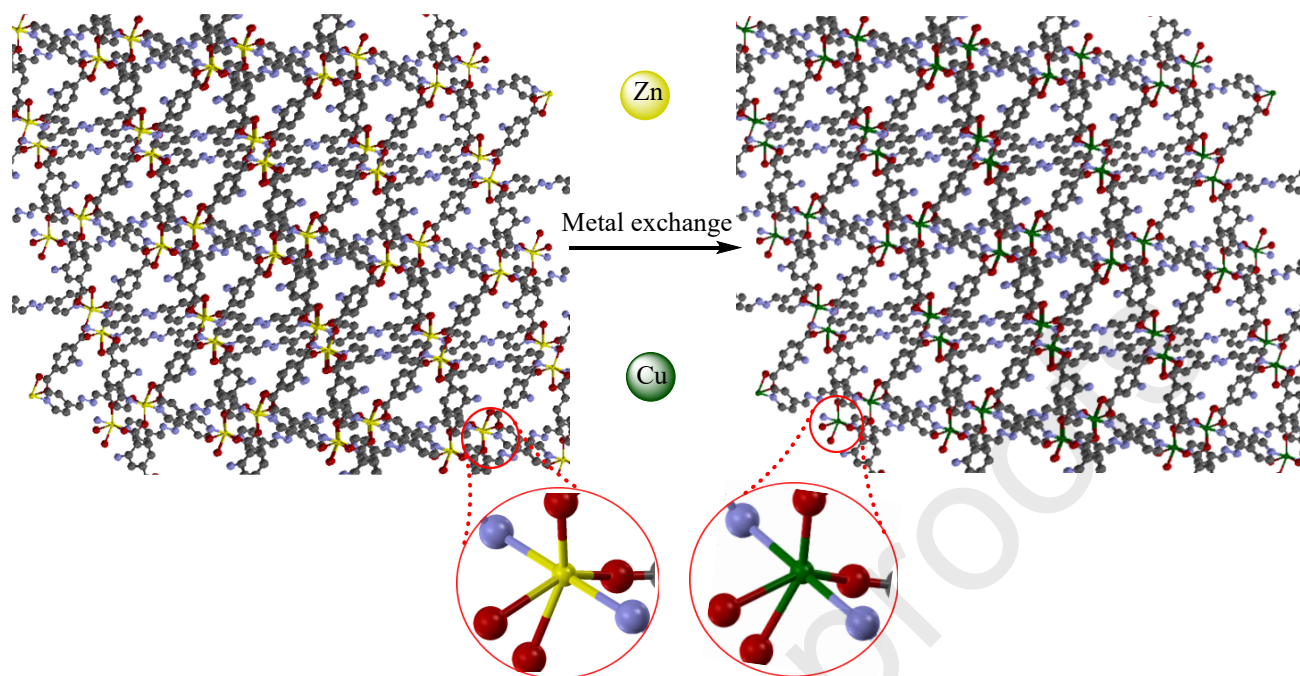
Catalyst characterization

[Zn(NH₂-BDC)(4-bpdb)].2DMF (TMU-17-NH₂ that in this work called Zn-MOF), consisting of ZnN₂O₄ clusters connected by 2-amino-1,4-benzendicarboxylic acid (NH₂-BDC) and 1,4-bis(4-pyridyl)-2,3-diaza-2,3-butadiene (4-bpdb), is a robust MOF which can undergo tandem post-synthetic modifications (PSMs). The uncoordinated amino groups in the linker make it a potential candidate for both covalent and subsequently dative post-synthetic modifications (Scheme 2). Accordingly, the covalent modification was carried out by grafting salicylaldehyde onto amine-tagged Zn-MOF to produce corresponding Schiff-base chelating attachment (Zn-MOF-Sc) followed by dative modification in which Zn-MOF-[Pd] was yielded by anchoring of Pd(II) species on Schiff-base complexation (Scheme 2). In the final stage of tandem modifications, post-synthetic metal exchange (inorganic modification) was occurred where the Zn(II) ions were exchanged with Cu(II) ions, achieving the Cu-MOF-[Pd] (Scheme 3).



Scheme 2. Covalent and dative post-synthetic modifications on Zn-MOF





Scheme 3. Preparation of the Cu-MOF-[Pd] by inorganic post-synthetic modification.

Figure 1 depicts the FT-IR spectra of synthesized Zn-MOF, Zn-MOF-Sc, Zn-MOF-[Pd] and Cu-MOF-[Pd]. The characteristic vibrational bands of the Zn-MOF were well matched with those of the reference.^[46] Two typical absorption peaks of Zn-MOF located at 3980 and 3364 cm^{-1} are ascribed to asymmetric and symmetric stretching vibrations of amino group of the NH_2 -BDC ligand (Figure 1a).^[47-48] However, significant reduction of N—H absorption peaks at 3980 and 3364 cm^{-1} can be related to appear imine groups yielded from reaction of the aldehyde group of the salicylaldehyde with the $-\text{NH}_2$ group of the NH_2 -BDC ligand (Figure 1 b, c and d).^[48-49] The broad absorption bands appearing at 2600—3600 cm^{-1} may be attributed to the stretching vibrations of the coordinated water molecules to Pd(II) ions (Scheme 2 and

3).^[26, 48] Comparison between FT-IR spectra of the Zn-MOF-[Pd] and Cu-MOF-[Pd] demonstrates that the structure remains stable after metal exchange.

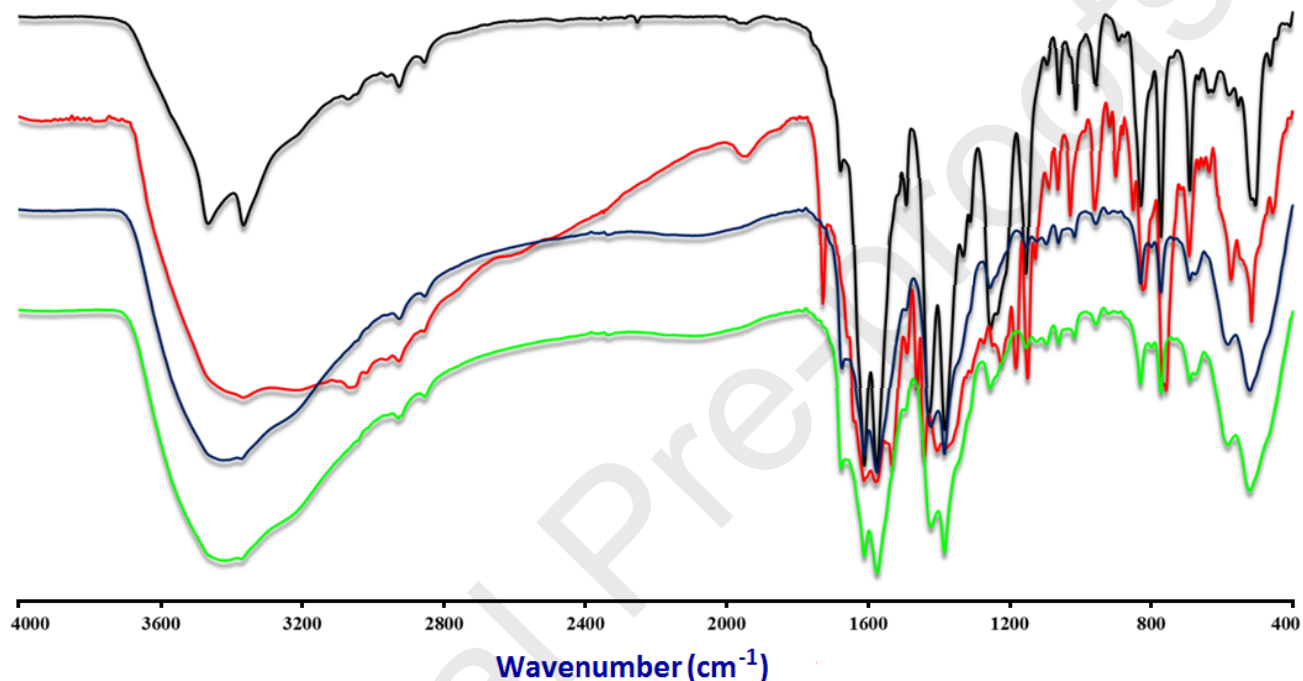


Figure 1. FT-IR spectra of a) Zn-MOF (black), b) Zn-MOF-Sc (red), c) Zn-MOF-[Pd] (blue) and d) Cu-MOF-[Pd] (green)

Powder X-ray diffraction patterns of the Zn-MOF (simulated), Zn-MOF, Zn-MOF-[Pd], and Cu-MOF-[Pd] are presented in Figure 2. The PXRD pattern of Zn-MOF corresponds well with the simulated pattern and the literature data.^[46] Comparing the PXRD patterns of the Zn-MOF, Zn-MOF-[Pd], and Cu-MOF-[Pd] show similar PXRD patterns for all the products; This clearly demonstrates that the framework of the

pristine MOF in each step remained intact, meaning that tandem organic transformation and Pd complexation did not affect the structure of the framework. However, a new peak appeared at $40.01^\circ 2\theta$ can be attributed to the successful anchoring of the zero-valent palladium nanoparticles, Pd (0) NPs, into the framework.^[50-52] Furthermore, the PXRD pattern of the transmetalated Cu-MOF-[Pd] was analogous to that of the pristine framework (Zn-MOF-[Pd]), indicating that the framework integrity remained unaffected during the metal-exchange process.

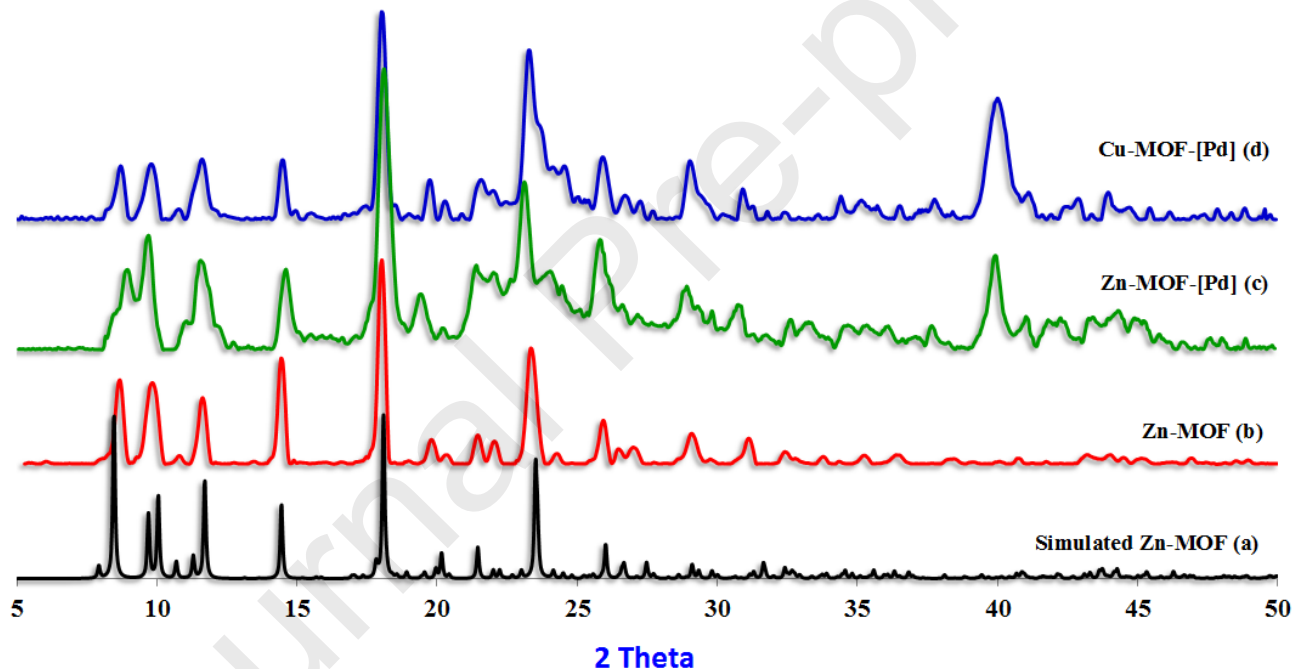
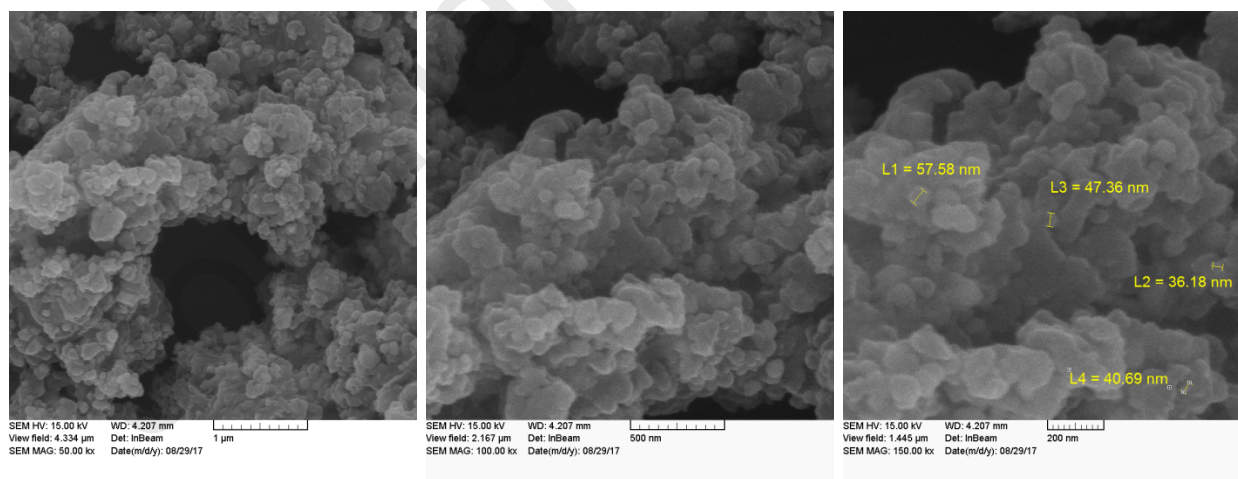


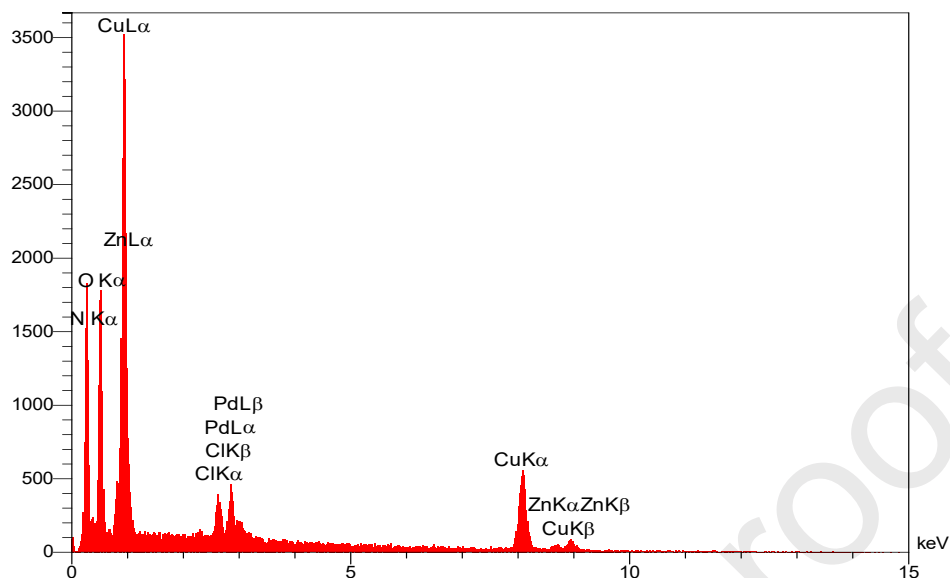
Figure 2. PXRD patterns of a) Zn-MOF, b) experimental Zn-MOF, c) Zn-MOF-[Pd], and d) Cu-MOF-[Pd]

The surface morphology and size of the Cu-MOF-[Pd] have been elucidated by field emission scanning electron microscopy (FE-SEM) (Figure 3, A). The images illustrate semi-spherical morphology with average particle size of 70 nm.

To further confirm the structure of the Cu-MOF-[Pd] after dative and inorganic post-synthetic modifications, SEM-EDS, AAS and EDS mapping techniques were carried out. According to energy dispersive X-ray (EDX) the presence of Zn, Cu, and Pd addition to C, N and O from organic ligands in the prepared catalyst were proven (Figure 3, B). In order to evaluate the metal quantities in the catalyst, Atomic Absorption Spectroscopy (AAS) was applied. In agreement with SEM-EDS results (Table S1), the weight percentages of Pd, Cu, and Zn in Cu-MOF-[Pd] were 5 %, 15% and 0.7%, respectively.



a)



b)

Figure 3. a) FE-SEM images and b) EDX analysis of Cu-MOF-[Pd]

Moreover, elemental mapping of the Cu-MOF-[Pd] catalyst reveals a well distribution of C, N, O, Cl, Cu, Zn, and Pd elements in the structure (Figure. 4), representing successful decoration of Pd on the MOF. Notably, the distribution of Pd element was uniform and the distribution area was the same as that of the Cl element. The presence of chlorine in the EDX map may also suggest an oxidation number of two, Pd(II), for the palladium in the structure of the Schiff-base compound. Furthermore, these observations confirm that dative and inorganic modifications of the MOF were successfully achieved.

Based on the FT-IR and EDX analyses it can be deduced that four coordinate square planar geometry of Pd(II) ion occupied by one chloride ion, nitrogen and oxygen

atoms of the Schiff-base scaffold, and an O atom of a water molecule (Scheme 2 and 3).

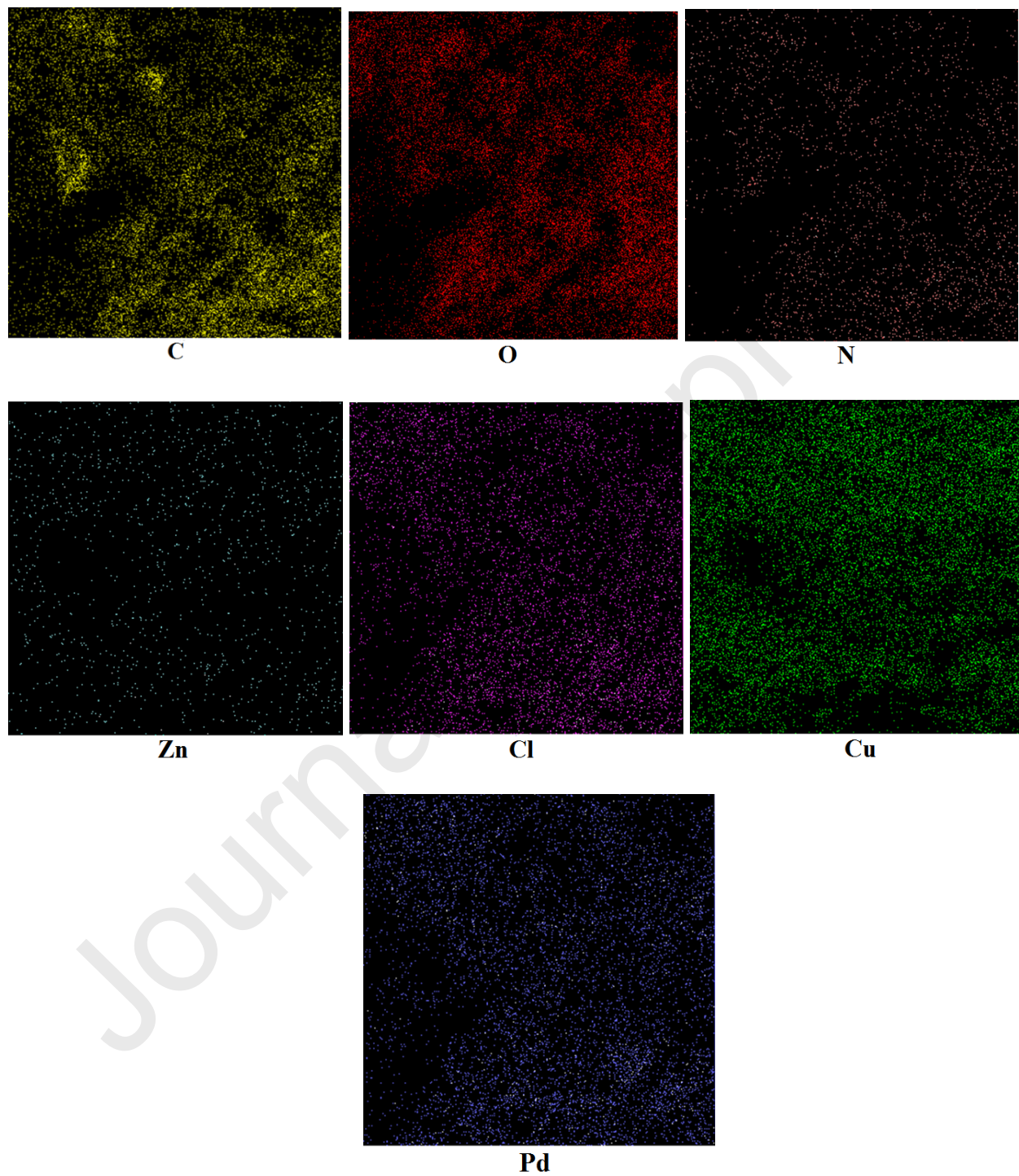


Figure 4. EDX Mapping of Cu-MOF-[Pd]

Catalytic activity

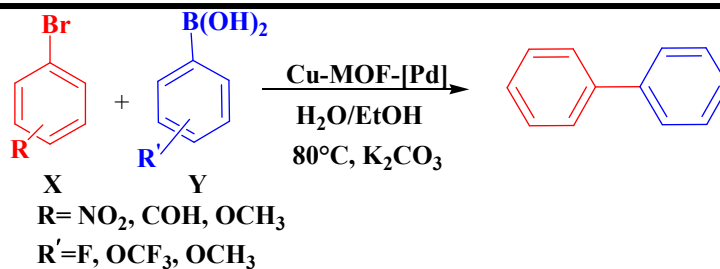
In order to demonstrate the catalytic activity of Cu-MOF-[Pd], 10 mg of the catalyst was examined in the Suzuki-Miyaura model reaction of bromobenzene and phenylboronic acid in different solvents (Table 1). The results revealed high catalytic performance of the Cu-MOF-[Pd] in 1:1 ratio of H₂O/EtOH mixture (Table 1, entry 5). To obtain the optimum reaction condition, different amount of catalysts in a wide range of temperature were screened. Evaluating precisely, it was found that using minor amount of the catalyst, lower than 10 mg, led to lower yield and longer reaction time (Table 1, entry 8).

On increasing the reaction temperature up to 80°C, the yield was increased to 98% (Table 1, entry 10). According to the results, the best performance was achieved in a mixture of H₂O/EtOH (1:1) as solvent in the presence of 10 mg of Cu-MOF-[Pd] at 80 °C.

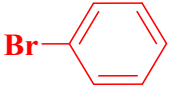
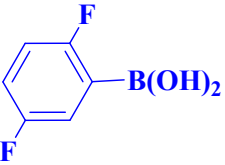
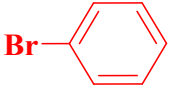
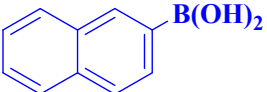
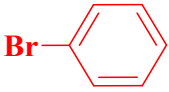
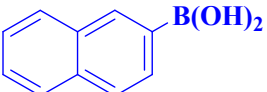
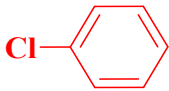
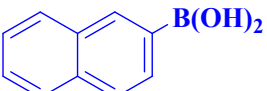

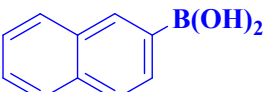
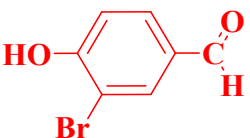
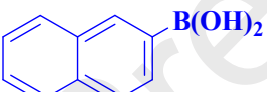
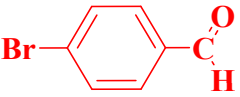
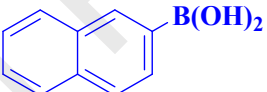
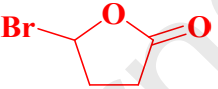
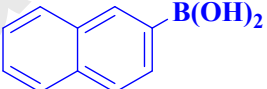
Table 1. The effect of solvent, catalyst and temperature in the coupling reaction of bromobenzene and phenylboronic acid

Entry	Catalyst (mg)	Solvent	Temperature (°C)	Time (min)	Yields (%)
1	15	H ₂ O	50	30	55
2	15	EtOH	50	30	85
3	15	PhCH ₃	50	30	trace
4	15	DMF	50	30	60
5	15	H ₂ O:EtOH	50	30	98
6	15	H ₂ O:DMF	50	30	95
7	10	H ₂ O:EtOH	50	30	88
8	7	H ₂ O:EtOH	50	30	70
9	10	H ₂ O:EtOH	80	20	80
10	10	H ₂ O:EtOH	80	15	98

To investigate the generality of the catalyst, the optimized protocol was applied for a collection of electronically diverse arylboronic acids as well as diverse aryl halides bearing a wide range of functional groups. The results are summarized in Table 2. Clearly, the catalyst promoted the coupling of iodinated and brominated aryl substrates, upon a slight increase of the reaction time (Table 1, entries 1, 2), whereas Suzuki–Miyaura cross-coupling of chlorobenzene, using the optimized procedure, resulted in longer reaction time and lower yield (Table 2, entry 3). The results presented in Table 2 point out that, excellent yields were obtained for both electron-rich and electron-deficient arylbromides. While the electron-deficient arylbromides gave desired products in high yield and shorter reaction time, the electron-rich ones required longer reaction time. For instance, formation of the nitro biaryl (Table 2, entry 4) was faster than the methoxy analogue (Table 2, entry 6). In general, having excellent functional group compatibility was found in this protocol. The structure of the products was confirmed by FT-IR, ^1H , ^{13}C NMR, melting point and compared with the corresponding reported data for the selected compounds (Figures S2-S14).

Table 4. Suzuki-Miyaura cross-coupling reactions catalyzed by Cu-MOF-[Pd]

Entry	X	Y	Yield (%)	Time (min)
1			90	10
2			98	15
3			30	60
4			95	10
5			85	15
6			85	20
7			90	10
8			80	30

9			95	10
10			90	10
11			95	15
12			10	60
13			98	10
14			85	25
15			58	20
16			95	10

Recyclability and leaching test of Cu-MOF-[Pd]

The recovery and reusability of the Cu-MOF-[Pd] were studied in the model reaction. Once the reaction was over, the catalyst was isolated from the reaction medium by centrifugation, washed with ethanol and water, dried and reused five times with no

significant loss in activity (Figure 5). Furthermore, powder X-ray diffraction pattern of five runs catalyst was compared with PXRD of fresh catalyst. According to Figure 6 the structure of catalyst remained intact even after five runs without losing of catalytic activity.

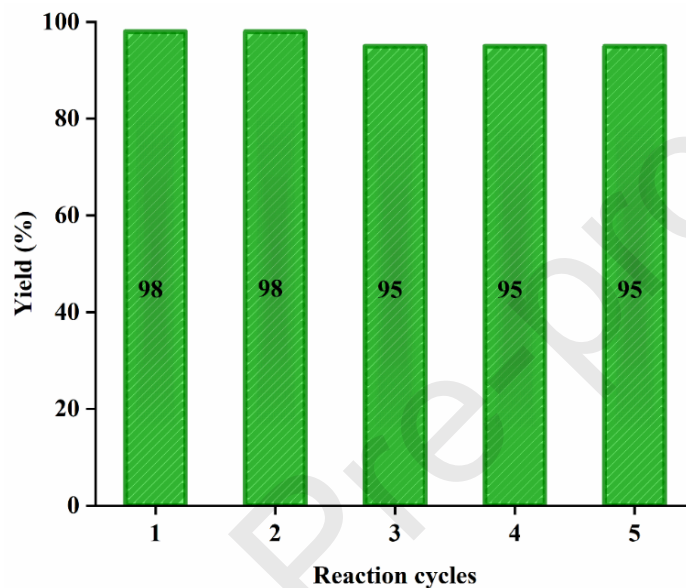


Figure 5. Reusability of the Cu-MOF-[Pd]

The possibility of homogeneous or semi-heterogeneous catalysis could be proved or disproved by hot filtration test. In the hot filtration test the model reaction of bromobenzene and phenylboronic acid in the presence of Cu-MOF-[Pd] were selected. After about 50% conversion (half time, 8 min), the catalyst was separated by centrifugation and the supernatant solution was allowed to react. The result showed no further conversion even after 30 min. Moreover, AAS analysis as additional evidence was applied in order to detect the presence of Pd ion in the filtrated in which no trace of Pd was appeared, indicating the heterogeneous catalytic behavior of Cu-MOF-[Pd].

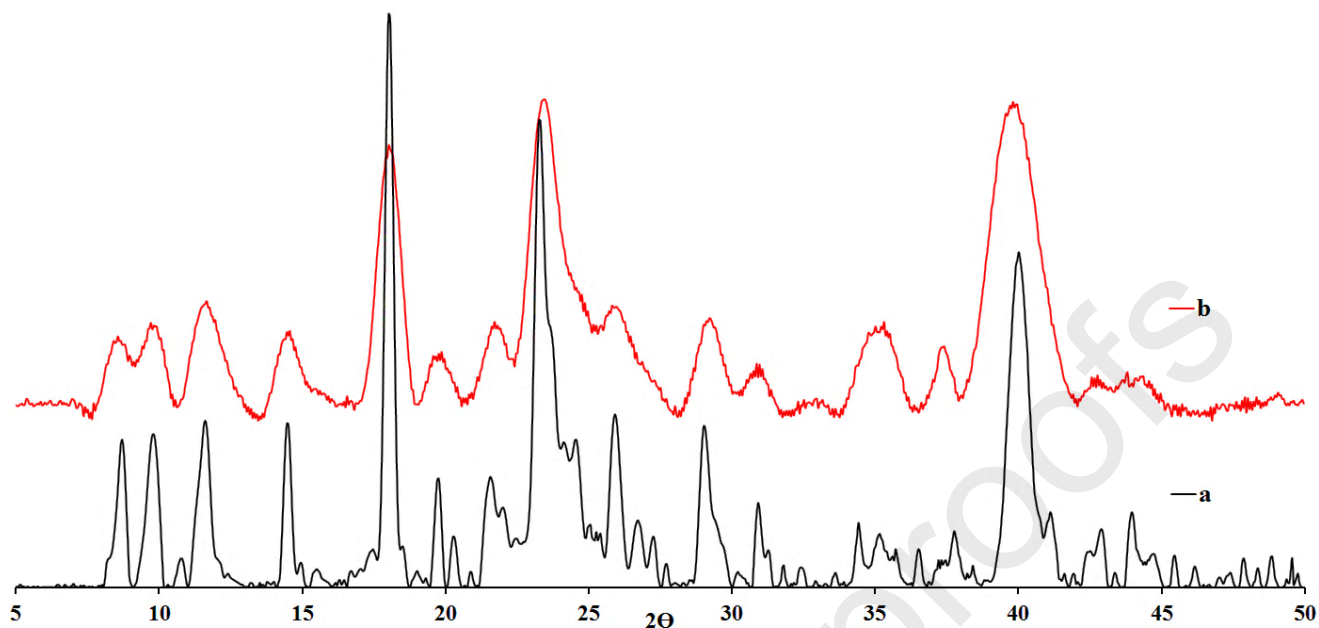
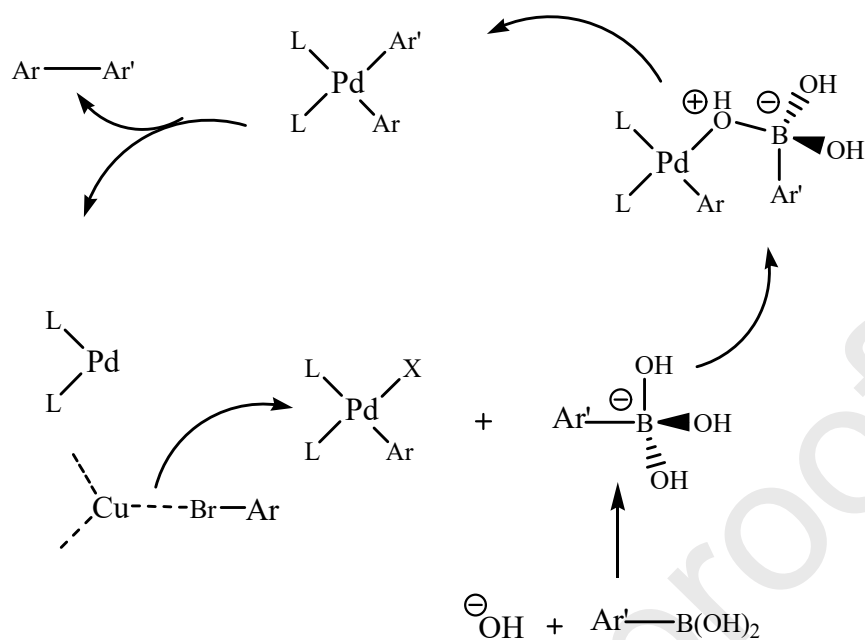


Figure 6. Powder XRD patterns of a) fresh and b) after five times reused Cu-MOF-[Pd]

A plausible mechanism for the Suzuki–Miyaura cross-coupling reaction catalyzed by the Cu-MOF-[Pd] is suggested in Scheme 4. Four-coordinate nucleophilic boronate species is generated in situ and substitute the halide ligand of the Pd intermediate, followed by the elimination of $B(OH)_3$ to form an intermediate and transfer the organic moiety to palladium species. In addition, the Cu centers can accelerate and activate the aryl halide. It should be mentioned that, as the pristine MOF has a very small pore size and it is known as non-porous MOF (proven by BET analysis),^[46] the Pd nanoparticles are expected to be on the surface of the composite, so the catalysis most likely occurs on the surface of the catalyst.



Scheme 4. A plausible mechanism for the Suzuki–Miyaura cross-coupling reaction catalyzed by the Cu-MOF-[Pd].

Comparison

The catalytic performance of Cu-MOF-[Pd] by considering the yield for the coupling reaction of bromobenzene and phenylboronic acid has been compared with several Pd-based catalysts in Table 3. It is resulted that Cu-MOF-[Pd] catalyst in the water/ethanol, as green solvents, provides excellent catalytic activities and performs the model reaction with yields up to 98%, in the shortest reaction time and highest reusability, while other procedures require prolong reaction time and toxic solvents with lower yields.

Table 5. Comparison of efficiency of Cu-MOF-[Pd] with other heterogeneous palladium catalysts in Suzuki–Miyaura cross-coupling of bromobenzene with phenylboronic acid

Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)	Ref
PdCl ₂ bpy–Cu	Toluene	95	4	94	[53]
IRMOF-3-PI-Pd (II)	Ethanol	80	5	88	[25]
UiO-67 Pdbpydc _{0.5} /bpdc _{0.5}	Toluene	95	16	89	[22]
MONT	Toluene	70	5	99	[54]
Pd/Y-MOF		96	8	89	[55]
MIL-NHC-Pd	DMF/Water	60	0.5	100	[27]
Pd(II) doped UiO-67	DMF/Water	120	20	95	[56]
Pd ²⁺ /AZC	Ethanol	80	8	99	[57]
Pd–phosphine complex	Water	100	0.5	99	[58]
Cu-MOF-[Pd]	Water/Ethanol	80	10 min	98	This work

Conclusion

In summary, we synthesized a new Cu/Pd bimetallic heterogenous catalyst through three steps tandem post-synthetic reactions including covalent, dative and inorganic modifications. The Cu-MOF-[Pd] with uniform distribution of the active site and high

density of the Pd illustrates highly heterogenous catalyst activity for the Suzuki-Miyaura cross-coupling reaction in the mixed water/ethanol solvent. The catalyst reuses at least for 5 times without loss in activity.

Acknowledgements

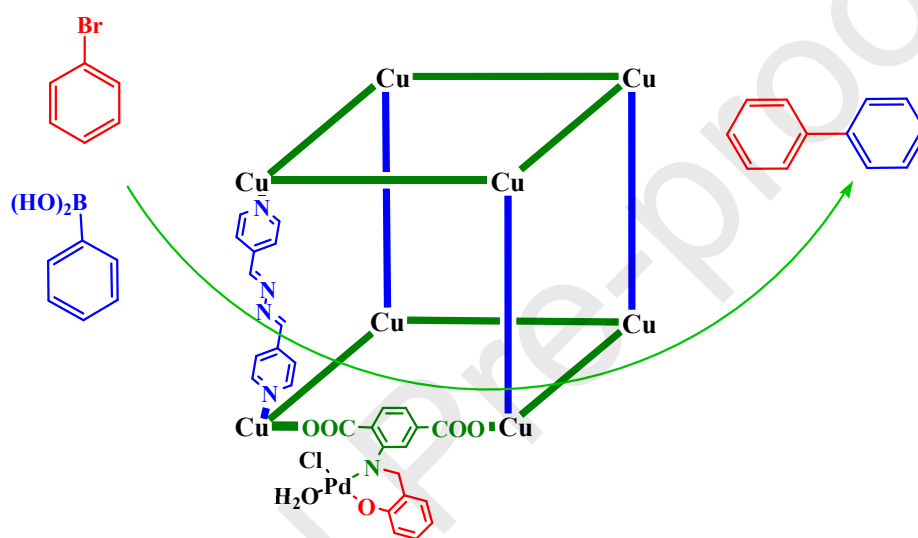
The authors thank Shahid Chamran University of Ahvaz for financial support (Grant No. SCU.SC98.251).

References

- [1] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276.
- [2] O. M. Yaghi, M. O'keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705.
- [3] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.
- [4] H.-C. Zhou, J. R. Long, O. M. Yaghi, ACS Publications, **2012**,
- [5] J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213.
- [6] R. W. Flaig, T. M. Osborn Popp, A. M. Fracaroli, E. A. Kapustin, M. J. Kalmutzki, R. M. Altamimi, F. Fathieh, J. A. Reimer, O. M. Yaghi, *J. Am. Chem. Soc.* **2017**, *139*, 12125.
- [7] J. L. Rowsell, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2005**, *44*, 4670.
- [8] A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov, F. Verpoort, *Chem. Soc. Rev.* **2015**, *44*, 6804.
- [9] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2011**, *112*, 1105.
- [10] Z. Neisi, Z. Ansari-Asl, S. Jafarinejad-Farsangi, M. E. Tarzi, T. Sedaghat, V. Nobakht, *Colloids Surf. B* **2019**.
- [11] A. Beheshti, E. S. Mousavi Fard, M. Kubicki, P. Mayer, C. T. Abrahams, S. E. Razatofighi, *CrystEngComm* **2019**, *21*, 251.
- [12] M. S. Ghasemzadeh, B. Akhlaghinia, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1119.
- [13] A. Alkaş, J. Cornelio, S. G. Telfer, *Chem. Asian J.* **2019**, *14*, 1167.
- [14] J. Cornelio, T.-Y. Zhou, A. Alkaş, S. G. Telfer, *J. Am. Chem. Soc.* **2018**, *140*, 15470.
- [15] L. Liu, T.-Y. Zhou, S. G. Telfer, *J. Am. Chem. Soc.* **2017**, *139*, 13936.
- [16] M. Yadollahi, H. Hamadi, V. Nobakht, *Appl. Organomet. Chem.* **2019**, *33*, e4819.
- [17] J.-P. Meng, Y. Gong, Q. Lin, M.-M. Zhang, P. Zhang, H.-F. Shi, J.-H. Lin, *Dalton Trans.* **2015**, *44*, 5407.
- [18] X.-G. Guo, S. Qiu, X. Chen, Y. Gong, X. Sun, *Inorg. Chem.* **2017**, *56*, 12357.
- [19] M. Yadollahi, H. Hamadi, V. Nobakht, *Appl. Organomet. Chem.* **2019**, *33*, e4629.
- [20] G. Xu, Q. D. Yang, F. Y. Wang, W. F. Zhang, Y. B. Tang, N. B. Wong, S. T. Lee, W. J. Zhang, C. S. Lee, *Adv. Mater.* **2011**, *23*, 5059.
- [21] G. Xu, K. Otsubo, T. Yamada, S. Sakaida, H. Kitagawa, *J. Am. Chem. Soc.* **2013**, *135*, 7438.

- [22] H. Fei, S. M. Cohen, *Chem. Commun.* **2014**, 50, 4810.
- [23] A. Beheshti, M. B. Pour, C. T. Abrahams, H. Motamedi, *Polyhedron* **2017**, 135, 258.
- [24] F. X. L. i Xamena, J. Gascon, J. Spivey, *Metal Organic Frameworks as Heterogeneous Catalysts*, Royal Society of Chemistry, **2013**.
- [25] D. Saha, R. Sen, T. Maity, S. Koner, *Langmuir*. **2013**, 29, 3140.
- [26] L. Lili, Z. Xin, G. Jinsen, X. Chunming, *Green Chem.* **2012**, 14, 1710.
- [27] M. Bahadori, S. Tangestaninejad, M. Moghadam, V. Mirkhani, A. Mechler, I. Mohammadpoor-Baltork, F. Zadehahmadi, *Microporous Mesoporous Mater.* **2017**, 253, 102.
- [28] H. Veisi, A. Nikseresht, N. Ahmadi, K. Khosravi, F. Saeidifar, *Polyhedron* **2019**, 162, 240.
- [29] M. Sarvestani, R. Azadi, *Appl. Organomet. Chem.* **2017**, 31, e3667.
- [30] J. Chakraborty, I. Nath, F. Verpoort, *Chem. Eng. Trans.* **2019**, 358, 580.
- [31] A. Zarnegaryan, Z. Dehbanipour, D. Elhamifar, *Polyhedron* **2019**.
- [32] B. Bhattacharyya, J. P. Biswas, S. Mishra, N. Gogoi, *Appl. Organomet. Chem.* **2019**, e5017.
- [33] I. Nath, J. Chakraborty, A. Khan, M. N. Arshad, N. Azum, M. A. Rab, A. M. Asiri, K. A. Alamry, F. Verpoort, *J. Catal.* **2019**, 377, 183.
- [34] S. Luo, Z. Zeng, G. Zeng, Z. Liu, R. Xiao, M. Chen, L. Tang, W. Tang, C. Lai, M. Cheng, *ACS Appl. Mater. Interfaces.* **2019**, 11, 32579.
- [35] V. Remya, M. Kurian, *Nano Lett.* **2019**, 9, 17.
- [36] A. Nuri, N. Vucetic, J.-H. Smått, Y. Mansoori, J.-P. Mikkola, D. Y. Murzin, *Catal. Lett.* **2019**, 149, 1941.
- [37] H. Alinezhad, M. Cheraghian, S. Ghasemi, *J. Organomet. Chem.* **2019**, 121069.
- [38] Y. Liang, Y. Liu, J. Deng, K. Zhang, Z. Hou, X. Zhao, X. Zhang, K. Zhang, R. Wei, H. Dai, *Environ. Sci. Technol.* **2019**.
- [39] L. Liu, X. Tai, X. Zhou, J. Hou, Z. Zhang, *J. Alloys Compd.* **2019**, 790, 326.
- [40] X. Yan, X. Yang, C. Xi, *Catal. Sci. Technol.* **2014**, 4, 4169.
- [41] B. Salahshournia, H. Hamadi, V. Nobakht, *Appl. Organomet. Chem.* **2018**, 32, e4416.
- [42] S. Rostamnia, H. Alamgholiloo, X. Liu, *J. Colloid Interface Sci.* **2016**, 469, 310.
- [43] M. Müller, O. I. Lebedev, R. A. Fischer, *J. Mater. Chem.* **2008**, 18, 5274.
- [44] W. Xu, H. Sun, B. Yu, G. Zhang, W. Zhang, Z. Gao, *ACS Appl. Mater. Interfaces.* **2014**, 6, 20261.
- [45] M. Homaee, H. Hamadi, V. Nobakht, M. Javaherian, B. Salahshournia, *Polyhedron* **2019**, 165, 152.
- [46] V. Safarifard, S. Beheshti, A. Morsali, *CrystEngComm* **2015**, 17, 1680.
- [47] T. Lu, L. Zhang, M. Sun, D. Deng, Y. Su, Y. Lv, *Anal. Chem.* **2016**, 88, 3413.
- [48] L. Liu, X. Tai, X. Zhou, L. Liu, *Chem. Res. Chin. Univ.* **2017**, 33, 231.
- [49] E. Ahmadi Feijani, A. Tavasoli, H. Mahdavi, *Ind. Eng. Chem. Res.* **2015**, 54, 12124.
- [50] C. I. Ezugwu, B. Mousavi, M. A. Asraf, Z. Luo, F. Verpoort, *J. Catal.* **2016**, 344, 445.
- [51] S. Verma, J. Le Bras, S. L. Jain, J. Muzart, *Dalton Trans.* **2013**, 42, 14454.
- [52] C. I. Ezugwu, B. Mousavi, M. A. Asrafa, A. Mehta, H. Vardhan, F. Verpoort, *Catal. Sci. Technol.* **2016**, 6, 2050.
- [53] S.-L. Huang, A.-Q. Jia, G.-X. Jin, *Chem. Commun.* **2013**, 49, 2403.
- [54] G.-Q. Kong, S. Ou, C. Zou, C.-D. Wu, *J. Am. Chem. Soc.* **2012**, 134, 19851.
- [55] J. Huang, W. Wang, H. Li, *ACS Catal.* **2013**, 3, 1526.
- [56] L. Chen, S. Rangan, J. Li, H. Jiang, Y. Li, *Green Chem.* **2014**, 16, 3978.
- [57] H. Choudhary, S. Nishimura, K. Ebitani, *J. Mater. Chem. A* **2014**, 2, 18687.
- [58] Y. M. Yamada, Y. Maeda, Y. Uozumi, *Org. Lett.* **2006**, 8, 4259.

Graphical Abstract



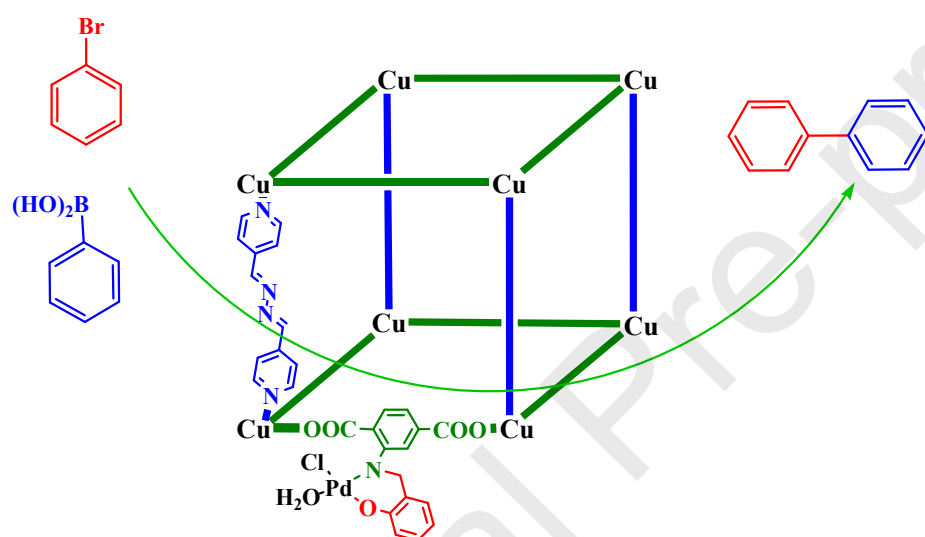
CRedit author statement

Behrang Salahshournia: Methodology. Investigation

Hosein Hamadi: Project administration, Supervision, Conceptualization, Writing - Original Draft

Valiollah Nobakht: Writing - Review & Editing, Validation

Graphical Abstract



Suzuki-Miyaura Cross-Coupling Reaction catalyzed by Cu-MOF-[Pd]

Highlights

- A new Cu/Pd bimetallic Cu-MOF-[Pd] was synthesized through covalent, dative and inorganic post-synthetic modifications.
- using Cu-MOF-[Pd] as a highly active recoverable catalyst was confirmed in the Suzuki–Miyaura cross-coupling reaction in a mixed water/ethanol solvent.
- The Cu-MOF-[Pd] with uniform distribution of the active site and high density of the Pd illustrates highly heterogenous catalyst activity

Journal Pre-proofs