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Simple synthesis of the novel Cu-MOF catalysts for the selective alcohol oxidation and the oxidative cross-coupling of amines and alcohols

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А novel porous metal-organic framework $\{Cu_2(bbda)_{0,5}(Hbbda)_{1,5}\}$ (OAc)_{1.5}.8H₂O} (UoB-5) was synthesized under ultrasound irradiation by employing a new Schiff base ligand H₂bbda (4,4'(1,4-phenylene bis (azanylylidene)) bis (methanylylidene))dibenzoic acid) and was fully characterized. The microporous nature of UoB-5 was confirmed by gas-sorption measurements. This framework acted as a highly effective heterogeneous catalyst for the alcohol oxidation reaction with tert-butyl hydroperoxide (t-BuOOH) as an oxidant. The presence of coordinatively unsaturated metal sites in UoB-5 could be the reason for high performance in this reaction. Furthermore, using the long linker with the free -N=C group and uncoordinated -N atom on the wall of the pores created UoB-5 an excellent candidate for the catalytic activities without activation of the framework. It was confirmed with the heterogeneous catalytic experiments on the one-pot tandem synthesis of imines from benzyl alcohols and anilines. Eventually, the new Cu-MOF (UoB-5) could be an alternative catalyst as a more economically favorable and environmentally friendly in the catalysis field.

K E Y W O R D S

alcohol oxidation, imine, MOF, oxidative cross-coupling, Schiff base

1 | INTRODUCTION

In the recent century, massive attention has been paid to the sustainable and green processes in the various fields of synthetic chemistry. One of the important chemical transformations in synthetic chemistry is the oxidation reaction, which produces the types of laboratory and industrially chemicals.^[1] The selective alcohol oxidation to the carbonyl compound especially is of great importance in both academic research and industries.^[2] Alcohol oxidation can be performed with the diversity of oxidants.^[3,4] Most of these oxidants are commercially available but are highly toxic and hazardous. Also, the other major concern associated with them in the alcohol oxidation is the overoxidation. To resolve these problems, researchers are focused on catalytic oxidation reactions. Recently, peroxides (e.g., H_2O_2 , TBHP) and oxygen have attracted attention because of the advantages such as inexpensive, green, and abundant. Furthermore, their only by-product (water or *t*-butanol) in the catalysis of the selective alcohol oxidation is environmentally friendly.^[5,6] However, it is essential to develop the suitable heterogeneous catalysts for the efficient activation of these oxidants due to the dynamic inertia of them.

Another of the most important oxidation reactions is oxidative cross-coupling reaction of alcohols with amine, which its production is imines. Imines are well-known to be key N-containing organic intermediates for the synthesis of different biological, pharmaceuticals, agricultural compounds, and other useful chemicals.^[7-10] The main methodologies for imine formation are oxidative cross-coupling of alcohols with amines,^[11,12] self-coupling of primary amines,^[13,14] and oxidative dehydrogenation of secondary amines,^[15,16] that the first of them seems to be one of the most promising approaches. Synthesis of imines in this way is associated with many advantages such as readily available, low toxicity, stable, inexpensive, and the wide substrate scope.^[17] Moreover, the only by-product is water in the oxidative cross-coupling of alcohols with amines. However, the main challenge for this reaction is the selective oxidation of alcohols into aldehyde intermediates under mild conditions. Recently, diverse heterogeneous catalysts had been reported for the oxidative cross-coupling of alcohols whit amines, including catalysts based on supported Au, Pd, Pt, and Ru.^[18-20] However, most of those reaction systems need pure O2 atmosphere, base additives, high temperatures, long reaction time which limited their large-scale application. Therefore, in the point of view of positive environmental impact, it will be an important breakthrough if a heterogeneous catalyst is introduced for the synthesis of imines from alcohols and amines via the oxidative cross-coupling reaction.

Metal-organic frameworks, a class of porous crystalline materials, assemble with metal ions and different organic linkers. They are structurally tunable and monodisperse materials that propose the capacity for the control of the molecular-level in the solid-state.^[21] Interestingly, the wide spectrum of MOFs with diverse structures and porosity can be synthesized by selecting the available various organic linkers. Recently, MOFs have attracted the considerable attention of chemists because they precede other heterogeneous catalysts in several significant ways, such as more accessible catalytic centers, high catalyst loading, and the more flexible design of structural building units.^[22–24] The active sites of catalytically in MOFs can be achieved at the organic linker or the inorganic component of frameworks by direct synthesis of the envisaged framework or postsynthetic modification. The metal sites can be created via the removal of coordinated solvent molecules, which can be used as catalytically active sites.^[25,26] MOFs with active metal sites have studied as a heterogeneous catalyst in some reactions such as cyanosilylation, photocatalysis, hydrogenation/isomerization, oxidation of organic substrates, and condensation reactions.^[27,28] On the other hand, it has been made clear that MOFs with a smaller size display the higher catalytic activities, because of the good exposure of active sites.^[29] As regards the traditional synthetic methods of MOFs prefer to form the large crystals of them, the preparation of MOFs with small size is a challenging task. Therefore, the purposeful and reasonable design of the architecture and composition of MOFs is needed to produce the desired nanostructures with the practical catalytic applications.

Considering the above points, we have successfully synthesized the novel Cu-MOF nanostructures, named as UoB-5, with а new Schiff base 4,4'(1,4-phenylene bis (azanylylidene))bis $(H_2 bbda:$ (methanylylidene))dibenzoic acid) as an organic linker by ultrasonic irradiation as a simple and green method. We have selected a novel Schiff base as an organic linker because of the basic nature of its azomethine group which can have a positive effect on catalytic activity, especially in the reactions that catalyzed generally in the basic medium. Also, we have chosen the copper as the node of MOF because the topology structure can effectively inhibit the leaching of the active sites by using the covalently linked metal centers as the nodes. Therefore, UoB-5 can be used as a chemical stable heterogeneous catalyst in different reactions. For this reason, and after our recent report about the synthesis and application of MOFs, we herein report our results for the application of UoB-5 as a suitable, efficient, and green catalyst for the alcohol oxidation and oxidative crosscoupling reactions (Scheme 1). Also, the reusability and stability of the catalyst during the reaction process have also been studied in detail.



SCHEME 1 Schematic illustration of the catalytic efficiency of UoB-5

2 | EXPERIMENTAL

2.1 | General information

All chemicals and solvents were purchased from commercial sources and used without further purification. All of them were analytical grade. Deionized water was used to prepare all the solutions.

FTIR spectra were recorded using a JASCO FTIR-4200 (KBr technique). CHN analyses were done by a vario EL III element analyzer. 1H NMR and electrospray ionization mass (ESIMS) measurements were made using Bruker DPX-250 Avance 300 MHz (in DMSO-d6 with tetramethylsilane as an internal standard.) and 3,200 QTRAP system, respectively. The content of Cu was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES,5300 DV, Perkin Elmer). Powder X-ray diffraction pattern was recorded on an XPert Pro MPD diffractometer with Cu Kα radiation $(\lambda = 0.15406 \text{ nm})$ and scanning speed of 10°/min from 2 to 50° at ambient temperature. Transmission electron microscopy (TEM) was carried out on a Philips EM 208S model. SEM images were taken with a Nova Nano SEM450 instrument. Thermogravimetric Analysis (TGA) was evaluated using a TG 209 F1 Nevio system from 30 to 700 °C with a temperature rate of 20 °C/min in air. The specific surface areas of the catalyst samples were measured by N₂ adsorption method at 77 K using a Belsorp-Mini II instrument. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2 mm huanghai silica gel plates using UV light as a visualizing agent. Melting points were recorded with a Veego VMP-D melting point apparatus and were uncorrected.

2.2 | Preparation of 4,4'(1,4-phenylene bis (azanylylidene)) bis (methanylylidene)) dibenzoic acid (H₂bbda)

To a solution of 4-formylbenzoic acid (2 mmol, 300 mg) in EtOH (10 ml) was gradually added a solution of 1,4-phenylene diamine (1 mmol, 108 mg) in EtOH (10 ml) at room temperature. The reaction mixture was mechanically stirred for 60 min. After that, the yellow crystalline precipitate of the product was filtered, washed with EtOH (3 × 10), and then dried in an oven overnight. The structural assignments of the synthesized Schiff base (H₂bbda: 4,4'(1,4-phenylene bis (azanylylidene))bis (methanylylidene))dibenzoic acid)) were based on FT-IR, ¹HNMR, Mass and analytical analysis of CHN data (Figure S1, S2, S3). FT-IR (KBr, cm⁻¹): ν : 1685, 1,623, 1,490, 1,430, 1,290, 852, 778. ¹HNMR (300 MHz, DMSO): $\delta = 7.45$ (s, 4H, Ar), 8.09 (m, 8H, Ar), 8.82 (s, 2H, CH=N), 13.10 (s, 2H, COOH). MS m/z (ESI) Calc. for C₂₂H₁₆N₂O₄ [M + H]⁺: 372.11, found: 372.06. Anal. Cal. for C₂₂H₁₆N₂O₄ (%): C: 70.96: H, 4.33, N: 7.52; found (%): C: 70.43, H: 4.13, N: 7.32.

2.3 | Preparation of cu-MOF nanoparticle (UoB-5)

NaOH (1 M, 1 ml) was added dropwise to a water solution (20 ml) of H₂bbda (1 mmol, 0.372 g) and the mixture stirred until a yellow and a clear solution was obtained. Then, a solution of copper acetate (2 mmol, 0.362 g) in water (10 ml) was gradually added to the above mixture at room temperature under ultrasonic irradiation. The reaction mixture remained in the same conditions for the more 30 min. Afterward, the product was centrifuged and washed by ethanol and water. Finally, $Cu_2(bbda)_{0.5}$ (Hbbda)_{1.5}(OAc)_{1.5}.8H₂O nanoparticles were obtained after drying for 12 hr at 70 °C.

2.4 | General procedure for alcohol oxidation using UoB-5

To a mixture of primary/secondary alcohols (1 mmol), UoB-5 (1.5 mol%) in a glass test tube was added TBHP (2 mmol), and the mixture reaction was heated at 40 °C without any solvent for the appropriate time. After completion of the reaction, UoB-5 was separated by centrifuging followed by decantation (3×3 ml EtOAc) and was used in the next run. The final product (liquid phase) was identified by comparison of their physical data with those of authentic samples because all of them are known.

2.5 | General procedure for oxidative cross-coupling using UoB-5

Benzyl alcohol (1 mmol), TBHP (2 mmol), and UoB-5 were magnetically stirred at 40 °C for an appropriate time under solvent-free conditions. After completion of the reaction, aniline (1.2 mmol) was subsequently added to the above reaction mixture and stirred for an additional appropriate time at room temperature to afford the corresponding products. After completion of the reaction as indicated by TLC. The final product was purified by recrystallization from absolute ethanol to yield pure secondary imine as yellowish solid. Also, UoB-5 was recovered by centrifugation, then washed several times with EtOAc, dried, and reused for the next run under the same reaction conditions.

3 | **RESULTS AND DISCUSSION**

3.1 | Syntheses and characterization

The novel Schiff base ligand was prepared by the condensation of 4-formylbenzoic acid and 1,4-phenylene diamine in EtOH at room temperature, which was then used as a suitable organic linker for the new MOF (Scheme 2). The Cu-MOF nanoparticles, as named UoB-5, was obtained as a light-brown powder from the combination of Cu (OAc)₂ and H₂bbda in water using ultrasonic irradiation as a simple method. The possibility



 $SCHEME\ 2$ Synthesis of UoB-5 by the prepared H_2bbda as a Schiff base linker

of large-scale synthesis is the most important aspect of this procedure; here, 6.54 grams of UoB-5 were produced with 3.6 grams of Cu (OAc)₂. The molecular formula of Cu₂(bbda)_{0.5}(Hbbda)_{1.5}(OAc)_{1.5}.8H₂O was proposed for UoB-5 by the EDS analysis (Figure 1a) (calc. (%): C: 51.2; O: 27.6; Cu: 11.45), which reasonably agrees with the real amounts (%) of C: 51.29, O: 28.07 and Cu (10.10).

The TGA curve of UoB-5 displayed its thermal stability up to 230 °C (Figure 1b). The material was released two main weight changes. The first step slope of mass loss happened (13.71%) around 310 °C due to the vaporization of water molecules residing in the pore (cal. 13.09%). The other sharp weight loss step occurred at 490 °C that signified the composition temperature of the MOF compound.

FTIR spectrum of UoB-5 compared with H₂bdda confirmed the coordination of linker to metal (Figure 2, Left). The OH stretching vibration at 2300-3000 cm⁻¹ from the organic ligand was disappeared that indicated the ligand deprotonation occurred and the ligand was coordinated to the metal ions. The absorption peaks at \approx 3,421 cm⁻¹ and \approx 3,120 cm⁻¹ could be attributed to the stretching vibration of hydroxyl and the N-H groups, respectively. Also, the peaks at 1702 and 1,414 cm^{-1} resulted from the symmetric and asymmetric vibration of the coordinated acetate group. The peaks at 1167 cm^{-1} symmetric and 1,589 cm⁻¹ asymmetric vibration corresponded to the carboxylate presence in the structure of UoB-5. Furthermore, they have been shifted to the lower value compared to the related vibration of the linker. which demonstrates the presence of H₂bdda as a linker in the framework. It is worth noting that the coordination mode of carboxylate groups to Cu have determined as a bridging mode based on the difference in the symmetric and asymmetric stretching vibrations of carboxylate groups (Δv) in UoB-5 and H₂bdda.^[30] Based on the



FIGURE 1 (a) EDS spectrum; (b) TGA curve of UoB-5





obtained results from FT-IR, the geometry around of the Cu center in UoB-5 was suggested (Figure 2, Right).

BET-BJH method was utilized to measure the surface area, pore-volume, and pore-size distribution of UoB-5 (Figure 3a, 3b). Moreover, the surface area and pore value of the synthesized UoB-5 based on N₂ adsorption at 77 K were 86 m²/g and 0.67 cm³/g, respectively. The results exhibited a type IV isotherm with an H₂ hysteresis loop, which revealed a hierarchically mesoporous structure of UoB-5. The relevant distribution curve of the pore diameter, calculated by BJH method, displayed that the dominant mesopores are centered approximately in the range of 2–10 nm with a peak maximum of 5 nm.

The crystal structure of the as-prepared UoB-5 was well characterized by PXRD (Figure 3c). The XRD pattern of UoB-5 indicated the sharp peaks at around 2θ of 6.8° that confirmed a highly crystalline material was produced. Furthermore, the appearance of the sharp peaks



FIGURE 3 (a) The adsorption-desorption curves, (b) The pore diameter distribution, (c) PXRD pattern of UoB-5



FIGURE 4 (a) TEM, (b) SEM image, (c) the size distribution of UoB-5



SCHEME 3 Model alcohol oxidation reaction catalyzed by UoB-5

at the low angel area $(2\theta < 10)$ displayed a high degree of mesoscopic ordering. The overall XRD pattern of the UoB-5 was in good agreement with those of IRMOF-3, as reported in the literature,^[31] indicating that both of them

(UoB-5 & IRMOF-3) are isostructural with the cubic lattice structure.

The cubic morphology of UoB-5 was confirmed via the TEM (Figure 4a) and the SEM (Figure 4b) analysis, which was an agreement with the obtained results of XRD pattern. Moreover, the images displayed relatively uniform size distribution and morphology for UoB-5. The average particle size of UoB-5 was obtained the range 20–21 nm by the particle size distribution based on TEM images, that was emphasized the observed data of SEM images (Figure 4c). Also, the TEM images revealed no amorphous component in the synthesized nanoparticle.

TABLE 1 Summary of the Alcohol Oxidation Reactions Based on Substituted Primary and Secondary Alcohols^[a]

С ^О н	ОН	но	но
1a, 95% ^b , 1.5 h	1b, 90% ^b , 2 h	1c, 95% ^b , 1.45 h	1d,87% ^b ,1.45 h
	CI	O H Br	Br
1e, 92% ^b , 1.5 h	1f, 95% ^b , 2 h	1 g, 90% ^b , 1.45 h	1 h, 85% ^b , 2 h
MO2	O ₂ N H	O ₂ N H	O H
1i, 80% ^b , 2 h	1j, 85% ^b , 2 h	1 k, 75% ^b , 2 h	1 l, 90% ^b , 1.45 h
U H	-O L H	NO THE REPORT OF	-o
1 m, 97% ^b , 1.5 h	1n, 85% ^b , 1.5 h	10, 95% ^b , 1.5 h	1p, 97% ^b , 1.5 h
€ C C C C C C C C C C C C C C C C C C C			
1q, 78% ^b , 1.45 h	1r, 98% ^b , 1.5 h	1 s, 98% ^b , 1.5 h	1 t, 83% ^b , 2 h

^aReaction conditions: Alcohols (1 mmol), TBHP (2 eq), UoB-5 (1.5 mol%), Solvent-free, 40 $^{\circ}$ C. ^bIsolated yields.

3.2 | Catalysis studies

3.2.1 | Alcohol oxidation reaction

As commented in the introduction, MOFs are characterized by their prominent thermal and chemical stability as well as providing unique catalytic activity and product selectivity. With these precedents, the catalytic performance of UoB-5 was explored for alcohol oxidation reaction in the first step of this work (Scheme 3). The benzyl alcohol was chosen as model substrate and the different reaction parameters, involving temperatures, the reaction medium, catalyst amount, and the type/ amount of oxidant, were screened. It should be noted that only a low conversion was obtained after a reaction time of 120 min without the addition of any catalyst or in the presence of the precursor salt. Firstly, the investigation of the reaction medium was displayed that the solvent-free condition was more effective with respect to the solvent medium (Figure S4). This reaction condition has some advantages such as easy reactors, facile, and efficient workup procedures that are often more environmentally friendly. The evaluation of the temperature effect revealed that the best yield of the product was obtained at 40 °C. With a further increase in the reaction temperature, the product yield decreased, which may be due to the decomposition of TBHP without oxidizing benzyl alcohol (Figure S5). The key factor of catalyst dosage investigated, the best result was achieved with using 1.5 mol% of UoB-5. Besides, a further increment of catalyst amount had no positive effect on the reaction progress (Figure S6). In an effort to optimize the oxidant amount, upon increasing TBHP amount from 0.5–2 equivalent, the conversion of benzyl alcohol increased. Also, it decreased with more increasing of TBHP that can be due to the over-oxidation (Figure S7). Moreover, the nature of the oxidant was evaluated as a crucial factor in the activity of this reaction system, and the results confirmed that the TBHP is the best choice (Figure S8).

With the optimized reaction conditions in hand, the scope and generality of the alcohol oxidation reaction were moreover extended. The obtained results are presented in Table 1. A lot of structurally diverse primary and secondary benzyl alcohols were oxidized by UoB-5 with TBHP in solvent-free conditions, producing excellent yields (75-98%) of aromatic aldehydes (2a-p, Table 1)/ ketones (2r-t, Table 1). The various benzyl alcohols with electron-donating and electron-withdrawing groups at ortho-/meta-/and para-position of the benzene ring were smoothly converted to corresponding aromatic aldehydes in a good to excellent yields under optimized reaction conditions, regardless of the electronic nature and position of the substituent. Secondary alcohols were effectively converted to corresponding ketones by UoB-5 with TBHP. Moreover, cinnamyl alcohol was selectively oxidized to cinnamaldehyde without any by-products in good yield (2q, 78%).

In scheme 4, a possible mechanism is presented for the alcohol oxidation catalyzed by UoB-5 in the case of the primary alcohol dehydrogenation. At first, the radicals t-BuOO• is generated by the metal-assisted, which



the Cu (II) center is oxidized t-BuOOH. Then, the formed Cu (I) center is reduced t-BuOOH and provided the radicals t-BuO•. Finely, the both radicals behave as hydrogen atom abstractors from the alcohols.^[32]

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3.2.2 | Oxidative cross-coupling reaction

The adoption of MOFs as a catalyst has been explored extensively in recent years, due to coordinatively

Catalysts	Catalyst amount	Conditions	Time (hr)	Yield (%)	Ref
RuO ₂ /GO	25 mg	toluene/air/100 °C	3	63	[33]
Au ₆ Ag ₁ /PAAS	2 mol%	$H_2O/O_2/60\ ^\circ C$	12	94	[34]
Ru (OH) _x /TiO ₂	2 mol%	toluene/O2/100 °C	2	91	[35]
Au-Pd/resin	2 mol%	$H_2O/O_2/40\ ^\circ C$	12	65	[20]
Cu _{0.9} Fe _{0.1} @RCAC	50 mg	toluene/air, LED/120 °C	3	92	[36]
Pd-Au@Mn (II)-MOF	2 mg	toluene/air/110 °C	30	99	[12]
MnO _x /TiO ₂ @SBA-15	100 mg	toluene/air/80 °C	24	92	[37]
γ-Fe ₂ O ₃	300 mg	toluene/air/80 °C	12	92	[10]
M-350 (amorphous manganese oxide)	50 mg	toluene/air/80 °C	2	97	[38]
Mo (CO) ₆	26.4 mg	mesitylene/ /164 °C	60	73	[39]
UoB-5	1.5 mol%	S.F./TBHP/40 °C	1	95	This work

TABLE 2 Comparison of the catalytic activity of UoB-5 towards the oxidative cross-coupling reaction

Summary of the Oxidative Cross-Coupling Reactions Based on Substituted Benzyl Alcohols and Anilines [a] TABLE 3



(Continues)

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TABLE 3 (Continued)



^aReaction conditions: Alcohols (1 mmol), Aniline (1.2 mmol), UoB-5 (1.5 mol%), Solvent-free, 40 °C. ^bIsolated yields.

unsaturated metal site and the microporous nature. It is believed that both the tunable pore structures and catalytically active sites of MOFs could be used at the same time to do the chemical synthesis in a one-pot manner. Therefore, UoB-5 was examined for its active role as a heterogeneous catalyst for oxidative cross-coupling reaction as a one-pot tandem reaction. The challenge of oxidative cross-coupling reaction is the optimization of the reaction conditions for the first step, and the following non-oxidation condensation step largely differ from each other. With good precedents of UoB-5 in the alcohol oxidation reaction, its catalytic activity was also examined in the formation imines by oxidative cross-coupling reaction (Scheme 5).

According to having the optimized reaction condition for alcohol oxidation, the imine formation was initially investigated in the same conditions by following to add aniline as a model substrate. Fortunately, the good result was achieved to produce the imine as a final product in previous conditions in terms of



SCHEME 6 The plausible mechanism for the oxidative cross-coupling reaction catalyzed by UoB-5

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temperature, catalyst amount, and reaction medium. It should be noted that the reaction progress was evaluated in the absence of catalyst, a negligible proceed was observed. Also, the precursor salt of Cu $(OAc)_2$ showed negligible catalytic activity for the oxidative cross-coupling reaction.

For the investigation that the nature of imine groups decorated UoB-5 and the important role of its synthetic components in oxidative cross-coupling reaction, the model reaction was carried out using H_2 bbda, Cu (OAc)₂ and UoB-5 as catalysts under optimized conditions. Cu (OAc)₂, as precursor salt of UoB-5, showed lower catalytic activity than UoB-5, with a conversion of 25% being obtained after 3 hr. Also, using H_2 bbda, the organic linker of UoB-5 afforded approximately 15% conversion after 3 hr (Figure S9). These results indicated that the simultaneous presence of the imine and metal groups in the framework enhanced the catalytic activity. Anyway, the role of the imine moiety in the structure of UoB-5 still requires further investigation.

To manifest the supremacy of our catalytic system, a comparison list was displayed in Table 2 to compare this work with other analogous reaction systems. In this work, the shortcoming of high temperatures, high catalyst amount, high reaction time, and the usage of organic solvents that go against green chemistry was eliminated. Therefore, UoB-5 can be a decent system deserved to develop further for industrial applications.

After that, the scope and limitations of UoB-5 were investigated using different amines and alcohols (Table 3). First, aniline was examined with the different benzyl alcohols with various functional groups as the coupling partner to form the desired imines. The substituted benzyl alcohols with halides (-Cl, -Br) revealed the excellent yields for the corresponding products (respectively 2b, 2c). p- nitoraniline gave the lowest yield for the corresponding imine (2d) after only 1.5 hr. Salicyl alcohol with aniline showed a high yield for the corresponding product (2e). Second, p-anisidine and benzyl alcohols with the electron-withdrawing (-NO₂) and electron-donating (-OMe) functional groups as well as displayed the excellent yields (respectively 2j, 2 k). The reaction of p-anisidine and other substituted benzyl alcohols (-OH, -Cl, -Br) gave the good yields for their products (respectively 2 g, 2 h, 2i). Finally, the benzyl alcohols with different functional groups and p-bromoaniline as the partner coupling produced the corresponding products with pleasant yields (2 l-20).



FIGURE 5 Recycling test of UoB-5 catalyst within kinetic-controlled region and under the optimized conditions

The oxidative cross-coupling reaction is two steps, which the mechanism of the first step is similar to what is given in the previous section. With respect to the catalysis of imine synthesis in the basic, a plausible mechanism was proposed for the second step (Scheme 6). Actually, the C=N groups of Schiff base linker could be act as highly reactive base sites and a Brønsted proton of aniline is absorbed by the nitrogen of imine. The generated stable anion is subjected to nucleophilic attack on the carbonyl carbon atom of the substituted aromatic aldehydes. Finally, UoB-5 come back to the initial structure after two runs of protonation and deprotonation, the product release from the surface of the catalyst. According to the proposed mechanism, the high catalytic activity of UoB-5 in the oxidative cross-coupling reaction can be attributed to the presence of the azomethine group in linker.

3.3 | The recyclability tests of UoB-5

One of the important factors for the heterogeneous catalyst in terms of sustainable chemistry is recyclability. Therefore, the used UoB-5 after the post-treatment (illustrated experimental section) was examined for the recycling reactions under the optimized conditions. As shown in Figure 5, the catalyst displayed a very stable activity for both reactions (alcohol oxidation: 5a, oxidative cross-coupling: 5c) after consecutive use of five cycles, as good as a fresh catalyst. Any possible saturation of catalytic sites because of the used optimized reaction conditions was also investigated during the kineticcontrolled region, i.e. 45 and 30 min after the starting alcohol oxidation and oxidative cross-coupling reactions, respectively. The catalyst indeed exhibited considerable stability. TEM of the reused catalyst from both reactions clearly revealed the integrity of its characteristic structure (Figure 5b, 5d). These observations can be attributed to the strong interaction between the nodes of Cu and H₂bbda as an organic linker which maintains the integrity and structure of the UoB-5 during the reaction progress.

4 | CONCLUSION

In summary, a novel Cu-MOF nanoparticles, UoB-5, were successfully synthesized through time-saving, low-cost methods *via* ultrasound irradiation by employing the new Schiff base as a linker precursor. Due to the presence of open metal sites and the mesoporous nature of the framework, it was used as an excellent heterogeneous catalyst toward alcohol oxidation reaction as well as

toward tandem oxidative cross-coupling reaction. Besides achieving high selectivity and activity to the target products, the heterogeneous nature of the catalyst was provided by the preservation of its structural integrity during both reactions. Furthermore, this framework can be simply separated and reused for five catalytic cycles without significant loss of its activity in both reactions. UoB-5 is an excellent candidate as a more economically favorable and environmentally friendly alternative to conventional catalysts. Also, we expect the approach of this work to be viable for the construction of many more interesting and practical MOF catalysts like this for green organic synthesis, and studies toward the synthesis of novel MOFs containing the Schiff base as linker are underway.

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AUTHOR CONTRIBUTIONS

Pouya Ghamari Kargar: Investigation. **sima aryanejad:** Investigation. **ghodsieh bagherzade:** Project administration.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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