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Metal-Organic Framework $Cu_2(OBA)_2(BPY)$ as efficient catalyst for C–O bond formation via oxidative cross-coupling reaction of benzaldehyde and 1,4-dioxane

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ABSTRACT

A metal-organic framework $Cu_2(OBA)_2(BPY)$ was synthesized, and was used as an efficient heterogeneous catalyst for the oxidative cross-coupling reaction of benzaldehyde and 1,4-dioxane to form 1,4-dioxan-2-yl benzoate as major product. The coupling reaction could proceed readily, with more than 80 % reaction yield being achieved after 24 h at 80 ^oC in the presence of 2 mol% $Cu_2(OBA)_2(BPY)$ catalyst and *tert*-butyl hydroperoxide in water as an oxidant. The $Cu_2(OBA)_2(BPY)$ was reutilized numerous times for the reaction without a noteworthy decline in catalytic efficiency. This Cu-MOF exhibited higher activity than other MOFs and traditional homogeneous catalysts in the oxidative coupling reaction. To the best of our knowledge, this transformation using heterogeneous catalyst was not previously mentioned in the literature.

Introduction

The direct activation and cleavage of C–H bonds for the construction of carbon-carbon and carbon-heteroatom bonds catalyzed by transition metals has become an attractive strategy in modern organic [1]. The transformation showed remarkable potential for step economy, atom economy, and environmental sustainability as compared with traditional cross couplings which usually required the prefunctionalization of the reactants [2-4]. Considerable attention has been paid to the oxidative couplings involving $C(sp^3)$–H bonds [5-10]. However, studies involving the activation of C-H bond adjacent to an ethereal oxygen atom are still rare [11-14]. α-acyloxy ethers are ubiquitous structural motifs found in natural products and pharmaceutically active molecules [15-19]. The traditional methods of the esterification of a hemiacetal, the nucleophilic substitution of a carboxylic acid and an α-halo substituted ether or the addition of a carboxylic acid to an alkenyl ether, represented many disadvantages because it required substrate prefunctionalization and it was not atom economic. Recently, some processes have been developed to address these problems [20-23]. The Patel group synthesized benzylic esters via cross dehydrogenative coupling of aldehydes with alkylbenzenes in the presence of $Cu(OAc)_2$catalyst and tert-butyl hydroperoxide as a oxidant [24]. The Patel group also reported an efficient Cu-catalyzed directed O-aroylation process (esterification) between alkylbenzenes and o-carbonylphenols and β-dicarbonyl compounds using TBHP as the oxidant [25]. The Sharma group developed an efficient method of synthesizing 2-carbonyl substituted benzoates via copper-catalyzed esterification of 2-carbonyl substituted phenols with aliphatic and benzylic alcohols [26]. By using of $Cu(OAc)_2$ as the catalyst and di-tert-butyl peroxide (DTBP) as the oxidant, the Pan group demonstrated that α-acyloxy ethers could be prepared by an iron-catalyzed oxidative esterification reaction between ethers and carboxylic acids [27]. The Yuan group previously reported the first illustration of a $Cu(OAc)_2$-catalyzed formation of C-O bonds via oxidative cross-coupling reaction of aldehydes and ethers [28]. From a viewpoint of green chemistry, the transformation should be conducted under heterogeneous catalysis condition. In addition, the use of solid catalysts would counteract the possibility of the contamination of the expected products with hazardous metals.

Metal-organic frameworks (MOFs) are crystalline materials constructed from metal clusters and organic linkers [29-30]. The characteristics of MOFs could be controlled by combining different metal cations with varied organic components. In the relation with conventional porous materials, MOFs showed outstanding benefits based on the combination of remarkable characteristics of both inorganic and organic components [31-32]. Because of their topological structures and special physical properties, MOFs have demonstrated to be promising materials for potential applications in many fields, ranging from gas storage to catalysis [33-35]. The utilization of MOFs as heterogeneous catalysts has recently received significant attention [36-40]. Over the past 10 years, an increasing number of organic transformations have been performed in the presence of MOFs as heterogeneous catalysts [41-43]. As compared to several popular MOFs, copper-based organic frameworks (Cu-MOFs) with their unsaturated open copper metal sites previously exhibited high activity in various organic reactions [44]. In this work, we would like to describe the synthesis of α-acyloxy ethers via C-H activations of ethers and aldehydes utilizing the metal–organic framework $Cu_2(OBA)_2(BPY)$ as a productive heterogeneous catalyst. To the best of our knowledge, this reaction using heterogeneous catalyst was not previously mentioned in the literature.

Materials and Methods

2.1. Materials and instrumentation

All reagents and starting materials were purchased from Sigma-Aldrich and Acros, and used as received without further purification. X-ray powder diffraction (XRD) patterns were recorded using a Cu Kα radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a S4800 Scanning Electron Microscope (SEM). Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument. Transmission electron microscopy studies were performed using a JEOL JEM 1010 Transmission Electron Microscope (TEM) at 80 kV.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 µm). The temperature program for GC analysis held samples at 100 ^oC for 1 min; heated them from 100 to 280 ^oC at 10 ^oC/min; held them at 280 ^oC for 2 min. Inlet and detector temperatures were set constant at 280 ^oC. Diphenyl ether was used as an internal standard to calculate reaction conversions. GC-MS analyses were performed using a Hewlett Packard GC-MS 5972 with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5 µm). The temperature program for GC-MS analysis heated samples from 60 to 280 ^oC at 10 ^oC/min and held them at 280 ^oC for 10 min. Inlet temperature was set constant at 280 ^oC. MS spectra were compared with the spectra gathered in the NIST library.

2.2. Synthesis of $Cu_2(OBA)_2(BPY)$

In a typical preparation, firstly, a solid of H_2OBA (H_2OBA = 4,4'-oxybis(benzoic acid) (0.258 g, 1 mmol) was dissolved in a mixture of DMF (DMF = *N,N'*-dimethylformamide; 3 mL), and water (1 mL). Secondly, 4,4'-bipyridine (BPY) (0.078 g, 0.5 mmol) was dissolved in 3 mL DMF. Thirdly, $Cu(NO_3)_2.3H_2O$ (0.242 g, 1 mmol) was dissolved in a mixture of DMF (5 mL), and water (2 mL). The solution of H_2OBA and BPY were added in the solution of $Cu(NO_3)_2.3H_2O$. The suspension was stirred to achieve a homogeneous solution. The resulting solution was then distributed to three 8 mL vials. The vials were then heated at 80 ^oC in an isothermal oven for 24 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 mL) for 3 days. Solvent exchange was carried out with ethanol (3 x 10 mL) at room temperature for 3 days. The material was then evacuated under vacuum at 150 °C for 6 h, yielding 0.29 g of $Cu_2(OBA)_2(BPY)$ in the form of green crystals (75 % based on BPY).

2.3. Catalytic studies

In a typical experiment, a predetermined amount of the $Cu_2(OBA)_2(BPY)$ was added to the vial containing a mixture of benzaldehyde (0.053 g, 0.50 mmol), 1,4-dioxane (1.760 g, 20 mmol), *tert*-butyl hydroperoxide (TBHP) (5.0-6.0 M in decade, 0.18 g, 4 equivalents) as an oxidant, and diphenyl ether (0.085 g, 0.05 mmol) as an internal standard. The catalyst amount was calculated with respect to the copper/benzaldehyde molar ratio. The reaction mixture was stirred at 80 °C under an oxygen atmosphere for 24 h. Reaction yield was monitored by withdrawing aliquots from the reaction mixture at different time intervals, quenching with distilled water (1 mL). The organic components were then extracted into ethyl acetate (2 mL), dried over anhydrous Na_2SO_4, analyzed by GC with reference to diphenyl ether. The product identity was further confirmed by GC-MS. To investigate the recyclability of $Cu_2(OBA)_2(BPY)$, the catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of DMF and ethanol, dried 150 °C under vacuum in 2 h, and reused if necessary.

Results and Discussion

In this work, the $Cu_2(OBA)_2(BPY)$ was prepared from the reaction of copper nitrate trihydrate, 4,4’-oxybis(benzoic acid) and 4,4’-bipyridine via a solvothermal method, following a literature protocol. The copper-organic framework was subsequently characterized by using various analysis techniques. A highly sharp peak with 2*θ* of 7.0 was recorded on the XRD diffractogram, revealing that a crystalline framework was generated (Figure 1). FT-IR spectra indicated the presence of bonded carboxylate organic linkers and BPY ligand (Figure 2). SEM exploration indicated that the $Cu_2(OBA)_2(BPY)$ crystals exhibited a needle-shaped morphology (Figure 3). TEM image indicated a porous structure (Figure 4). Thermal gravimetric analysis (TGA) of activated $Cu_2(OBA)_2(BPY)$ shows high thermal stability (>250 ∘C).

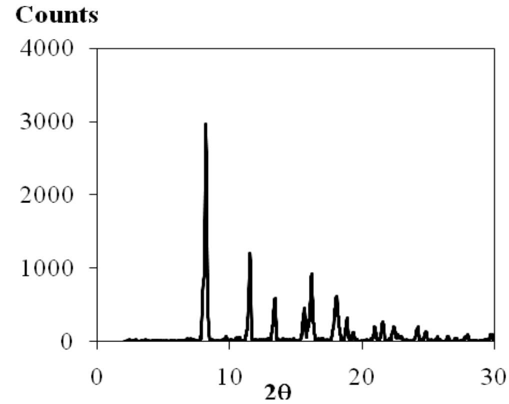


Figure 1: X-ray powder diffractograms of the $Cu_2(OBA)_2(BPY)$

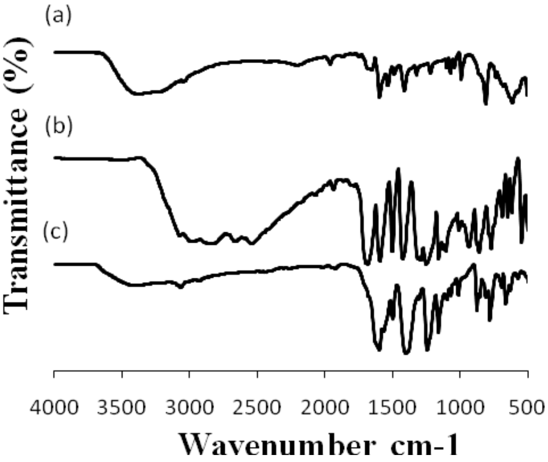


Figure 2: FT-IR spectra of 4,4’-bipyridine (a), 4,4’-oxybis(benzoic acid) (b) and the $Cu_2(OBA)_2(BPY)$ (c)

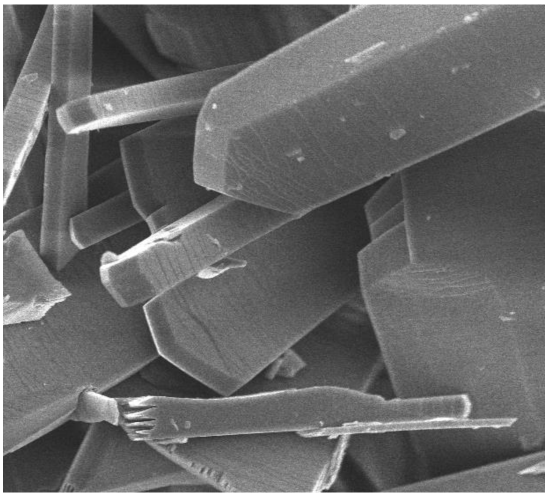


Figure 3: SEM micrograph of the $Cu_2(OBA)_2(BPY)$

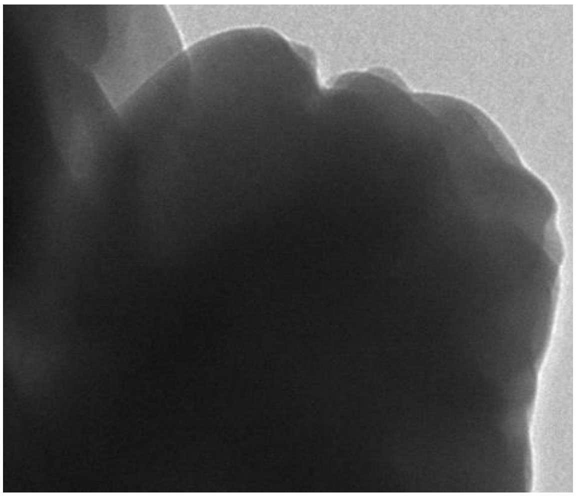
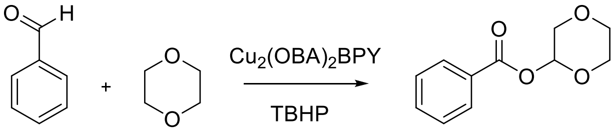


Figure 4: TEM of the $Cu_2(OBA)_2(BPY)$

The $Cu_2(OBA)_2(BPY)$ was tested as a heterogeneous catalyst for the oxidative esterification of benzaldehyde with 1,4-dioxane to form 1,4-dioxan-2-yl benzoate as the principal product (Scheme 1). Its structures were confirmed by ^1H NMR, and ^{13}C NMR.



Scheme 1: The coupling reaction of benzaldehyde and 1,4-dioxane using $Cu_2(OBA)_2(BPY)$ catalyst

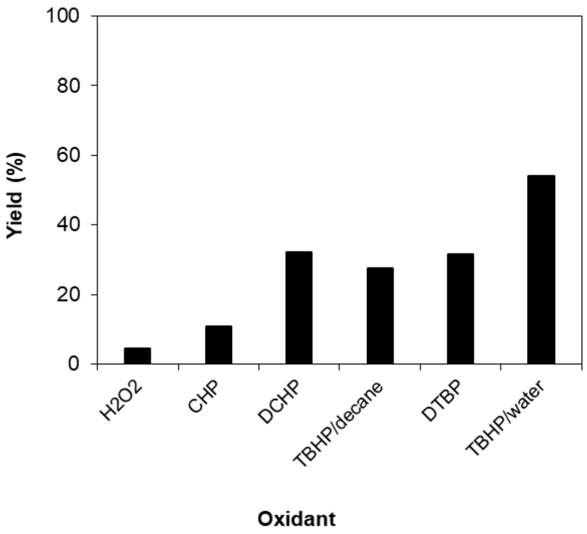


Figure 5: Effect of oxidant on reaction yield

Initial studies addressed the effect of different oxidants on the reaction yield. The coupling reaction was carried out at 140 °C, using 2 mol% $Cu_2(OBA)_2(BPY)$ as the catalyst, in the presence of 4 equivalents of different oxidants, including hydro peroxid (H_2O_2), cumyl hydroperoxide (CHP), dicumyl peroxide (DCHP), *tert*-butyl hydroperoxide in decane (TBHP/decane), di-*tert*-butyl peroxide (DTBP) and *tert*-butyl hydroperoxide in water (TBHP/water), respectively. Experimental results showed that TBHP/water should be the oxidant of choice for the $Cu_2(OBA)_2(BPY)$-catalyzed coupling reaction of benzaldehyde with 1,4-dioxane, affording more than 54% yield after 24 h. Almost no reaction yield was observed when using H_2O_2 as the oxidant. The reaction using CHP as the oxidant proceeded with significantly more difficulty, though 10% yield was still observed after 24 hours. DCHP, TBHP/decane, DTBP were found to be unsuitable for the reaction, with the reaction yields of 32, 27 % and 31%, respectively, being observed after 24 hours. These results could be rationalized based on the fact that the catalytically active copper sites on the Cu–MOF could be poisoned by small amount of water in the oxidants (Figure 5).

With this result in mind, the influence of different concentrations of the *tert*-butyl hydroperoxide in water (TBHP/water) on reaction yield was also investigated. The reaction was carried out at 140 °C, in the presence of 2 mol% $Cu_2(OBA)_2(BPY)$ catalyst, using 0, 2, 3, 4, 5, and 6 equivalents of TBHP/water as the oxidant, respectively. Experimental results revealed that the concentration of the TBHP/water exhibited a profound effect on the reaction yield. Indeed, it was found that almost no reaction yield was observed for the oxidative esterification of benzaldehyde with 1,4-dioxane in the absence of TBHP/water. As expected, increasing the oxidant concentration to 2 and 4 equivalents led to a dramatic enhancement in reaction yield, with 39% and 54% yields, respectively, being achieved after 24 hours. Noticeably, the reaction yield decreased significantly when using 5 and 6 equivalents of TBHP/water (Figure 6).

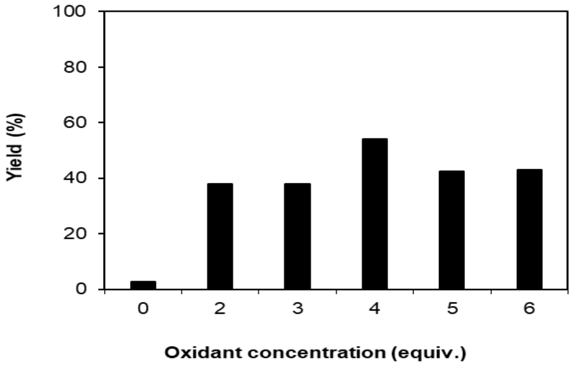


Figure 6: Effect of the TBHP equivalent on reaction yield

Another factor that must be discussed for the reaction between benzaldehyde and 1,4-dioxane to produce 1,4-dioxan-2-yl benzoate was the influence of temperature on the reaction yield. The coupling reaction was conducted using 2 mol% $Cu_2(OBA)_2(BPY)$ catalyst, in the presence of 4 equivalents of TBHP/water as the oxidant, at room temperature, 80 ^{o}C, 100 ^{o}C, 120 ^{o}C, and 140 ^{o}C, respectively. It was found that the reaction performed at 80 ^{o}C could lead to 80% yield after 24 h. As expected, there was no product formed at room temperature. Increasing the reaction temperature to 120 ^{o}C and 140 ^{o}C resulted in a significant drop in the reaction yield, with only 65% and 54 % yields being observed after 24 h.

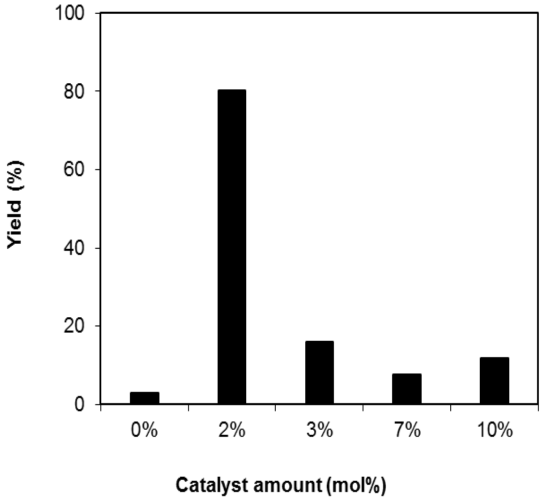


Figure 7: Effect of catalyst amount on reaction yield

One important factor that should be addressed in an investigation of the coupling reaction between benzaldehyde and 1,4-dioxane with $Cu_2(OBA)_2(BPY)$ as the catalyst is the catalyst amount. The catalyst amount, with respect to the copper content in the $Cu_2(OBA)_2(BPY)$, was studied in the range of 0mol% – 10mol% relative to benzaldehyde at a reaction temperature of 80 $^{\circ}$C. It was found that the coupling reaction afforded to more than 80% yield within 24 h with 2 mol% catalyst. Interestingly, increasing the catalyst concentration beyond 2 mol% resulted in a significant decrease in the reaction yield. It should be noted that almost no coupling reaction was detected in the absence of $Cu_2(OBA)_2(BPY)$, confirming the necessity of using the Cu–MOF as the catalyst for the coupling reaction (Figure 7).

For liquid-phase organic reaction, the possibility that some of catalytically active sites on the solid catalyst could dissolve into the solution during the course of the reaction might be a serious problem. Therefore, the transformation could proceed under either homogeneous or partially homogeneous catalysis conditions. In order to determine whether active copper species dissolved from the solid $Cu_2(OBA)_2(BPY)$ catalyst contributed to the yield of the coupling reaction between benzaldehyde and 1,4-dioxane, a control experiment was carried out using a simple centrifugation during the course of the reaction. Apparently, if the reaction yield was still recorded after the solid catalyst was separated from the reaction mixture, this behavior would verify that the coupling reaction actually occurred either under homogeneous or partially homogeneous catalysis conditions. The reaction was performed at 80 ^{o}C, using 2 mol% catalyst, in the presence of 4 equivalents of TBHP/water as the oxidant. The $Cu_2(OBA)_2(BPY)$ catalyst was removed from the reaction mixture after 12 h of reaction time by simple centrifugation. The liquid phase was then transferred to a new reactor vessel, stirred for an additional 12 h at 80 ^{o}C. It was noticed that no further reaction yield was recorded, verifying that the reaction only occurred in the presence of the solid $Cu_2(OBA)_2(BPY)$ catalyst (Figure 8).

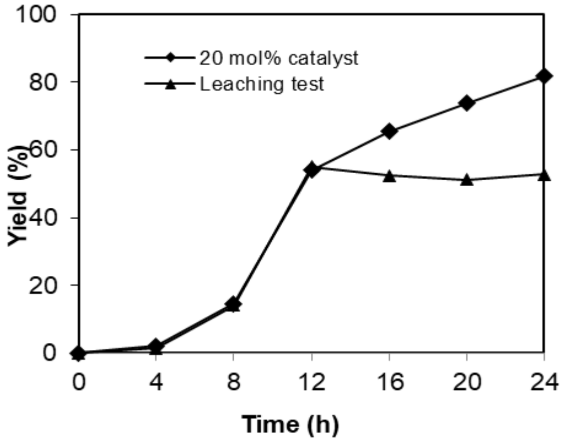


Figure 8: No donation from homogeneous catalysis to the generation of 1,4-dioxan-2-yl benzoate was detected

To clarify the benefit of using the $Cu_2(OBA)_2(BPY)$ as the heterogeneous catalyst for the oxidative esterification of benzaldehyde with 1,4-dioxane, the catalytic activity of $Cu_2(OBA)_2(BPY)$ was compared to that of many homogeneous catalysts, including

$FeCl_3.6H_2O$, $Fe_2(SO_4)_3$, $Cu(OAc)_2.H_2O$, $Cu(OAc)_2$, $CuCl_2.6H_2O$ and $Cu(NO_3)_2$. The coupling reaction was conducted at 80 °C, using 2 mol% catalyst, in the presence of 4 equivalents of TBHP/water as the oxidant. It was noted that copper salts demonstrated greater catalytic activity over the iron salts. $FeCl_3.6H_2O$ and $Fe_2(SO4)_3$ were found to be unsuitable as catalysts for the reaction, with the reaction yields of 9% and 10%, respectively, being observed after 24 hours. The Cu salts exhibited high catalytic activities for the reaction. The $Cu(OAc)_2.H_2O$-catalyzed coupling reaction could afford 81% yield after 24 h. Surprisingly, $Cu(OAc)_2$ was found to be less active with 65% yield being obtained after 24 hours. The reaction using $CuCl_2.6H_2O$ and $Cu(NO_3)_2$ as the catalysts proceeded with significantly more difficulty , with the reaction yields of 25% and 19%, respectively, being observed after 24 h. It was apparent that the coupling reaction occurred with higher yield in the presence of the $Cu_2(OBA)_2(BPY)$ catalyst, thus emphasizing the advantages of using this Cu-MOF as the catalyst. Although several homogeneous Cu salts exhibited reasonable activities for the coupling reaction of benzaldehyde with 1,4-dioxane, the use of $Cu_2(OBA)_2(BPY)$ is clearly advantageous for the reaction in terms of catalyst separation, recovery, and recycling (Table 1).

Table 1: Different homogeneous catalysts for the coupling reaction.

Entry	Catalyst	GC yield (%)
1	$Cu_2(OBA)_2(BPY)$	82
2	$Cu(NO_3)_2$	20
3	$Cu(OAc)_2$	66
4	$CuCl_2$	56
5	$FeCl_3$	9
6	$Fe_2(SO_4)_3$	11
7	ligand	-

The catalytic activity of $Cu_2(OBA)_2(BPY)$ in the coupling reaction of benzaldehyde with 1,4-dioxane to form 1,4-dioxan-2-yl benzoate was also compared to that of other heterogeneous catalysts, including Cu-MOF-74, Cu(OBA), MOF-235, $Fe_3O(BPDC)_3$ and $CuFe_2O_4$, respectively. These Cu-MOFs and $CuFe_2O_4$ were synthesized and characterized according to literature procedures. It was observed that Cu-MOFs were found to be more active than Fe-MOFs for the esterification reaction. Indeed, the reaction using $Fe_3O(BPDC)_3$ and MOF-235 proceeded with significantly difficulty, with reaction yields of 6% and 8% being observed after 24 h. Experimental results revealed that the $Cu_2(OBA)_2(BPY)$ exhibited significantly higher activity than other two Cu-MOFs, affording more than 81% yield after 24 h. The Cu(OBA) offered slightly lower catalytic activity for the coupling reaction as compared to the Cu-MOF-74, with only 65% yield being achieved after 24 h. Noticeably, the $CuFe_2O_4$ exhibited higher catalytic activity than Fe-MOFs for the reaction, with more than 59% yield being observed after 24 h, indicating the crucial role of copper sites for the oxidative esterification of benzaldehyde with 1,4-dioxane to form 1,4-dioxan-2-yl benzoate as the principal product (Table 2).

Table 2: Different heterogeneous catalysts for the coupling reaction.

Entry	Catalyst	GC yield (%)
1	$Cu_2(OBA)_2(BPY)$	82
2	Cu-MOF-74	74
3	Cu(OBA)	65
4	MOF-235	9
5	$Fe_3O(BPDC)_3$	7
6	$CuFe_2O_4$	59

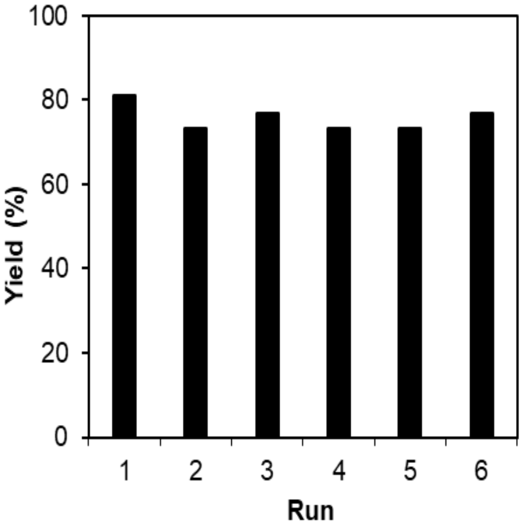


Figure 9: Catalyst recycling studies

For the development of more environmentally benign synthetic procedures, heterogeneous catalysts should offer advantages of the ease of recyclability and reusability. The $Cu_2(OBA)_2(BPY)$ catalyst was therefore investigated for recoverability and reusability in the coupling reaction between benzaldehyde and 1,4-dioxane over 6 successive runs, by repeatedly separating the Cu-MOF catalyst from the reaction mixture, washing it, and then reusing it. The coupling reaction was carried out at 80 ^{O}C, using 2 mol% catalyst, in the presence of 4 equivalents of TBHP/water as the oxidant. After that, the catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of DMF and ethanol, dried 150 ^{O}C under vacuum in 2 h, and reutilized. It was observed that the $Cu_2(OBA)_2(BPY)$ catalyst could be recovered and reused many times. Certainly, a yield of 77% was still achieved in the 6th run (Figure 9).

Conclusions

In conclusion, the $Cu_2(OBA)_2(BPY)$ was synthesized, and could be employed as a recyclable catalyst for the reaction between benzaldehye and 1,4-dioxane to form 1,4-dioxan-2-yl benzoate. High reaction yield of 82% to 21,4-dioxan-2-yl benzoate was obtained in the presence of 2 mol% $Cu_2(OBA)_2(BPY)$ catalyst, utilizing 4 equivalents of *tert*-butyl hydroperoxide (TBHP) in water at 80 ºC after 24 h. This Cu-MOF displayed superior catalytic productivity than other MOFs as well as homogeneous catalysts. This framework was reutilized six times for the transformation without a remarkable decline in catalytic activity. Heterogeneous catalysis was confirmed for the reaction utilizing the solid catalyst, and 1,4-dioxan-2-yl benzoate was not generated via the contribution of leached copper species.

Acknowledgements

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