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Expanding applications of copper-based metal–organic frameworks in catalysis: Oxidative C–O coupling by direct C–H activation of ethers over $Cu_2(BPDC)_2(BPY)$ as an efficient heterogeneous catalyst

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ABSTRACT

A crystalline porous metal–organic framework $Cu_2(BPDC)_2(BPY)$ was synthesized and characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) spectra, atomic absorption spectrophotometry (AAS), hydrogen temperature-programmed reduction (H_2-TPR), and nitrogen physisorption measurements. The Cu-MOF could be used as an efficient heterogeneous catalyst for the copper-catalyzed cross-dehydrogenative coupling reaction of ethers with 2-carbonyl-substituted phenols. The $Cu_2(BPDC)_2(BPY)$ exhibited significantly higher catalytic activity than that of other Cu-MOFs such as $Cu_3(BTC)_2$, Cu(BDC), and Cu(BPDC). The Cu-MOF also offered advantages over several copper salts such as $CuCl_2$, CuCl, CuI, $Cu(NO_3)_2$, and $Cu(OAc)_2$ in terms of the catalytic activity as well as the catalyst reusability. To the best of our knowledge, the cross-dehydrogenative coupling reaction of ethers with 2-carbonyl-substituted phenols via C–H activation under oxidative conditions using a heterogeneous catalyst was not previously mentioned in the literature.

1. Introduction

Transition metal-catalyzed cross-coupling reactions have attracted significant attention as a powerful method for the formation of carbon–carbon and carbon–heteroatom bonds [1–5]. Conventional approaches require the preparation of prefunctionalized starting materials, being a major concern from atom-economical and environmental aspects [6–8]. Apparently, the cross-dehydrogenative coupling reaction by the direct activation of C–H bonds would eliminate such drawbacks and thus could offer shorter and more efficient synthetic schemes [6,9]. Li and co-workers previously explored the homogeneous copper-catalyzed cross-dehydrogenative coupling via C–H activation under oxidative conditions to efficiently achieve C–C and C–X (X = O, N) bonds [6,7,10,11]. Recently, several homogeneous copper [10–13]-, iron [14–19]-, palladium [20–22]-, or ruthenium [23–27]-based catalysts have been employed for this transformation in the presence of oxidants such as organic peroxides, H_2O_2, and oxygen. Moreover, molecular iodine [28,29] and *N*-tetrabutylammonium iodide (*n*Bu_4NI) [30–33] have also been reported as efficient transition metal-free catalytic protocols for the cross-dehydrogenative couplings. In terms of green chemistry, more environmentally benign protocols should be investigated to improve the green credentials of the reaction [34]. For the development of greener processes, reactions using heterogeneous catalysts should be targeted in terms of the ease of handling, simple workup, recyclability, and reusability [35]. Furthermore, using solid catalysts also decreases contamination of the desired products with hazardous or harmful metals [36,37].

Metal–organic frameworks (MOFs) have recently emerged as promising materials for their potential applications in gas separation and storage, sensors and luminescence, drug storage and delivery, templated low-dimensional material preparation, and catalysis [38–43]. Although the application of MOFs in catalysis is a young research area, MOFs have been employed as solid catalysts or catalyst supports for a variety of organic transformations [44,45], ranging from carbon–carbon [46–51] to carbon–heteroatom [52–55] forming reactions. Among several popular MOFs, copper-based materials such as $Cu_3(BTC)_2$ [56–59] and Cu(BDC) [60,61] previously offered high activity in various organic transformations due to their unsaturated open copper metal sites. In this work, we wish to report a copper-catalyzed cross-dehydrogenative coupling reaction of ethers with 2-carbonyl-substituted phenols using $Cu_2(BPDC)_2(BPY)$ as an efficient heterogeneous catalyst. The $Cu_2(BPDC)_2(BPY)$ also offered significantly higher catalytic activity than that of other Cu-MOFs such as $Cu_3(BTC)_2$, Cu(BDC), and Cu(BPDC). Indeed, Kappe and co-workers have recently reported *the first example* of this transformation using $Cu(OAc)_2$ as a

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homogeneous catalyst [62]. To the best of our knowledge, the coupling reaction of ethers with 2-carbonyl-substituted phenols in the presence of a heterogeneous catalyst was not previously mentioned in the literature.

2. Experimental

2.1. Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 150 °C for 3 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 °C/min under a nitrogen atmosphere. 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). Transmission electron microscopy studies were performed using a JEOL JEM 1400 Transmission Electron Microscope (TEM) at 100 kV. The $Cu_2(BPDC)_2(BPY)$ sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with atomic absorption spectrophotometry (AAS) was performed on an AA-6800 Shimadzu. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pallets. The chemisorption experiments were studied in a Micromeritics 2020 analyzer. For hydrogen temperature-programmed reduction (H_2-TPR), the sample was outgassed at 100 °C for 30 min with helium, then cooled down to room temperature, and exposed to 50 ml/min of 10% H_2/Ar as the temperature ramped at 2.5 °C/min to 600 °C. The amount of hydrogen consumption was determined from TCD signal intensities, which were calibrated using an Ag_2O reference sample.

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 °C for 1 min, heated them from 100 to 180 °C at 40 °C/min, held them at 180 °C for 1 min, heated them from 180 to 280 °C at 50 °C/min, and held them at 280 °C for 2 min. Inlet and detector temperatures were set constant at 280 °C. *n*-Hexadecane 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 °C at 10 °C/min and held them at 280 °C for 2 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library.

2.2. Synthesis of the metal–organic framework $Cu_2(BPDC)_2(BPY)$

In a typical preparation, a solid mixture of H_2BPDC (H_2BPDC = 4,4′-biphenyldicarboxylic acid; 0.1039 g, 0.4 mmol), bpy (bpy = 4,4′-bipyridine; 0.033 g, 0.2 mmol), and $Cu(NO_3)_2 \cdot 3H_2O$ (0.105 g, 0.4 mmol) was dissolved in a mixture of DMF (DMF = *N,N′*-dimethylformamide; 30 ml), pyridine (0.3 ml), and methanol (3 ml). The resulting solution was stirred at 70 °C for 5 min and then distributed to four 20-ml vials. The vials were then heated at 120 °C 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 × 10 ml) for 3 days. Solvent exchange was carried out with methanol (3 × 10 ml) at room temperature for 3 days. The material was then evacuated under vacuum at 140 °C for 6 h, yielding 0.103 g of $Cu_2(BPDC)_2(BPY)$ in the form of blue crystals (67.5% based on copper nitrate).

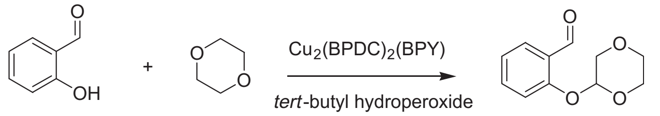
2.3. Catalytic studies

In a typical experiment, a mixture of 2-hydroxybenzaldehyde (0.143 ml, 1.0 mmol) and *n*-hexadecane (0.1 ml) as an internal standard in 1,4-dioxane (4 ml, 50 mmol) was added into a 25-ml flask containing the pre-determining amount of $Cu_2(BPDC)_2(BPY)$ catalyst and *tert*-butyl hydroperoxide (70 wt.% in water; 0.436 ml, 3.0 mmol) as an oxidant. The catalyst concentration was calculated with respect to the copper/2-hydroxybenzaldehyde molar ratio. The reaction mixture was stirred at 100 °C for 2 h. Reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, quenching with water (1 ml). The organic components were then extracted into diethyl ether (2 ml), dried over anhydrous Na_2SO_4, and analyzed by GC with reference to *n*-hexadecane. The product identity was further confirmed by GC–MS. To investigate the recyclability of $Cu_2(BPDC)_2(BPY)$, the catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of methanol, dried under air, and reused if necessary. For the leaching test, a catalytic reaction was stopped after 20 min, analyzed by GC, and centrifuged to remove the solid catalyst. The reaction solution was then stirred for a further 40 min. Reaction progress, if any, was monitored by GC as previously described.

3. Results and discussion

3.1. Catalyst synthesis and characterization

In this work, the $Cu_2(BPDC)_2(BPY)$ was synthesized in a yield of 67.5% by a solvothermal method, according to a modified literature procedure [63]. The material was then characterized by a variety of different techniques. The X-ray diffraction patterns of the $Cu_2(BPDC)_2(BPY)$ (Fig. S1) showed the presence of a sharp peak at $2\theta = 6°$, being consistent with the simulated pattern of single crystals previously reported by James and co-workers [63]. Elemental analysis by AAS indicated that a copper loading of 2.5 mmol/g was obtained. The SEM micrograph of the $Cu_2(BPDC)_2(BPY)$ revealed that well-shaped, high-quality cubic crystals were formed (Fig. S2). Moreover, the TEM observation showed that the $Cu_2(BPDC)_2(BPY)$ possessed a porous structure (Fig. S3). However, nitrogen physisorption measurements indicated a complicated pore structure for the $Cu_2(BPDC)_2(BPY)$. A pore size distribution of the $Cu_2(BPDC)_2(BPY)$ revealed two peaks in the range of 5–15 Å (using the Horvath–Kawazoe method) and another peak at a pore size between 15 Å and 50 Å (using the Dubinin–Astakhov method) (Fig. S4). A type I adsorption isotherm with a hysteresis loop was achieved for the $Cu_2(BPDC)_2(BPY)$. Langmuir surface areas of 1547 m^2/g were achieved for the material, as calculated from nitrogen adsorption–desorption isotherm data (Fig. S5). TGA result indicated that the material was stable up to over 300 °C (Fig. S6). FT-IR spectra of the $Cu_2(BPDC)_2(BPY)$ exhibited a significant difference as compared to those of the H_2BPDC and the BPY, showing the coordination of copper cations and organic linkers (Fig. S7). The H_2-TPR experiment revealed the nature of copper species within $Cu_2(BPDC)_2(BPY)$ structure. Two broad reduction peaks being at 340 °C and 410 °C could be attributed to the reduction of Cu^{2+} and Cu^{+} ions, respectively (Fig. S8). Although these assignments were previously reported in several copper-based catalytic systems



Scheme 1. The cross-dehydrogenative coupling reaction of 2-hydroxybenzaldehyde and 1,4-dioxane using $Cu_2(BPDC)_2(BPY)$ as a solid catalyst.

[64,65], further investigations would be needed to elucidate the nature of copper sites in the MOF structure.

3.2. Catalytic studies

The $Cu_2(BPDC)_2(BPY)$ was assessed for its catalytic activity in the cross-dehydrogenative coupling reaction by studying the coupling of 2-hydroxybenzaldehyde and 1,4-dioxane to form 2-(1,4-dioxan-2-yloxy)benzaldehyde as the principal product (Scheme 1). Initial studies addressed the effect of temperature on the reaction conversion, having carried out the coupling reaction at 5 mol% catalyst, using the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50, in the presence of three equivalents of *tert*-butyl hydroperoxide as an oxidant, at 80 °C, 90 °C, and 100 °C, respectively. Aliquots were withdrawn from the reaction mixture at different time intervals and analyzed by GC, giving kinetic data during the course of the reaction. It was found that the coupling reaction proceeded with difficulty at 80 °C, affording a conversion of only 15% after 120 min. As expected, increasing the temperature led to a significant enhancement in reaction rate. A conversion of more than 99% was achieved after 120 min for the reaction carried out at 90 °C. Furthermore, it was observed that the coupling reaction could proceed to quantitative conversion after 80 min at 100 °C (Fig. 1). Indeed, in the first example of the homogeneous copper-catalyzed coupling reaction of 2-hydroxybenzaldehyde and 1,4-dioxane, a full substrate conversion was achieved after 180 min at 100 °C [62].

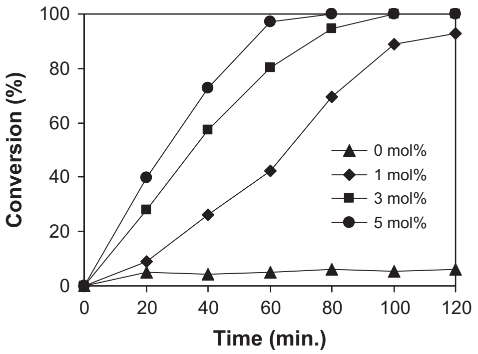


Fig. 2. Effect of catalyst concentration on reaction conversion.

With this result in mind, we then decided to investigate the effect of catalyst concentration on the reaction conversion. The reaction was carried out at 100 °C, using the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with 1 mol%, 3 mol%, and 5 mol% catalyst, respectively. It was found that the coupling reaction of 2-hydroxybenzaldehyde and 1,4-dioxane could proceed readily in the presence of a catalytic amount of the $Cu_2(BPDC)_2(BPY)$. Using 1 mol% catalyst, a reaction conversion was obtained after 120 min. As expected, when increasing the catalyst concentration from 1 mol% to 3 mol%, the reaction rate went up significantly, affording more than 99% conversion after 100 min. The reaction rate could be improved with qualitative conversion being achieved after 80 min for the reaction using 5 mol% catalyst (Fig. 2). It should be noted that almost no reaction occurred in the absence of the $Cu_2(BPDC)_2(BPY)$, indicating the necessity of using the Cu-MOF as catalyst for the cross-dehydrogenative coupling reaction. Indeed, Kappe and co-workers previously reported that the cross-dehydrogenative coupling reaction of 2-hydroxybenzaldehyde and 1,4-dioxane could occur readily in the presence of 5 mol% $Cu(OAc)_2$ catalyst [62]. In some other oxidative C–O coupling reactions by direct C–H activation, the copper catalyst concentration required for the reaction could vary from 1 mol% to 10 mol%, depending on the nature of the catalyst as well as that of the substrate. These reactions included the coupling of *N*,*N*-dialkylformamides with β-keto esters and 2-carbonyl-substituted phenols (1 mol% CuCl [66], 5 mol% $CuBr_2$ or 5 mol% $Cu(OAc)_2$ [8]), and the coupling of carboxylic acids with *N*,*N*-dialkylformamides (10 mol% $Cu(ClO_4)_2{\cdot}6H_2O$) [67]. The catalyst concentrations used for the cross-dehydrogenative coupling via C–H activation in this study were therefore comparable with those in the literature.

Another factor that should be considered for the cross-dehydrogenative coupling reaction using the $Cu_2(BPDC)_2(BPY)$ catalyst is the reagent molar ratio. The coupling of 2-hydroxybenzaldehyde with 1,4-dioxane could proceed under solvent-free condition, and a large excess of 1,4-dioxane should be required to act as the reaction medium. The reaction was carried out at 100 °C, using 3 mol% catalyst, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50, 1:37.5, and 1:25, respectively. It was found that decreasing the reagent molar ratio resulted in a drop in the reaction conversion. However, the reaction using 25 equivalents of 1,4-dioxane could still proceed to 95% conversion after 120 min, while this value could be improved to 98% for the case of 37.5 equivalents. Increasing the reagent molar ratio to 1:50 led to an enhancement in the reaction rate, affording more than 99% conversion after 100 min (Fig. 3). For organic transformations using a solid catalyst, reaction solvents could have a profound

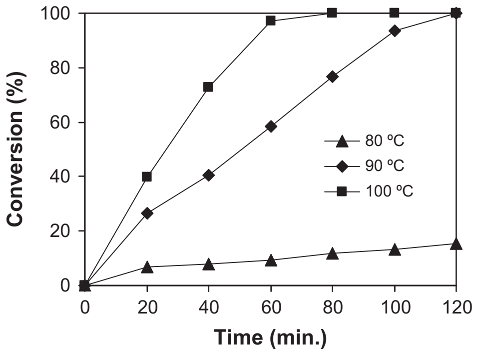


Fig. 1. Effect of temperature on reaction conversion.

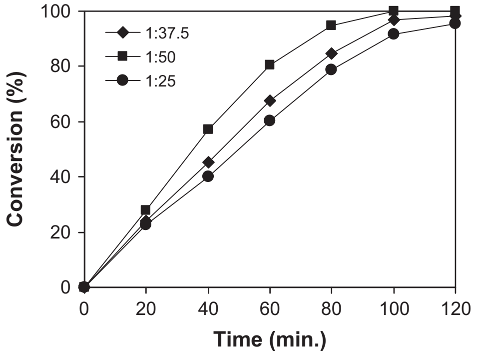


Fig. 3. Effect of reagent molar ratio on reaction conversion.

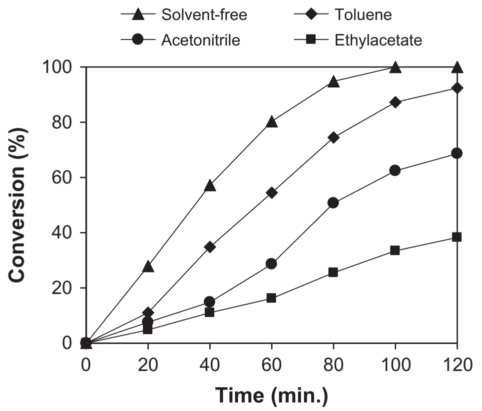


Fig. 4. Effect of co-solvent on reaction conversion.

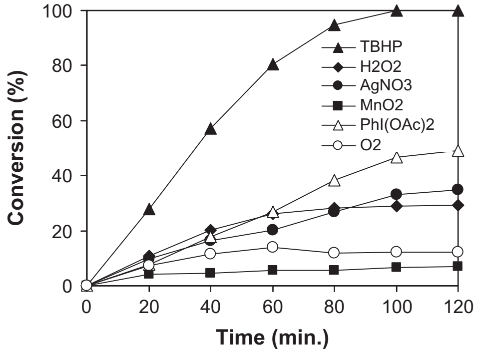


Fig. 5. Effect of oxidant on reaction conversion.

influence on the reaction rate, depending on the nature of the catalyst [68,69]. We therefore decided to investigate the effect of different co-solvents on the coupling reaction using the $Cu_2(BPDC)_2(BPY)$ catalyst. The reaction was carried out in the mixture of 1,4-dioxane and the co-solvent (1:1 by volume) at 100 °C, using 3 mol% catalyst, in the presence of three equivalents of *tert*-butyl hydroperoxide as an oxidant, with the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50. It was found that the reaction rate was decreased significantly in the presence of the co-solvent, confirming the advantages of the solvent-free condition. Indeed, reaction conversions of 92%, 68%, and 38% were observed after 120 min for the transformation carried out in the mixture of 1,4-dioxane and toluene, acetonitrile, and ethyl acetate, respectively (Fig. 4).

As for other cross-dehydrogenative coupling reaction by the direct activation of C–H bonds [6], the presence of at least one equivalent of an oxidant should be required for the coupling of 2-hydroxybenzaldehyde with 1,4-dioxane using the $Cu_2(BPDC)_2(BPY)$ catalyst. It was therefore decided to investigate the effect of different oxidants on the reaction conversion. The coupling reaction was carried out at 100 °C, using the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50, with 3 mol% catalyst, in the presence of three equivalents of an oxidant including *tert*-butyl hydroperoxide, hydrogen peroxide, $AgNO_3$, MnO_2, $PhI(OAc)_2$, and oxygen in air, respectively. Experimental results showed that *tert*-butyl hydroperoxide should be the oxidant of choice for the $Cu_2(BPDC)_2(BPY)$-catalyzed reaction of 2-hydroxybenzaldehyde with 1,4-dioxane, affording more than 99% conversion after 100 min. The reaction using $PhI(OAc)_2$ as the oxidant proceeded with significantly more difficulty, though 49% conversion was still observed after 120 min. Hydrogen peroxide, $AgNO_3$, MnO_2, and oxygen in air were found to be unsuitable for the coupling reaction, with a conversion of 29%, 34%, 7%, and 12%, respectively, being observed after 120 min (Fig. 5). Indeed, *tert*-butyl hydroperoxide was previously employed as the oxidant in the first example of the homogeneous copper-catalyzed coupling reaction of 2-hydroxybenzaldehyde and 1,4-dioxane [62]. Chang and co-workers previously used several oxidants for the cross-dehydrogenative coupling of *N*,*N*-dialkylformamides with β-keto esters and 2-carbonyl-substituted phenols and also showed that *tert*-butyl hydroperoxide offered significantly better performance than other oxidants [66].

Moreover, it was also found that the concentration of the *tert*-butyl hydroperoxide exhibited a profound influence on the reaction rate, having carried out the coupling reaction in the presence of one, two, and three equivalents of *tert*-butyl hydroperoxide as the oxidant, respectively. The coupling reaction using three equivalents of *tert*-butyl hydroperoxide could proceed to completion after 100 min, while 94% conversion was obtained after 120 min for the case of two equivalents. Decreasing the amount of the oxidant to one equivalent resulted in a drop in the reaction rate, with 79% conversion being observed after 120 min (Fig. 6). To verify the necessity of the oxidant in the cross-dehydrogenative coupling reaction between 2-hydroxybenzaldehyde and 1,4-dioxane, ascorbic acid or phloroglucinol as the antioxidant was added to the reaction mixture after the first 20 min. If the reaction conversion was not observed in the presence of the antioxidant, this behavior would indicate that the catalytically active metal sites could be poisoned or the radicals in the catalytic cycle could be decomposed. The coupling reaction was carried out at 100 °C, using 3 mol% catalyst, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50. After 20 min, 0.15 mol% of ascorbic acid as the antioxidant was then added to the reaction mixture, and the mixture was stirred for an additional 100 min at 100 °C with aliquots being sampled at different time intervals and analyzed by GC. It was found that the coupling reaction was significantly affected by the antioxidant. Similarly, adding phloroglucinol as the antioxidant to the reaction mixture also led to a dramatic drop in the reaction rate (Fig. 7). As the total amount of the copper was 20 times higher than that of the ascorbic acid or the phloroglucinol, it could be proposed that the reaction stopped owing to the interaction of the radicals in the catalytic cycle with the antioxidant. It should be noted that almost no reaction occurred in the absence of the $Cu_2(BPDC)_2(BPY)$ but with the presence of *tert*-butyl hydroperoxide, thus emphasizing the function of the copper sites in the catalytic cycle.

In order to check the possibility that the adsorption of the 2-(1,4-dioxan-2-yloxy)benzaldehyde product on the active copper sites in the $Cu_2(BPDC)_2(BPY)$ could hinder the reaction, a reaction

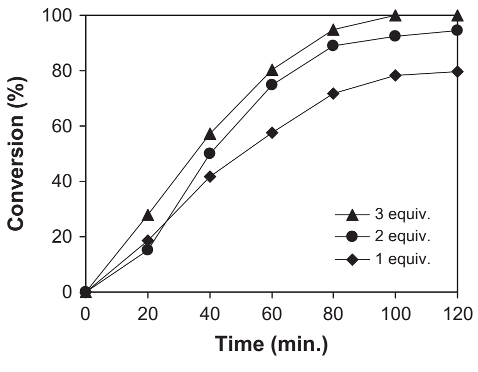


Fig. 6. Effect of oxidant concentration on reaction conversion.

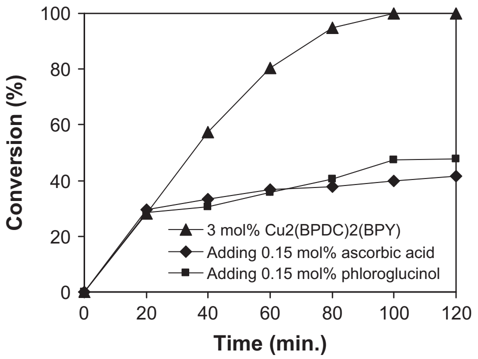


Fig. 7. Adding antioxidant to the reaction mixture after 20 min.

solution at 20% conversion of 2-hydroxybenzaldehyde was prepared and was then added into a second reaction mixture in the presence of 3 mol% $Cu_2(BPDC)_2(BPY)$ catalyst after 20 min. The resulting mixture was stirred for another 100 min at 100 °C, with aliquots being sampled at different time intervals, and analyzed by GC. Interestingly, it was found that the coupling reaction stopped immediately, indicating the inhibition role of the product. It should be noted that the coupling reaction using 3 mol% catalyst could proceed to completion after 100 min at 100 °C. In a second experiment, the $Cu_2(BPDC)_2(BPY)$-catalyzed coupling reaction was carried out for 40 min, affording 55% conversion. The solution at 20% conversion of 2-hydroxybenzaldehyde was then added, and the resulting mixture was stirred for another 80 min at 100 °C. It was also observed that adding product to the reaction mixture stopped the cross-dehydrogenative coupling between 2-hydroxybenzaldehyde and 1,4-dioxane immediately. Interestingly, adding the solution at 20% conversion of 2-hydroxybenzaldehyde to the $Cu(NO_3)_2$-catalyzed coupling reaction did not change the reaction rate significantly (Fig. 8). To further verify this observation, two controlled experiments were also carried out at 100 °C using 3 mol% catalyst, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50. In the first experiment, the pre-purified 2-(1,4-dioxan-2-yloxy)benzaldehyde product was added to the reaction mixture after 20 min. Experimental result showed that almost no further reaction was observed after the addition of the product to the reaction mixture. In the second experiment, the mixture of 2-hydroxybenzaldehyde and 1,4-dioxane (molar ratio of 1:50) was added to the reaction mixture after 20 min. It was observed that the addition of the substrates to the reaction mixture did not affect the reaction rate significantly (Fig. 9). These observations suggested that the adsorption of a large amount of the 2-(1,4-dioxan-2-yloxy)benzaldehyde product on the copper sites of the solid catalyst could inhibit the coupling reaction. However, the fact that the original reaction mixture could proceed to 100% conversion led us to believe that there would be an adsorption–desorption equilibrium during the course of the reaction. Indeed, Kholdeeva and co-workers previously employed MOF-based catalysts for the oxidation reaction and also reported similar observation, in which the reaction stopped completely after the product was added to the reaction mixture [70]. However, further studies on the adsorption–desorption equilibrium of the product on the Cu-MOF catalyst would be needed.

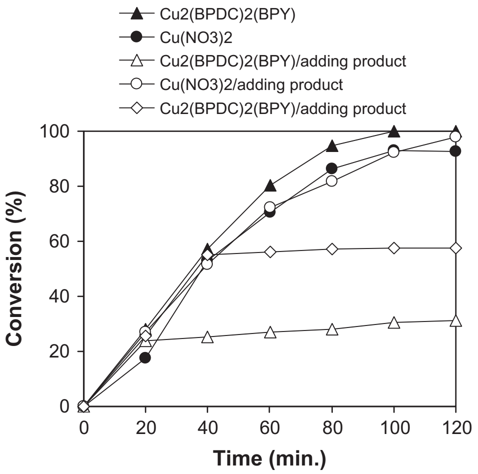


Fig. 8. Adding product to the reaction mixture when using $Cu_2(BPDC)_2(BPY)$ or $Cu(NO_3)_2$ as catalyst.

To clarify the advantages of using the $Cu_2(BPDC)_2(BPY)$ as catalyst for the cross-dehydrogenative coupling reaction, the catalytic activity of the $Cu_2(BPDC)_2(BPY)$ was compared with that of other Cu-MOFs, including $Cu_3(BTC)_2$, Cu(BDC), and Cu(BPDC). The coupling reaction was carried out at 100 °C, using 3 mol% catalyst, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50. Interestingly, it was found that the $Cu_2(BPDC)_2(BPY)$ could offer significantly higher activity than other three Cu-MOFs, with more than 99% conversion being achieved after 100 min. Although the well-known $Cu_3(BTC)_2$ previously exhibited high activity in several copper-catalyzed organic reactions [54,71–77], the cross-dehydrogenative coupling reaction using this Cu-MOF proceeded to only 48% conversion after 120 min. Ether cyclic solvents were previously reported to be able to coordinate with active copper centers in the $Cu_3(BTC)_2$, thus significantly blocking catalytically active sites [78]. Low conversions were also observed for the cross-dehydrogenative coupling reaction using Cu(BDC) or Cu(BPDC) as catalyst (Fig. 10). Indeed, Tannenbaum and co-workers previously proposed that the desolvated Cu(BDC) would possess a compact structure, and this phase could be converted into a lamellar form in solvents containing carbonyl groups such as DMF and NMP [79]. Similarly, Corma and co-workers also demonstrated that the transformation of Cu(BDC) from the catalytically inactive compact structure to the lamellar form upon DMF adsorption could generate the catalytically active phase [76]. In the cross-dehydrogenative coupling reaction between 2-hydroxybenzaldehyde and 1,4-dioxane, the Cu(BDC) structure would remain compact in excess 1,4-dioxane, thus offering lower activity. The performance of the Cu(PBDC) as catalyst in the cross-dehydrogenative coupling reaction could be explained based on similar reasons.

In the $Cu_2(BPDC)_2(BPY)$ structure, the BPDCs act as grid-forming ligands and the BPYs as pillars [63], thus preventing the formation of catalytically inactive compact structure. To gain insight into the

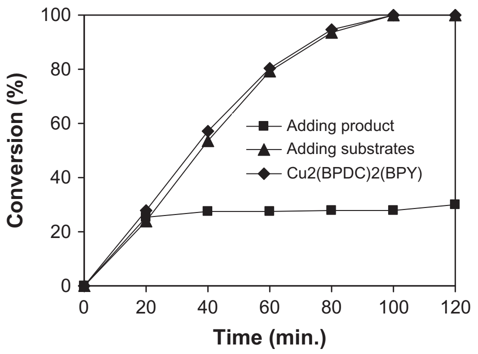


Fig. 9. Adding substrates to the reaction mixture using $Cu_2(BPDC)_2(BPY)$ as catalyst.

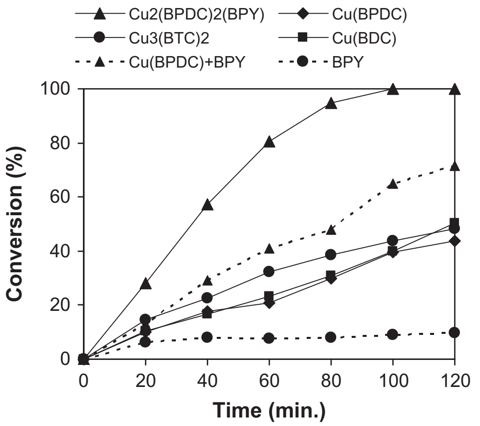


Fig. 10. Effect of different Cu-MOFs as catalyst on reaction conversion.

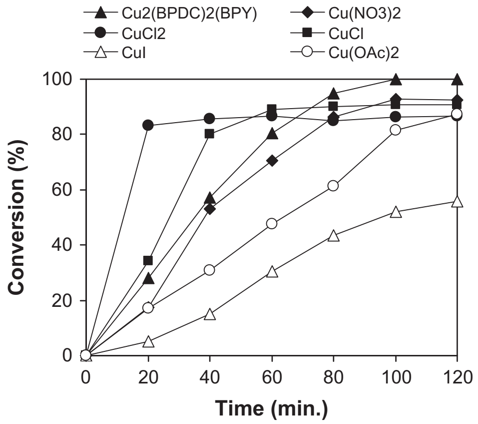


Fig. 11. Effect of different copper salts as catalyst on reaction conversion.

possible reasons for the higher activity of the $Cu_2(BPDC)_2(BPY)$ in comparison with other Cu-MOF catalysts, a controlled experiment was also carried out at 100 °C, using 3 mol% Cu(BPDC) and 1.5 mol% BPY ligand as the catalyst system, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50. Interestingly, it was observed that the presence of the BPY ligand in the reaction mixture led to an enhancement in the reaction rate, with 72% conversion being obtained after 120 min. It should be noted that the Cu(BPDC)-catalyzed coupling reaction afforded only 44% conversion after 120 min in the absence of the BPY ligand and that the BPY itself was inactive for the reaction. However, using Cu(BPDC) and BPY ligand (molar ratio of 2:1) as the catalyst system still offered lower activity for the coupling reaction than the case of the $Cu_2(BPDC)_2(BPY)$ (Fig. 10). It could be proposed that the combination of Cu(BPDC) and BPY ligand might produce $Cu_2(BPDC)_2(BPY)$ phase during the course of the coupling reaction [80], resulting in a medium catalytic performance. An amount of the BPY would not be coordinated with the Cu(BPDC); therefore, lower catalytic activity was observed as compared to that of the $Cu_2(BPDC)_2(BPY)$ [80,81]. However, further investigations would be necessary to elucidate the reaction mechanism of the $Cu_2(BPDC)_2(BPY)$-catalyzed cross-dehydrogenative coupling reaction of 2-hydroxybenzaldehyde with 1,4-dioxane.

To further emphasize the advantages of employing the $Cu_2(BPDC)_2(BPY)$ catalyst in the cross-dehydrogenative coupling reaction, we also carried out the reaction in the presence of several copper salts as catalyst, including $CuCl_2$, CuCl, CuI, $Cu(NO_3)_2$, and $Cu(OAc)_2$, respectively. The coupling reaction was carried out at 100 °C, using 3 mol% catalyst, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50. As expected, the $Cu(OAc)_2$-catalyzed coupling reaction could afford 87% conversion after 120 min. Interestingly, it was observed that higher conversions were obtained for the reaction using $CuCl_2$ or CuCl as catalyst for the first 60 min. However, the reaction did not proceed any further, and conversions of 86% and 90%, respectively, were observed after 120 min. The $Cu(NO_3)_2$-catalyzed coupling reaction could afford 92% conversion after 120 min, while CuI exhibited significantly lower activity, with 55% conversion being observed after 120 min (Fig. 11). The fact that the $Cu_2(BPDC)_2(BPY)$-catalyzed coupling reaction could proceed to completion after 100 min therefore would offer advantages over that using copper salts as catalyst.

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 reaction would not proceed under real heterogeneous catalysis condition [69]. In order to determine whether active copper species dissolved from the solid $Cu_2(BPDC)_2(BPY)$ catalyst contribute to the total conversion of the coupling reaction of 2-hydroxybenzaldehyde and 1,4-dioxane, a control experiment was carried out using a simple centrifugation during the course of the reaction. Apparently, if the reaction conversion was still observed after the solid catalyst was separated from the reaction mixture, this behavior would confirm that the reaction would not occur under real heterogeneous catalysis condition. The coupling reaction was carried out at 100 °C, using 3 mol% catalyst, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50. The $Cu_2(BPDC)_2(BPY)$ catalyst was removed from the reaction mixture after 20 min reaction time by simple centrifugation. The liquid phase was then transferred to a new reactor vessel, stirred for an additional 100 min at 100 °C with aliquots being sampled at different time intervals, and analyzed by GC. It was found that almost no further conversion was observed after the $Cu_2(BPDC)_2(BPY)$ catalyst was separated from the reaction mixture (Fig. 12). These observations would indicate that cross-dehydrogenative coupling reaction between 2-hydroxybenzaldehyde and 1,4-dioxane could only proceed in the presence of the solid $Cu_2(BPDC)_2(BPY)$ catalyst, and no contribution from catalytically active species soluble in the solution was detected.

Although several copper salts exhibited reasonable conversions in the coupling reaction between 2-hydroxybenzaldehyde and 1,4-dioxane, it was apparent that the catalyst could not be reused. For the development of more environmentally benign processes, the ability to recover and reuse the catalyst should be taken into

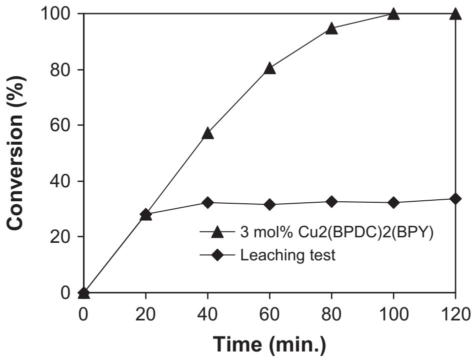


Fig. 12. Leaching test indicated no contribution from homogeneous catalysis of active species leaching into reaction solution.

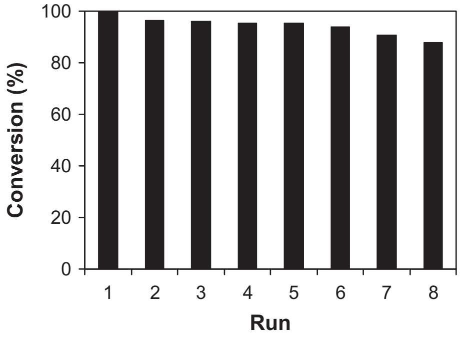


Fig. 13. Catalyst recycling studies.

accounts. It is expected that the solid catalyst can be separated from the reaction mixture and reused several times before it eventually deactivates completely. The $Cu_2(BPDC)_2(BPY)$ catalyst was therefore investigated for recoverability and reusability in the coupling reaction between 2-hydroxybenzaldehyde and 1,4-dioxane over eight 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 100 °C, using 3 mol% catalyst, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with the 2-hydroxybenzaldehyde:1,4-dioxane molar ratio of 1:50. After the coupling reaction was complete, the $Cu_2(BPDC)_2(BPY)$ catalyst was separated by simple centrifugation, then washed with copious amounts of methanol to remove any physisorbed reagents, and dried at room temperature under air. The recovered $Cu_2(BPDC)_2(BPY)$ was then reused in further reactions under identical conditions to those of the first run. It was observed that the $Cu_2(BPDC)_2(BPY)$ catalyst could be recovered and reused several times without a significant degradation in catalytic activity. Indeed, a conversion of 88% was still achieved in the 8th run (Fig. 13). The XRD result of the reused $Cu_2(BPDC)_2(BPY)$ catalyst indicated that the crystallinity of the Cu-MOF could be maintained during the course of the reaction (Fig. 14). Furthermore, the FT-IR spectra of the reused $Cu_2(BPDC)_2(BPY)$ showed a similar absorption as compared to that of the fresh catalyst (Fig. 15). These observations confirmed that the $Cu_2(BPDC)_2(BPY)$ catalyst offered excellent reusability in the coupling reaction between 2-hydroxybenzaldehyde and 1,4-dioxane.

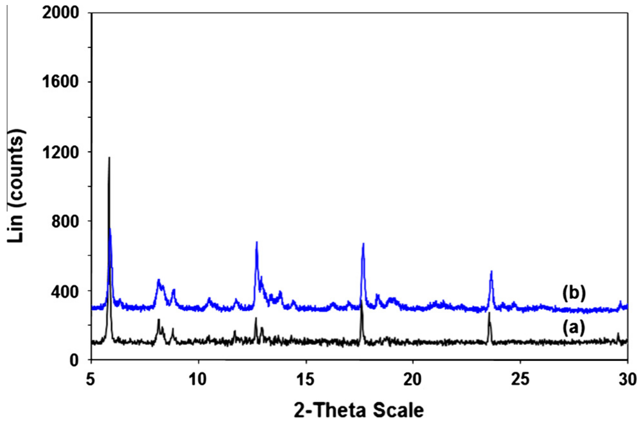


Fig. 14. X-ray powder diffractograms of the fresh (a) and reused (b) $Cu_2(BPDC)_2(BPY)$ catalyst.

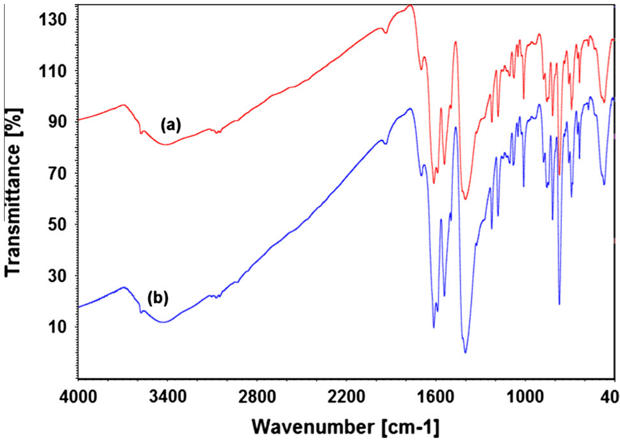


Fig. 15. FT-IR spectra of the fresh (a) and reused (b) $Cu_2(BPDC)_2(BPY)$ catalyst.

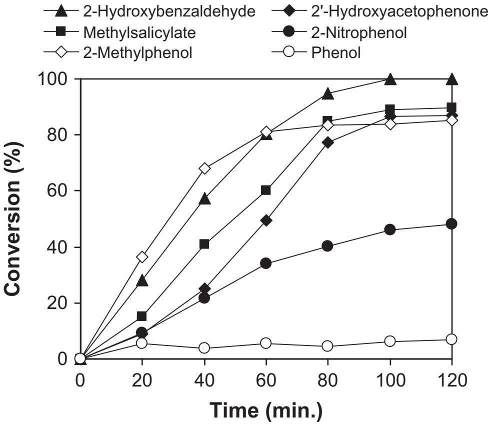


Fig. 16. Effect of different phenols on reaction conversion.

The study was then extended to the coupling reaction between different phenols with different ethers, respectively. In the first experiment series, the $Cu_2(BPDC)_2(BPY)$-catalyzed coupling reaction between 1,4-dioxane and 2-hydroxybenzaldehyde, methylsalicylate, 2-methylphenol, 2′-hydroxyacetophenone, 2-nitrophenol, and phenol, respectively, was carried out at 100 °C, using 3 mol% catalyst, in the presence of three equivalents of *tert*-butyl hydroperoxide as the oxidant, with the reagent molar ratio of 1:50. It was found that the phenol structure exhibited a profound effect on the coupling reaction. Phenol was almost unreactive in the $Cu_2(BPDC)_2(BPY)$-catalyzed coupling reaction with 1,4-dioxane, with only 7% conversion being observed after 120 min. The presence of a substituent at the *ortho* position led to a significant improvement in the reaction rate. Conversions of 48%, 85%, 87%, 90%, and more than 99% were obtained for the coupling reaction of 2-nitrophenol, 2-methylphenol, 2′-hydroxyacetophenone, methylsalicylate, and 2-hydroxybenzaldehyde, respectively (Fig. 16). These observations indicated the importance of the substituent at the *ortho* position in the phenol structure. However, further investigations would be needed to clarify the effect of the phenol structure on the coupling reaction. The coupling reaction between 2-hydroxybenzaldehyde and 1,4-dioxane, diethyl ether, dimethoxymethane, and tetrahydrofuran, respectively, was also investigated. Owing to the low boiling point of diethyl ether, dimethoxymethane, and tetrahydrofuran, the reaction was carried out at reflux temperature instead of 100 °C. As a sequence, the reaction resulted in significantly lower conversion than the case of 1,4-dioxane (Fig. 17).

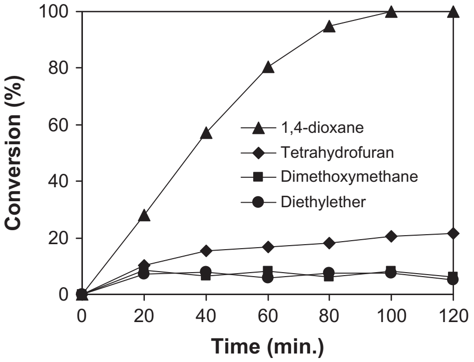


Fig. 17. Effect of different ethers on reaction conversion.

4. Conclusions

In summary, the metal–organic framework $Cu_2(BPDC)_2(BPY)$ was synthesized by a solvothermal method and was characterized by several techniques including XRD, SEM, TEM, FT-IR, TGA, AAS, H_2-TPR, and nitrogen physisorption measurements. The Cu-MOF could be used as an efficient heterogeneous catalyst for the copper-catalyzed cross-dehydrogenative coupling reaction of ethers with 2-carbonyl-substituted phenols. Excellent conversions were obtained in the presence of a catalytic amount of the Cu-MOF. The $Cu_2(BPDC)_2(BPY)$ exhibited significantly higher catalytic activity than that of other Cu-MOFs such as $Cu_3(BTC)_2$, Cu(BDC), and Cu(BPDC). The $Cu_2(BPDC)_2(BPY)$ also offered advantages over several copper salts such as $CuCl_2$, CuCl, CuI, $Cu(NO_3)_2$, and $Cu(OAc)_2$ in terms of the catalytic activity as well as the ability to recover and reuse the catalyst. The $Cu_2(BPDC)_2(BPY)$ could be recovered and reused several times without a significant degradation in catalytic activity. The cross-dehydrogenative coupling reaction could only occur in the presence of the solid Cu-MOF catalyst, and no contribution from leached copper sites present in the solution was detected. To the best of our knowledge, the cross-dehydrogenative coupling reaction of ethers with 2-carbonyl-substituted phenols via C–H activation under oxidative conditions using a heterogeneous catalyst was not previously mentioned in the literature.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.06.006.

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