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# Application of iron-based metal-organic frameworks in catalysis: Oxidantpromoted formation of coumarins using Fe<sub>3</sub>O(BPDC)<sub>3</sub> as an efficient heterogeneous catalyst

Thien N. Lieu, Khoa D. Nguyen, Dung T. Le, Thanh Truong<sup>\*</sup>, Nam T. S. Phan<sup>\*</sup>

Department of Chemical Engineering, HCMC University of Technology, VNU-HCM,

268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

\*Email: tvthanh@hcmut.edu.vn, ptsnam@hcmut.edu.vn

Ph: (+84 8) 38647256 ext. 5681 Fx: (+84 8) 38637504

#### Abstract

An iron-based metal-organic framework Fe<sub>3</sub>O(BPDC)<sub>3</sub> was synthesized, and was characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), atomic absorption spectrophotometry (AAS), and nitrogen physisorption measurements. The Fe-MOF could be used as an efficient heterogeneous catalyst for the synthesis of coumarins from salicylaldehydes and activated methylene compounds in the presence of *tert*-butyl hydroperoxide as the oxidant under base-free condition. The Fe<sub>3</sub>O(BPDC)<sub>3</sub> was more catalytically active for the synthesis of coumarins than other MOFs such as Cu<sub>2</sub>(BDC)<sub>2</sub>(BPY), Cu<sub>3</sub>(BTC)<sub>2</sub>, Cu<sub>2</sub>(BDC)<sub>2</sub>(DABCO), Ni<sub>2</sub>(BDC)<sub>2</sub>(DABCO), and Fe<sub>3</sub>O(BDC)<sub>3</sub>. This Fe-MOF also offered significantly higher catalytic activity for the transformation than that of common metal salts such as FeCl<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, FeSO<sub>4</sub>, CuCl<sub>2</sub>, CuCl, Cu(NO<sub>3</sub>)<sub>2</sub>, and Ni(NO<sub>3</sub>)<sub>2</sub>. The Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst could be recovered and reused several times without a significant degradation in catalytic

activity. To the best of our knowledge, the oxidant-promoted formation of coumarins under heterogeneous catalysis conditions was not previously mentioned in the literature.

Keywords: Metal-organic framework; coumarins; Fe<sub>3</sub>O(BPDC)<sub>3</sub>; heterogeneous catalyst; oxidant-promoted.

#### 1. Introduction

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Coumarins and their derivatives have emerged as important structural motifs in many pharmaceutical candidates, fragrances, cosmetics, food additives, agrochemicals, and molecular photonic devices [1, 2]. Classically, these structures could be synthesized by numerous methods, including the Pechmann condensation [3, 4], the Knoevenagel condensation [5, 6], the Perkin condensation [7], the Wittig reaction [8], and the Claisen rearrangement [9]. These approaches still suffer from some drawbacks such as drastic acidic or basic conditions, tedious manipulation, and lengthy work-up procedures [10]. Transition metal-catalyzed formation of coumarins and their derivatives was also reported. Kirai and Yamamoto previously demonstrated the synthesis of coumarins via the Cu(OAc)<sub>2</sub>-catalyzed hydroarylation reaction between arylpropionic acid methyl esters having a MOM-protected hydroxy group at the *ortho* position and arylboronic acids [11]. Alper and co-workers performed the Pd(OAc)<sub>2</sub>-catalyzed oxidative cyclocarbonylation of 2-vinylphenols to produce various coumarins in the presence of low pressures of CO, and air or 1,4- benzoquinone as the oxidant [12]. Iwasawa and co-workers pointed out that coumarins could be formed by the Pd(OAc)<sub>2</sub>-catalyzed direct carboxylation of alkenyl C-

H bonds of 2-hydroxystyrenes under atmospheric pressure of  $CO_2$  [13]. Recently, Shang and co-workers reported the synthesis of coumarins via FeCl<sub>3</sub>-catalyzed cascade reactions of salicylaldehydes and activated methylene compounds with or without using a base [14]. To develop greener protocols for the synthesis of coumarins in terms of the ease of handling, simple workup, recyclability and reusability, heterogeneous catalysts should be investigated.

Crystalline porous metal-organic frameworks (MOFs) have attracted significant attention in the last decade due to their potential applications in many fields, including energy technologies, gas storage, gas separation, sensors, optics, biomedicals, and catalysis [15-20]. Containing both organic linkers and metal ions in the frameworks, MOFs possess several interesting properties, such as well-defined structures, high surface areas, high porosity, structural diversity, the ability to tune the pore size, and the possibility to modify the surface hydrophobicity/hydrophilicity [15, 16, 21-28]. Although the application of MOFs in catalysis is relatively lagging behind the application in gas capture and storage, it is expected that organic transformations using MOFs as heterogeneous catalysts or catalyst supports would be extensively investigated in the near future [29-31]. Either the catalytically active sites could be present on the framework or they could be achieved via post-functionalization [30, 32-38]. During the last few years, a variety of MOFs have been explored for catalysis applications, including both carboncarbon [39-50] and carbon-heteroatom forming transformations [51-59]. The application of iron-based metal-organic frameworks in catalysis was previously mentioned in the literature, focusing on oxidation transformations [60-65]. In this work, we wish to report the synthesis of coumarins from salicylaldehydes and activated methylene compounds using the iron-based metal-organic framework Fe<sub>3</sub>O(BPDC)<sub>3</sub> as an efficient heterogeneous catalyst in the presence of an oxidant under base-free condition. To the best of our knowledge, the oxidant-promoted formation of coumarins under heterogeneous catalysis conditions was not previously mentioned in the literature.

#### 2. Experimental

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#### 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 K $\alpha$ radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a Hitachi S-4800 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1400 Transmission Electron Microscope (TEM) at 100 kV. The Fe<sub>3</sub>O(BPDC)<sub>3</sub> 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.

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  $\mu$ m). The temperature program for GC analysis held samples at 100 °C for 1 min; heated them from 100 to 280 °C at 40 °C/min; held them at 280 °C for 2 min. Inlet and detector temperatures were set constant at 280 °C. Diphenyl ether was used as an internal standard to calculate reaction conversions. GC-MS analyses were performed using a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25  $\mu$ m). The temperature program for GC-MS analysis held samples at 50 °C for 2 min; heated samples from 50 to 280°C at 10 °C/min and held them at 280 °C for 10 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library. The <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference.

# 2.2. Synthesis of the metal-organic framework Fe<sub>3</sub>O(BPDC)<sub>3</sub>

In a typical preparation, a solid mixture of H<sub>2</sub>BPDC (H<sub>2</sub>BPDC = biphenyl-4,4'dicarboxylic acid; 0.08g, 0.33mmol), acetic acid (CH<sub>3</sub>COOH; 0.4ml, 7mmol), and FeCl<sub>3</sub>·6H<sub>2</sub>O (0.1665g, 0.62mmol) was dissolved in DMF (DMF = N,N'dimethylformamide; 39 ml). The mixture was magnetically stirred for 1 h to achieve a clear solution. The resulting solution was then distributed in ten 8-ml vials. The vials were heated at 120 °C in an isothermal oven for 48 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed with DMF ( $3 \times 10$  ml) for three days. Solvent exchange was carried out with dichloromethane ( $3 \times 10$  ml) at room temperature for three days. The material was then dried at 120 °C for 24 h, and then at 150 °C for 2 h under vacuum, yielding 0.0755g of the Fe<sub>3</sub>O(BPDC)<sub>3</sub> as orange crystals (76 % based on H<sub>2</sub>BPDC).

#### 2.3. Catalytic studies

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In a typical experiment, a mixture of salicylaldehyde (0.122 g, 1 mmol), and diphenylether (0.1 ml, 0.8 mmol) as an internal standard in DMF (4 ml) was added into a 25 ml round bottom flask containing the Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst (0.015 g, 5 mol%). The catalyst loading was calculated with respect to the iron/salicylaldehyde molar ratio. The mixture was magnetically stirred for 3 min to disperse the Fe-MOF catalyst in the liquid phase. Methyl acetoacetate (0.348 g, 3 mmol) and tert-butyl hydroperoxide in water (0.032 g, 0.25 mmol) were then added. The resulting mixture was magnetically stirred at 60 °C for 3 h. Reaction yield was monitored by withdrawing aliquots from the reaction mixture at different time intervals, quenching with pure water (1 ml). The organic components were then extracted into ethyl acetate (2 ml), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, analyzed by GC with reference to diphenylether. The product identity was further confirmed by GC-MS, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. To investigate the recyclability of the Fe<sub>3</sub>O(BPDC)<sub>3</sub>, the catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of dichloromethane, activated under vacuum at 150 °C for 3 h, and reused if necessary. For the leaching test, a catalytic reaction was stopped after 60 min, analyzed by GC, and centrifuged to remove the solid

catalyst. The reaction solution was then stirred for a further 120 min. Reaction progress, if any, was monitored by GC as previously described.

#### 3. Results and discussion



Scheme 1. The synthesis of 3-acetylcoumarin from salicylaldehyde and methyl acetoacetate using Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst.

The iron-based metal-organic framework Fe<sub>3</sub>O(BPDC)<sub>3</sub> was synthesized according to a slightly modified literature procedure [66], and was characterized by several techniques, including XRD, SEM, TEM, TGA, FT-IR, AAS, and nitrogen physisorption measurements (Fig. S1 – Fig. S7). The Fe-MOF was assessed for its catalytic activity in the reaction of salicylaldehyde with methyl acetoacetate to form 3-acetylcoumarin as the principal product (Scheme 1). Initial studies addressed the effect of temperature on the yield of 3-acetylcoumarin. Shang and co-workers previously carried out the synthesis of coumarins via FeCl<sub>3</sub>-catalyzed cascade reactions of salicylaldehydes and activated methylene compounds at 80 °C [14]. Kittakoop and co-workers demonstrated that the same reaction using a tendon hydrolysate as an organocatalyst could occur at 50 °C, though the reaction time was extended to more than 24 h [67]. The reaction was then carried out at 5 mol% Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst in DMF for 180 min, using 3 equivalents of methyl acetoacetate and 0.75 equivalent of *tert*-butyl hydroperoxide as the oxidant, at

room temperature, 50, 60, 70, 80, 90, and 100 °C, respectively. It was observed that the reaction could not occur at room temperature, with no trace amount of 3-acetylcoumarin being detected while reactions at 50 °C afforded 45 % yields. Increasing the reaction temperature to 60 °C led to a significant enhancement in the reaction rate, with 75% GC yield being achieved after 180 min. Performing the reaction at higher temperature was found to be unnecessary as the yield of 3-acetylcoumarin was not improved any further (Fig. 1 and Fig. S8). It is noted that less than 2 % of other products in the reaction mixture according to GC and LC analysis, indicating the excellent reaction selectivity at tested conditions.

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Fig. 1. Effect of temperature on the reaction yield.

Effect of the catalyst concentration on the reaction yield was then kinetically investigated. The reaction was then carried out at 1 mol%, 3 mol%, and 5 mol%  $Fe_3O(BPDC)_3$  catalyst, respectively. It should be noted that only 6% yield was detected after 180 min in the absence of the  $Fe_3O(BPDC)_3$  catalyst, confirming the necessity of the Fe-MOF for the reaction of salicylaldehyde with methyl acetoacetate. The reaction using 1 mol%  $Fe_3O(BPDC)_3$  catalyst proceeded with difficulty, affording 48% yield after 180 min. The reaction yield could be improved to 64% in the presence of 3 mol%  $Fe_3O(BPDC)_3$  catalyst. Increasing the catalyst concentration to 5 mol% led to 75% yield 3-acetylcoumarin (Fig. 2). Previously, the FeCl<sub>3</sub>-catalyzed cascade reactions of salicylaldehydes and activated methylene compounds to form coumarins also required 5 mol% catalyst [14]. It was also observed that the amount of methyl acetoacetate exhibited a dramatic effect on the reaction yield. The  $Fe_3O(BPDC)_3$ -catalyzed reaction using 2 equivalents of methyl acetoacetate proceeded to only 60% yield, while only 34% yield was observed for the case of 1 equivalent of methyl acetoacetate (Fig. 3).





Fig. 2. Effect of catalyst concentration on the reaction yield.

Fig. 3. Effect of reagent molar ratio on the reaction yield.

As mentioned earlier, coumarins were classically synthesized under basic or acidic conditions. In this work, it was found that the Fe<sub>3</sub>O(BPDC)<sub>3</sub>-catalyzed reaction of salicylaldehyde with methyl acetoacetate to form 3-acetylcoumarin could be promoted by an oxidant under base-free condition. In order to investigate the impact of an oxidant on the transformation, the reaction was carried out using 0.125, 0.25, 0.75, and 1.5 equivalents of *tert*-butyl hydroperoxide as the oxidant, respectively. It should be noted that no reaction occurred in the absence of the oxidant with no trace amount of product being detected. Interestingly, experimental data indicated that the amount of the *tert*-butyl hydroperoxide as the oxidant. The reaction using 0.75

equivalent of *tert*-butyl hydroperoxide afforded 75% yield. Unexpectedly, increasing the amount of *tert*-butyl hydroperoxide led to a significant drop in the reaction rate, with only 62% yield being observed. It was found that the Fe<sub>3</sub>O(BPDC)<sub>3</sub>-catalyzed reaction of salicylaldehyde with methyl acetoacetate could proceed readily to 91% yield in the presence of 0.25 equivalent of *tert*-butyl hydroperoxide. However, using less than 0.25 equivalent of *tert*-butyl hydroperoxide resulted in only 64% yield (Fig. 4). These observations indicated that the oxidant would play an important role in the catalytic cycle for the formation of coumarins.



Fig. 4. Effect of oxidant concentration on the reaction yield.



Fig. 5. Effect of oxidant on the reaction yield.

Moreover, it was also found that the nature of the oxidant also exhibited a significant impact on the formation of coumarins. The reactions using various types of oxidants including hydrogen peroxide, *tert*-butyl hydroperoxide in water, *tert*-butyl hydroperoxide in decane, cumyl hydroperoxide, and  $K_2S_2O_8$  as the oxidant were carried out. It was found that hydrogen peroxide was not suitable for the Fe<sub>3</sub>O(BPDC)<sub>3</sub>-catalyzed reaction of salicylaldehyde with methyl acetoacetate, with only 11% yield being detected after 180 min. *Tert*-butyl hydroperoxide in decane was found to be significantly less active than *tert*-butyl hydroperoxide in water, affording only 64% yield for the reaction. It should be noted that the reaction using *tert*-butyl hydroperoxide in water as the oxidant could proceed to 91% yield. This could be rationalized based on the fact that using *tert*-

butyl hydroperoxide in decane would decrease the polarity of the reaction solvent. The reaction using cumyl hydroperoxide as the oxidant also proceeded with slower yield than that using *tert*-butyl hydroperoxide in water, though 72% yield was still observed after 180 min.  $K_2S_2O_8$  was found to be totally ineffective for the reaction, with no trace amount of 3-acetylcoumarin being detected (Fig. 5). Indeed, the oxidation of salicylaldehyde to its corresponding carboxylic acid as the by-reaction would be one of the reasons leading to these observations.



Fig. 6. Effect of ascorbic acid and TEMPO on the reaction yield.

To gain insights into the pathway of the Fe<sub>3</sub>O(BPDC)<sub>3</sub>-catalyzed reaction of salicylaldehyde with methyl acetoacetate, further mechanistic studies were carried out. The reaction was carried out at 60 °C in DMF for 180 min, using 3 equivalents of methyl acetoacetate, in the presence of 5 mol% Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst, with 0.25 equivalent of *tert*-butyl hydroperoxide as the oxidant. After the first 60 min reaction time with 49%

vield, 15 mol% of ascorbic acid as the antioxidant was added to the reaction solution. The resulting mixture was stirred for an additional 120 min at 60 °C with aliquots being sampled at different time intervals, and analyzed by GC. The reaction was stopped in the presence of the antioxidant, with no further 3-acetylcoumarin being produced. In a second experiment, 15 mol% of (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO), was introduced to the reaction mixture after the first 60 min. It was also observed that the transformation was significantly affected by the radical trapping reagent (Fig. 6). It could be proposed that the interaction of the radicals in the catalytic cycle with ascorbic acid or TEMPO would stop the transformation. In a third experiment, the reaction was carried out in the presence of pyridine as the catalyst poison. No reaction occurred in the presence of pyridine, with no trace amount of product being detected after 180 min. It should be noted that the reaction could not proceed in the absence of the  $Fe_3O(BPDC)_3$ catalyst, even when *tert*-butyl hydroperoxide was present in the reaction mixture. These observations would confirm the function of the iron sites in the catalytic cycle. With these mechanistic results, the tentative reaction route was proposed (Scheme 2). Specifically, Knoevenagel condensation of acidic carbon in 1,3-diketones with aldehyde resulted in  $\alpha$ ,  $\beta$ -unsaturated diketone [68]. Formation of *tert*-butoxide radical from TBHP under iron catalyst is well-known [69]. It was also reported that phenol derivative in the presence of alkoxide radical and iron catalyst was converted into phenoxide radical through hydrogen abstraction [70]. Subsequently, transesterification of phenoxide radical with ester functional group in starting material via sequential single electron transfer led to the formation of desired product [71].

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Scheme 2. Proposed reaction mechanism.

To further explore where the catalytic transformation occurred for the Fe<sub>3</sub>O(BPDC)<sub>3</sub>catalyzed reaction of salicylaldehyde with methyl acetoacetate, experiments using grinded Fe<sub>3</sub>O(BPDC)<sub>3</sub> were performed under identical conditions with aliquots being sampled at different time intervals, and analyzed by GC. Indeed, smaller size crystals normally exhibit higher catalytic activity due to the increased external surface of smaller crystals [72]. DLS analysis showed the particle size distribution of the catalyst, with a mean size of 35.8 µm and 25.6 µm being observed for the as-synthesized and the grinded Fe<sub>3</sub>O(BPDC)<sub>3</sub>, respectively (Fig. S9, Table S1). It was observed that slightly higher yields of 3-acetylcoumarin were obtained during the course of the reaction in the presence of the grinded  $Fe_3O(BPDC)_3$  as catalyst, though the difference was not significant. Serri and co-workers previously reported that Fe<sub>3</sub>O(BPDC)<sub>3</sub> possessed 1D channels of  $10 \times 11$  Å<sup>2</sup> along c axis [66]. In addition, based on MM2 calculation, the 3acetylcoumarin has the size of  $4 \times 9$  Å<sup>2</sup>. Furthermore, pore flexibility in MOFs upon temperature and guest molecules has been previously mentioned in the literature [73]. These observations would suggest that the Fe<sub>3</sub>O(BPDC)<sub>3</sub>-catalyzed reaction of salicylaldehyde with methyl acetoacetate to form 3-acetylcoumarin would occur inside the cavities as well as on the external surface of the Fe-MOF. However, further studies would be necessary to elucidate the issue.



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Fig. 7. Reactions with grinded Fe<sub>3</sub>O(BPDC)<sub>3</sub>.

Reaction solvents could have a profound impact on the rate of many organic transformations using solid catalysts, depending on the nature of the catalyst [74, 75]. Shang and co-workers previously carried out the synthesis of coumarins via FeCl<sub>3</sub>-catalyzed cascade reactions of salicylaldehydes and activated methylene compounds in several solvents, and pointed out that ethanol was the solvent of choice for the transformation [14]. We therefore decided to investigate the effect of different solvents on the Fe<sub>3</sub>O(BPDC)<sub>3</sub>-catalyzed reaction of salicylaldehyde with methyl acetoacetate to

form 3-acetylcoumarin. In particular, DMF, DEF, DMAc, DMSO, 1,4-dioxane, acetonitrile, dichloromethane, toluene, and ethanol were subsequently employed. Interestingly, it was found that all DMAc, DMSO, 1,4-dioxane, acetonitrile, dichloromethane, toluene, and ethanol were totally ineffective for the reaction, with no trace amount of 3-acetylcoumarin being detected after 180 min. DEF was also found to be unsuitable for the reaction, affording only 19% yield after 180 min. Among these solvents, DMF exhibited the best performance, with 91% yield being achieved after 180 min. We also tried to increase the polarity of the solvent by adding water to the system. However, the reaction carried out in the mixture of DMF/water proceeded with lower yield, producing 3-acetylcoumarin in 58% and 49% yields for the case of 95/5 and 90/10 (v/v) DMF/water system (Fig. 8).



Fig. 8. Effect of solvent on the reaction yield.

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To emphasize the significant benefit of using the  $Fe_3O(BPDC)_3$  as catalyst, the catalytic activity of the Fe<sub>3</sub>O(BPDC)<sub>3</sub> was compared with that of other MOFs, including MIL-100(Fe),  $Fe_3O(BDC)_3$ ,  $Cu_2(BDC)_2(BPY)$ ,  $Cu_3(BTC)_2$ ,  $Cu_2(BDC)_2(DABCO)$ , and Ni<sub>2</sub>(BDC)<sub>2</sub>(DABCO). The reaction was carried out in DMF at 60 °C for 180 min, using 3 equivalents of methyl acetoacetate, in the presence of 5 mol% MOFs catalyst, with 0.25 equivalent of *tert*-butyl hydroperoxide as the oxidant. It was found that the reaction using Fe<sub>3</sub>O(BDC)<sub>3</sub> catalyst proceeded to 56% yield after 180 min, while 91% yield was achieved for the case of  $Fe_3O(BPDC)_3$ . MIL-100(Fe) was found to be less active for the transformation than  $Fe_3O(BPDC)_3$ , though 79% yield of 3-acetylcoumarin was still obtained. Other MOFs offered lower cataytic activity for the reaction than Fe-MOFs. Indeed, 51%, 45%, and 42% yields were obtained after 180 min for the reaction using  $Cu_2(BDC)_2(BPY)$ ,  $Cu_3(BTC)_2$  $Cu_2(BDC)_2(DABCO)$ , respectively. and Ni<sub>2</sub>(BDC)<sub>2</sub>(DABCO) exhibited no catalytic activity for the transformation, with no trace amount of product being detected after 180 min (Table 1). To further highlight the advantages of the approach, the catalytic activity of the Fe<sub>3</sub>O(BPDC)<sub>3</sub> was also compared with that of several metal salts, including FeCl<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, FeSO<sub>4</sub>, CuCl<sub>2</sub>, CuCl,  $Cu(NO_3)_2$ , and Ni(NO<sub>3</sub>)<sub>2</sub>. The reaction using  $Cu(NO_3)_2$  as catalyst afforded 22% yield after 180 min, while less than 5% yields were detected for that using FeCl<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>,  $FeSO_4$ ,  $CuCl_2$ ,  $CuCl_3$ , and  $Ni(NO_3)_2$  (Fig. 9). Indeed, Shang and co-workers previously carried out the synthesis of coumarins via FeCl<sub>3</sub>-catalyzed cascade reactions of salicylaldehydes and ethyl acetoacetate, and reported that the presence of  $Na_2CO_3$  as a

base was necessary for the transformation, though the base was not employed for the case of other activated methylene compounds [14].

Table 1. Reactivity of other MOFs for 3-acetylcoumarin synthesis under optimized conditions <sup>a</sup>.

MOFs	Metal content	BET	Pore volume	CC Viold	
	(%)	$(m^2/g)$	(cm <sup>3</sup> /g)	GC Heiu	
Fe <sub>3</sub> O(BPDC) <sub>3</sub> (MIL-126)	16.2	1641	0.655	91	
Fe <sub>3</sub> O(BDC) <sub>3</sub> (MOF-235)	25.3 [76]	540 [76]	0.359[76]	56	
FeBTC (MIL-100)	21.29	876	0.41	79	
Cu <sub>2</sub> (BDC) <sub>2</sub> (DABCO)	22.53	1085 [77]	0.529 [77]	42	
Cu <sub>2</sub> (BDC) <sub>2</sub> (BPY)	20.83	447.82 [78]	0.232 [78]	51	
Cu <sub>3</sub> (BTC) <sub>2</sub> (MOF-199)	29.5 [79]	1507 [80, 81]	0.41 [82]	45	
Ni <sub>2</sub> (BDC) <sub>2</sub> (DABCO)	21.06	1474 [83]		<2	

<sup>a</sup> Kinetic studies of reactions using these catalysts were placed in Supporting Information (Fig. S8)



Fig. 9. Different homogeneous catalysts for the synthesis of 3-acetylcoumarin.

With these results in mind, we then carried out the leaching test to confirm if the catalysis of active iron species leached from the solid Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst, if any, could contribute to the total yield of the reaction between salicylaldehyde and methyl acetoacetate to form 3-acetylcoumarin. In many cases, the leached species from the solid catalyst could contribute significantly to the reaction, and therefore the reaction would not proceed under real heterogeneous catalysis conditions [75]. A control experiment was carried out using a simple centrifugation during the course of the reaction. Apparently, if more product was formed after the solid catalyst was separated from the reaction mixture, this observation would indicate that there should be contribution from homogeneous catalysis. The reaction was carried out under optimized condition. After the first 60 min

reaction time, with 49% yield being detected, the Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst was removed from the reaction mixture by simple centrifugation. The liquid phase was then transferred to a new reactor vessel, and magnetically stirred for an additional 120 min at 60 °C with aliquots being sampled at different time intervals, and analyzed by GC. Experimental results showed that the formation of 3-acetylcoumarin could not proceed after the Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst was separated from the reaction mixture, and 91% yield of 3acetylcoumarin was owing to the heterogeneous catalysis (Fig. 10).



Fig. 10. Leaching test indicated no contribution from homogeneous catalysis of active species leaching into reaction solution.

One of the issues that should be seriously addressed for organic reactions carried out under heterogeneous catalysis conditions is the ability to recover and reuse the catalyst. It would be expected that the solid catalyst could be reused several times for the transformation before it lost activity completely. The Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst was therefore

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investigated for recoverability and reusability in the reaction between salicylaldehyde and methyl acetoacetate to form 3-acetylcoumarin over six successive runs, by repeatedly separating the Fe-MOF catalyst from the reaction mixture, washing it and then reusing it. The reaction was carried out in DMF at 60 °C for 180 min, using 3 equivalents of methyl acetoacetate, in the presence of 5 mol% Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst, with 0.25 equivalent of tert-butyl hydroperoxide as the oxidant. After 180 min reaction time with 91% yield of 3acetylcoumarin being achieved, the Fe-MOF catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of dichloromethane to remove any physisorbed reagents, activated under vacuum at 150 °C for 3 h, and reused in further reactions under identical conditions to those of the first run. It was found that the  $Fe_3O(BPDC)_3$  catalyst could be recovered and reused several times for the reaction between salicylaldehyde and methyl acetoacetate to form 3-acetylcoumarin without a significant degradation in catalytic activity. Indeed, 94% yield of 3-acetylcoumarin was still achieved in the 6<sup>th</sup> run (Fig. 11). As compared to the FT-IR spectra of the fresh Fe<sub>3</sub>O(BPDC)<sub>3</sub>, similar absorption was observed for the 4<sup>th</sup> used Fe-MOF catalyst (Fig. S11). The XRD result of the the 2<sup>nd</sup> and the 4<sup>th</sup> used Fe<sub>3</sub>O(BPDC)<sub>3</sub> revealed that the crystallinity of the Fe-MOF catalyst could be maintained, though slight difference in the diffractogram was detected (Fig. S12).



Fig. 11. Catalyst recycling studies.

Table 2. The formation of several coumarins containing different substituents in the presence of Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst.



R1= -CI, -OH, -OCH<sub>3</sub>, -NO<sub>2</sub> R2= -CH<sub>3</sub>, -C<sub>6</sub>H<sub>5</sub>, -OCH<sub>3</sub> R3= -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>

Fe <sub>3</sub> O(BPDC) <sub>3</sub>				
TBHP in water				
	60 - 80 °C. 3-9 h			



Entry	Salicylaldehydes	1,3-Diketones	Products	Yields (%) <sup>a</sup>
1	СНО			89
2	СІСНООН		CI	94 <sup>b</sup>



<sup>a</sup> Reaction conditions: aldehyde (1 mmol), methyl acetoacetate (3 mmol), *tert*-butyl hydroperoxide (70% in water) (0.25 eqv.),  $Fe_3O(BPDC)_3$  (5 mol%), DMF (4 ml), 60 -80 °C, 3 - 9 h in open air, isolated yield. See Supporting Information for details. <sup>b</sup> GC yield due to poor separation.

The scope of this work was also expanded to the formation of several coumarins containing different substituents in the presence of Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst. The reaction

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was carried out in DMF at 60 °C for 180 min, using the reagent molar ratio of 1:3, in the presence of 5 mol%  $Fe_3O(BPDC)_3$  catalyst, with 0.25 equivalent of *tert*-butyl hydroperoxide as the oxidant. In the first series of experiments, we carried out the reaction between methyl acetoacetate and different salicylaldehyde derivatives, including salicylaldehyde. 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 5nitrosalicylaldehyde, 5-methoxysalicylaldehyde, and 4-methoxysalicylaldehyde, respectively. The product was purified by column chromatography using ethyl acetate/*n*hexane (2/1, v/v) mixture. The Fe<sub>3</sub>O(BPDC)<sub>3</sub>-catalyzed reaction of salicylaldehyde with methyl acetoacetate could afford 3-acetylcoumarin in 89% isolated yield after 180 min. It was observed that the presence of a substituent in salicylaldehyde decreased the yield of the transformation. However, by increasing the temperature and the reaction time, high yields of the desired products were achieved (See Supporting Information for details). Furthermore, the reaction of salicylaldehyde with ethyl acetoacetate using  $Fe_3O(BPDC)_3$ catalyst was also studied under the same reaction condition. Ethyl acetoacetate was found to be less reactive in this transformation, with 80% isolated yield of 3-acetylcoumarin being achieved after 180 min. Dimethyl malonate was also tested in the Fe<sub>3</sub>O(BPDC)<sub>3</sub>catalyzed transformation, affording methyl 2-oxo-2H-chromene-3-carboxylate in a yield of 28% after 180 min. It was found that the reaction between salicylaldehyde and methyl 3-oxo-3-phenylpropanoate using Fe<sub>3</sub>O(BPDC)<sub>3</sub> catalyst could proceed to 44% yield of 3benzoylcoumarin after 180 min (Table 2).

### 4. Conclusions

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In summary, the iron-based metal-organic framework  $Fe_3O(BPDC)_3$  was synthesized by a solvothermal method, and was characterized by several techniques including XRD, SEM, TEM, FT-IR, TGA, AAS, and nitrogen physisorption measurements. The Fe-MOF could be used as an efficient heterogeneous catalyst for the synthesis of coumarins from salicylaldehydes and activated methylene compounds in the presence of *tert*-butyl hydroperoxide as the oxidant. The transformation could proceed readily in the presence of a catalytic amount of the Fe-MOF without using a base. The Fe<sub>3</sub>O(BPDC)<sub>3</sub> was more catalytically active for the synthesis of coumarins than other MOFs such as  $Cu_2(BDC)_2(BPY)$ ,  $Cu_3(BTC)_2$ ,  $Cu_2(BDC)_2(DABCO)$ , Ni<sub>2</sub>(BDC)<sub>2</sub>(DABCO), and Fe<sub>3</sub>O(BDC)<sub>3</sub>. This Fe-MOF also exhibited significantly higher activity for the transformation than that of common metal salts such as FeCl<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, FeSO<sub>4</sub>, CuCl<sub>2</sub>, CuCl,  $Cu(NO_3)_2$ , and  $Ni(NO_3)_2$ . The coumarin formation could only be detected in the presence of the solid  $Fe_3O(BPDC)_3$  catalyst, and the contribution of leached active iron species, if any, was negligible. The Fe-MOF catalyst could be recovered and reused several times for the synthesis of coumarins from salicylaldehydes and activated methylene compounds without a significant degradation in catalytic activity. The fact that this transformation could proceed under heterogeneous and base-free conditions should be of advantages, and might be interested to the chemical industry.

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# Application of iron-based metal-organic frameworks in catalysis: Oxidant-

promoted formation of coumarins using Fe<sub>3</sub>O(BPDC)<sub>3</sub> as an efficient heterogeneous

catalyst

Thien N. Lieu, Khoa D. Nguyen, Dung T. Le, Thanh Truong<sup>\*</sup>, Nam T. S. Phan<sup>\*</sup>

Department of Chemical Engineering, HCMC University of Technology, VNU-HCM,

268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

\*Email: tvthanh@hcmut.edu.vn, ptsnam@hcmut.edu.vn

Ph: (+84 8) 38647256 ext. 5681

Fx: (+84 8) 38637504

