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Claisen–Schmidt Condensation Catalyzed by Metal-Organic Frameworks

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Abstract: Metal-organic framework [Fe(BTC) (BTC = 1,3,5-benzenetricarboxylic acid)] is a convenient heterogeneous catalyst for the carbon-carbon bond forming reaction in toluene between acetophenone and benzaldehyde to give selectively chalcone in high yield. Fe(BTC) appears as a general catalyst able to synthesize selectively different chalcone derivatives bearing various functionalities. Fe(BTC) could be recycled with no significant loss of catalytic efficiency and crystallinity in subsequent runs.

Keywords: chalcones; Claisen–Schmidt condensation; green chemistry; heterogeneous catalysis; metal-organic frameworks

Introduction

The Claisen–Schmidt reaction is the aldol condensation between an aromatic aldehyde and a ketone leading to carbon-carbon bond formation yielding a conjugated enone as the final product.[1] The most studied example of the Claisen–Schmidt condensation is the reaction of benzaldehydes with acetophenones to form chalcones (1,3-diarylpropenones). Chalcone and its derivatives have gained increasing attention due to numerous pharmacological applications such as anticancer,[2] anti-inflammatory,[3] nitric oxide regulation[4] and antihyperglycemic agents.[5] The Claisen–Schmidt reaction requires the use as catalyst of Lewis acids or bases, frequently in over stoichiometric amounts. Typically, work-up of the reaction mixture requires neutralization of the acid or base leading to the formation of large amounts of waste. Even though homogeneous catalysts exhibit high catalytic activity and selectivity in many organic reactions,[6] their practical application is limited by the difficulty in catalyst/product separation, the need to destroy the catalyst during the reaction work-up and hence the impossibility to reuse it. To overcome some of these problems and operate under continuous flow, some approaches have been developed to transform homogeneous into heterogeneous catalytic systems,[7] the simplest one being to support the active sites on large surface area inert inorganic matrices or organic polymers as supports or performing the reactions in some non-conventional media such as ionic liquids or supercritical CO_2 fluid.

For example, recyclable SO_3H-functionalized ionic liquids have been used recently as catalysts for the synthesis of chalcone and its derivatives.[8] In addition, reusable catalysts based on bamboo char sulfonic acid[9] and sulfonic acid silicas[10] have similarly shown to produce chalcone in good yields. Also, Brønsted acidic ionic liquids as catalyst and solvent have been reported as a potential substitute for conventional homogeneous/heterogeneous catalysts and solvents to produce chalcones.[11] Besides example of acid catalysts, hydrotalcites modified with ionic liquid have exhibited catalytic activity as base catalysts for the synthesis of chalcones.[12–15] Analogously, many zeolite-based catalysts, either acidic or basic, have been reported as heterogeneous catalysts for the synthesis of chalcone and its substituted derivatives.[16–18] The development of practical catalysts for the efficient synthesis of fine chemicals and biologically important molecules is a continuous task of large relevance for the chemical industry.[19]

Zeolites are among preferred materials in the field of heterogeneous catalysis, petrochemistry and fine chemical synthesis for the last few decades and find now extensive applications in many reactions.[20] Recently, in this context, a new class of materials termed metal organic frameworks (MOFs) have emerged with similar or improved properties than zeolites and other inorganic matrices in terms of porosity and content of transition metal.[21] MOFs are crystalline solids which are constructed by metal ions or clusters coordinated to polytopic organic ligands.[22] Depending on the coordination geometry around the metal ion or

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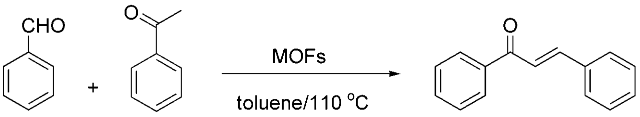
cluster and the bonding preference of donating atoms as well as the geometry of the bridging ligand, polymeric structures may result in different dimensionalities with high porosity, stability and surface area.[23] Typical pore sizes in MOFs are from 0.7 to 1.0 nm and, therefore, they expand the pore dimension range available in large pore zeolites and bridge the gap between zeolites and structured mesoporous silicas. The easy accessibility to the internal pores and the large metal content make MOF very attractive in the field of catalysis.[24]

As a result of their high dimensionality, the resulting MOF can be insoluble in conventional reaction media and therefore may potentially be useful in heterogeneous catalysis. There is currently a debate about whether or not MOFs can be applied as heterogeneous catalysts.[21] The lower thermal and chemical stability of MOFs represent a serious drawback with respect to zeolites. In addition, to act as catalytic sites the constitutional nodal metals need to have a reversible coordination position not compromised with the crystal structure. However, for reactions carried out under mild conditions and employing adequate solvents, there are certain MOFs that have exhibited a remarkable catalytic activity. We have recently shown that a MOF based on iron is a convenient heterogeneous catalyst for the oxidation of benzylic compounds with *tert*-butyl hydroperoxide[25] and that an aluminium-based MOF is a suitable non-noble metal solid catalyst for the hydrogenation of carbon-carbon multiple bonds using hydrazine as reducing agent.[26] In the present work, we will show the catalytic activity of a series of commercial MOFs as heterogeneous catalysts for carbon-carbon bond forming reaction useful for the synthesis of biologically important chalcones. In addition, this reaction also illustrates the activity of MOFs as solid Lewis acids.[27]

One point of interest is to address if the porosity in the catalysts plays any beneficial role or is detrimental with respect to similar catalytic sites in the homogeneous or heterogeneous phase. There are precedents in the literature showing that non-porous solids can be active in promoting the reaction. Therefore, catalyst microporosity is not a prerequisite to catalyze the Claisen–Schmidt reaction. In this context, it would be important to assess whether, in the case of MOFs, porosity is advantageous or not with respect to analogous catalytic sites. This could be addressed by comparing the activity of similar acids dissolved in the reaction phase or present in a non-porous material.

Results and Discussion

The Claisen–Schmidt reaction between benzaldehyde and acetophenone was selected in the first place to determine the catalytic activity of various MOFs and to optimize the reaction conditions with respect to temperature and solvent (Scheme 1). The results are as summarized in Table 1.



Scheme 1. Claisen–Schmidt condensation of benzaldehyde with acetophenone using MOFs as heterogeneous catalyst.

The blank reaction between benzaldehyde and acetophenone at 150 °C in chlorobenzene as solvent resulted in the formation of 10% chalcone after 24 h reaction time (Table 1, entry 1). The GC analysis of the reaction mixture showed also the presence of benzoic acid (16% selectivity), which originated by the aerobic oxidation of benzaldehyde. This control clearly shows that in order to promote selectively for the formation of chalcone a catalyst is required. We were interested in determining the catalytic activity of some commercially available MOFs. The structure of Fe(BTC) (BTC = 1,3,5-benzenetricarboxylic acid) is con-

Table 1. Claisen–Schmidt condensation reaction between benzaldehyde and acetophenone under various conditions.[a]

Entry	Catalyst	T [°C]	Solvent	Chalcone [%][b]
1	–	150	Chlorobenzene[c]	10
2	Fe(BTC)[d]	90	Chlorobenzene[c]	22
3	Fe(BTC)[d]	110	Chlorobenzene[c]	43
4	Fe(BTC)[d]	130	Chlorobenzene[c]	55
5	Fe(BTC)[d]	150	Chlorobenzene[c]	77
6	Fe(BTC)[e]	150	Chlorobenzene[c]	82
7	Fe(BTC)[e]	110	Toluene[f]	98
8	Fe(BTC)	110	Toluene[f]	90[g]
9	Iron citrate[h]	110	Toluene	<2
10	$FeCl_3\cdot 6H_2O$[i]	110	Toluene	20
11	Fe(BTC)[e]	150	Decane[c]	38
12	Fe(BTC)[e]	100	Acetonitrile[c]	15
13	$Al_2(BDC)_3$[d]	150	Chlorobenzene[c]	63
14	$Al_2(BDC)_3$[e]	110	Toluene[f]	71
15	$Cu_3(BTC)_2$[d]	150	Chlorobenzene[c]	8
16	$Cu_3(BTC)_2$[e]	110	Toluene[f]	6
17	Zn-MOF[d]	150	Chlorobenzene[c]	4
18	Zn-MOF[e]	110	Toluene[f]	<2

[a] *Reaction conditions*: Benzaldehyde (0.47 mmol), acetophenone (0.466 mmol), catalyst (150 mg), 24 h.
[b] Determined by GC using nitrobenzene as external standard.
[c] 3 mL of solvent.
[d] 100 mg of catalyst.
[e] 150 mg of catalyst.
[f] 6 mL of solvent.
[g] After third reuse.
[h] 150 mg were used.
[i] 50 mg were used.

stituted by the trimers of iron octahedra sharing a common vertex μ_3-O linked by the benzene-1,3,5-tricarboxylate moities in such a way that this leads to two types of mesoporous cages having free apertures of 25 and 29 Å, accessible through microporous windows of 5.5 and 8.6 Å.[28] Fe(BTC) is iso-structural to MIL-101[29] and exhibits a remarkable structural stability. Importantly, the coordination sphere of iron has an exchangeable coordination position that can be occupied by a solvent molecule but that can also participate in a catalytic cycle without compromising the crystal structure of Fe(BTC).[28] Compared to other conventional catalysts, such as large pore iron-containing zeolites, the major advantages of Fe(BTC) are the well defined single-site in which all the iron ions exhibit the same environment and coordination sphere, together with a very large surface area (more than double that of a Y zeolite) and larger pore size [0.7 nm windows with cavities of 1.3 nm for zeolite Y compared to 0.86 nm and cages of 2.9 nm for Fe(BTC)].

Using Fe(BTC) as catalyst, the yield of chalcone after 24 h reaction time increased gradually with increasing the reaction temperature (Figure 1) and also with the amount of catalyst present in the mixture from 100 to 150 mg (Table 1). Under the best conditions tested using chlorobenzene as solvent the maximum yield of chalcone achieved was 82% (Table 1, entry 6).

The same reaction in toluene at 110°C with Fe(BTC) as catalyst the yield of chalcone increased further to 98% (Table 1, entry 7) and hence these parameters were chosen as the optimum reaction conditions for further studies. Interestingly, in contrast to the blank control, benzoic acid was absent in the MOF-catalyzed reaction under identical conditions, increasing notably the selectivity of the process towards the target chalcone. Apparently Fe(BTC) by promoting the reaction towards the formation of chalcone avoids the slower, uncatalyzed formation of benzoic acid.

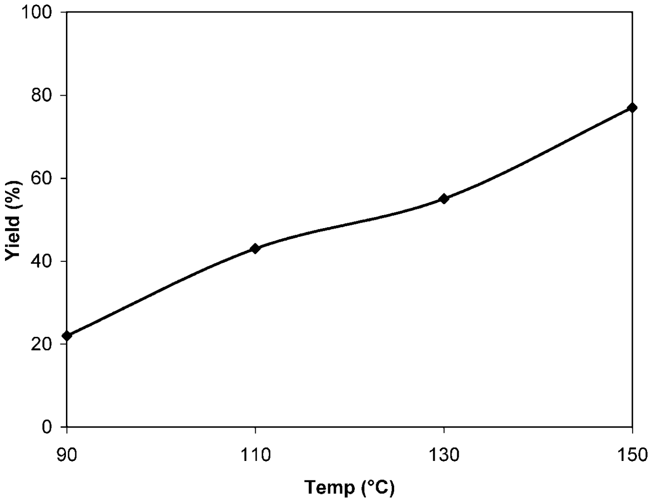


Figure 1. Effect of temperature on the condensation of benzaldehyde with acetophenone in chlorobenzene using Fe(BTC) as catalyst after 24 h reaction time.

The inherent instability of MOFs limits the range of solvents that can be used as reaction medium at high temperatures. Nevertheless, besides the two aromatic solvents, we also performed the reaction with Fe(BTC) in other solvents like decane and acetonitrile. The yield of chalcone decreased with respect to toluene to 38 and 15% for decane and acetonitrile, respectively (Table 1, entries 11 and 12).

To verify whether the observed catalysis is derived from Fe(BTC) or leached iron species, the reaction was carried out in toluene at 110°C under the optimized conditions described in Table 1 and the Fe(BTC) catalyst was filtered in hot from the reaction mixture at approximately 54% formation of chalcone after 2 h. After removal of the Fe(BTC) catalyst, the solution in the absence of solid was again stirred at 110°C. After 24 h, the chalcone formation was slightly improved to 62% but still far from the 98% observed when Fe(BTC) is not removed from the reaction mixture (Figure 2).

We believe that the additional increase in chalcone formation in the filtrate was mostly due to non-catalytic thermal condensation since the increase in the filtrate (8%) must have been contributed by the uncatalyzed reaction as observed in the control without Fe(BTC) (2%). A control experiment in toluene at 110°C in the absence of catalyst showed that benzaldehyde was converted to 5% with the formation of chalcone (2%) and benzoic acid (3%). In any case,

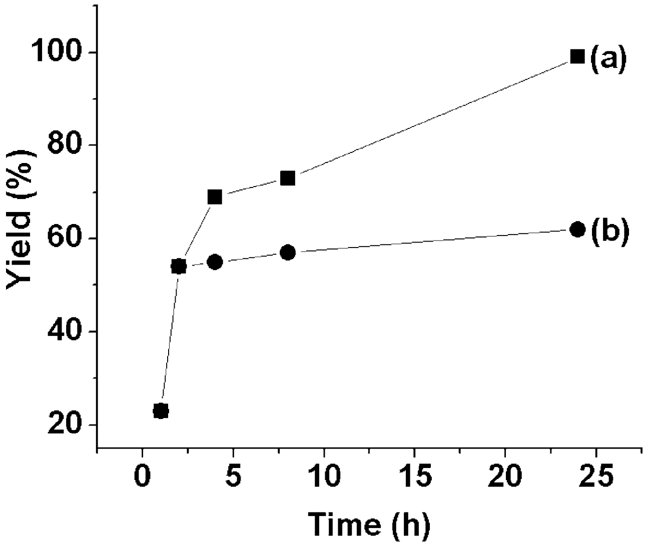


Figure 2. Time conversion plot for the reaction between benzaldehyde and acetophenone in toluene at 110°C: (a) in the presence of Fe(BTC), and (b) after filtration in hot of the solid at 54% conversion.

these results indicate that the presence of Fe(BTC) acting as heterogeneous catalyst is necessary to achieve high product yield. The occurrence of a low degree of homogeneous catalysis cannot, however, be conclusively ruled out.

In order to check the reusability of Fe(BTC) as heterogeneous catalyst, benzaldehyde and acetophenone were allowed to react in toluene at 110 °C for 24 h. After the reaction time, the solid was filtered, washed with acetonitrile, dried at 70 °C and used for another consecutive run without further treatment. After three consecutive reuses, the catalyst exhibited a minor decrease in the yield of chalcone and the selectivity remained unchanged. A comparison of the powder XRD patterns of the fresh and three times used Fe(BTC) is provided in Figure 3. It can be seen from Figure 3 (a) and (b) that the diffraction pattern of Fe(BTC) is maintained during its use as catalyst without any major changes in the peak pattern. These data demonstrate that the crystal structure of Fe(BTC) is not damaged upon its reuse as a heterogeneous catalyst. The catalyst structure was also not altered when the reaction was carried out in chlorobenzene and reused as shown in Figure 3 (c). This structural stability of Fe(BTC) is in agreement of previous studies that have shown that iso-structural MIL-101 is one of the most stable and robust MOF solids.[29] Surface area measurements of Fe(BTC) before and after its use as catalyst show a reduction from 1040 to 260 $m^2 g^{-1}$. This decrease in surface area could be due to the presence in the Fe(BTC) of some reaction (by)-products that are not volatile enough to be removed under the conventional outgassing procedure to which the sample is submitted prior to the isothermal nitrogen adsorption.

To address the structure of the catalytic sites and the role of the porosity of Fe(BTC), we selected iron citrate as model for a non-porous, insoluble iron carboxylate and performed a catalytic test in the heterogeneous phase for the reaction between benzaldehyde and acetophenone. In the solid state, the crystals of iron citrate show an iron-carboxylate coordination sphere that can be considered similar in many aspects to the one present in Fe(BTC). The catalytic results obtained are given in Table 1 (entry 9) and show that at the same substrate/iron ratio as for Fe(BTC), iron citrate does not promote the reaction towards the formation of chalcone. This clearly indicates that the porosity of Fe(BTC) allowing access to the catalytic site is a prerequisite to observe catalytic activity. To further address the ability of iron acting as a Lewis acid site to promote the Claisen condensation, the reaction of acetophenone and benzaldehyde was also carried out with ferric chloride hexahydrate (Table 1, entry 10). Interestingly, we observed the formation of chalcone (20%) in this case indicating iron can act as catalytic sites, but their activity is much lower than when iron is coordinated to carboxylate groups as in Fe(BTC). This lower catalytic activity of iron could be due to the absence of free coordination positions in $FeCl_3$ and the formation of dimeric iron species making the sites unstable in the homogeneous phase. Clearly immobilization of iron sites in the crystal structure of Fe(BTC) and the presence of a single site catalyst renders the system more active. It is well known that MOFs crystallize in large micrometric particles of defined cubic morphology and intergrowths. The presence of large crystallites in microporous materials could introduce diffusion limitations that restrict the access to the micropores. However, the fact that Fe(BTC) is considerably more active that $FeCl_3$ suggests that no severe diffusion limitations are taking place in the system under the reaction conditions. These experiments clearly prove that the presence of acidic sites in Fe(BTC) and their accessibility are the key features responsible for the high activity of Fe(BTC).[28]

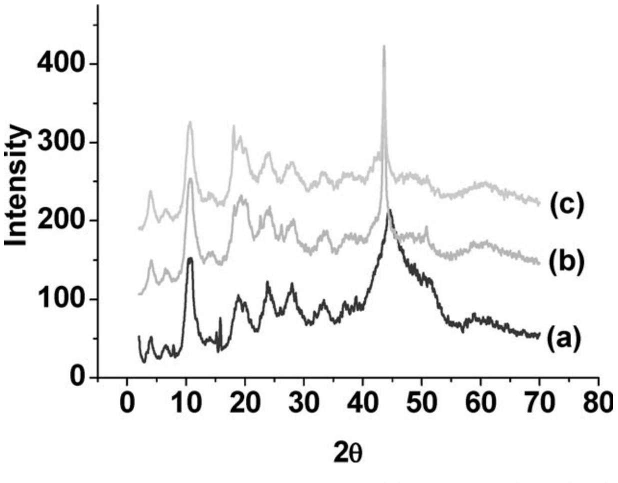


Figure 3. Powder XRD patterns of (a) fresh Fe(BTC); (b) three times-used Fe(BTC) in toluene and (c) reused Fe(BTC) in chlorobenzene

After elucidating the suitable conditions to achieve high yields of chalcone using Fe(BTC) as heterogeneous catalyst, we were also interested in determining the activity of other MOFs with aluminium, copper and zinc as the central metal atom. The crystal structure of $Al_2(BDC)_3$ (BDC = *p*-benzenedicarboxylate) is constructed from corner sharing octahedral Al linked by BDC ligands.[30] $Al_2(BDC)_3$ has the pore dimension of 8.5 Å with the surface area of 1590 $m^2 g^{-1}$with good thermal stability.[30] The structure of $Cu_3(BTC)_2$ is constituted by a cluster of two metal atoms with paddle wheel shape that has a square planar coordination.[31] The BTC ligand acts as a trigonal planar ligand connecting the diatomic metal clusters which defines nano cages of about 2.5 nm with windows of 0.8 nm. $Al_2(BDC)_3$ has also triggered the reaction towards the formation of chalcone with 71% yield in toluene and the same solid resulted in a slightly lower yield when chlorobenzene is used as solvent (Table 1, entries 13 and 14). Finally, the copper- and zinc-based MOFs have been tested for this reaction and these MOFs were found to be inefficient in promoting the desired reaction towards the formation of chalcone in toluene and chlorobenzene as solvents at 110 °C. These contrasting results indicate the role of the metal ion and its coordination defining the catalytic site (iron carboxylate the most active) and the role of the crystal structure permitting the accessibility to the site (Zn-MOF has too small pore size). We propose that the higher activity of Fe(BTC) with respect to other related MOFs derives from the coordinatively unsaturated vacancies in the iron coordination sphere and its larger porosity and surface area.

Fe(BTC) as General Claisen–Schmidt Catalyst

The remarkably simple and convenient reaction conditions, easy work-up, and high yield for the formation of chalcone prompted us to extend the scope of the Fe(BTC) as heterogeneous catalyst for the synthesis of various chalcones. The observed results are summarized in Table 2. Substituted and heterocyclic benzaldehydes were treated with substituted acetophenones, cyclic ketones and one aliphatic ketone. For instance, moderate to good yields of substituted chalcones were obtained when benzaldehyde was treated with 4-iodo- and 4-methoxy-substituted acetophenones (Table 2, entries 1 and 2) but the reaction of hydroxyacetophenone with benzaldehyde resulted in the formation of the corresponding chalcone in low yield (Table 2, entry 3). Apparently the free phenolic hydroxy group stops the reaction, probably by strong coordination with iron.

A reasonably good yield of heterocyclic chalcone was obtained between benzaldehyde and 4-acetylpyridine (Table 2, entry 4). Then, a series of cyclic ketones with different ring sizes was subjected to reaction with benzaldehyde to form enones with di- and mono-condensation to benzaldehyde. We notice that the ring size of the ketone determines the di/mono ratio of the condensed enone. In general as the size of the ketone is increased, formation of the mono derivative increases and formation of disubstituted one decreases. We propose that this trend in the product distribution clearly exemplifies the influence of the pore dimension of Fe(BTC) on the outcome of the reaction. For instance, the reaction between cyclohexanone and 4-methylcyclohexanone has resulted predominantly in the dibenzylidene product with similar selectivity (Table 2, entries 5 and 6). Cycloheptanone gives more mono- than di-products (Table 2, entry 7) and in the case of cyclooctanone α,α'-disubstituted cyclooctanone is a very minor product (Table 2, entry 8).

Then substituted benzaldehydes were reacted with acetophenone and tetralone to give their respective chalcones in high to moderate yields. In particular, reaction between 4-phenylbenzaldehyde and acetophenone resulted in a high yield (Table 2, entry 11) showing that linear-shaped long products can be formed in Fe(BTC). Similarly, the reaction of 4-pyridinecarboxaldehyde with tetralone and acetophenone resulted in the formation of the corresponding chalcones in moderate yields (Table 2, entries 12 and 13). Finally, 2-octanone was treated with benzaldehyde to obtain the corresponding enone through the less substituted methyl group in a moderate yield (Table 2, entry 14). Hence, the present study nicely demonstrates with a variety of substrates the general activity of Fe(BTC) to promote carbon-carbon bond formation reactions between aromatic aldehydes and ketones with reasonably good yields.

Conclusions

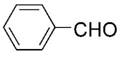
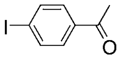
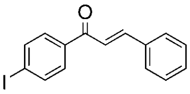
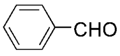
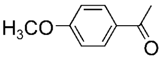
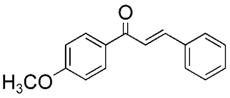
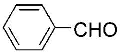
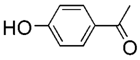
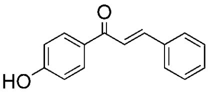
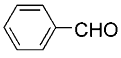
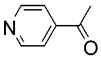
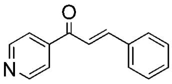
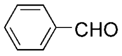
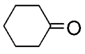
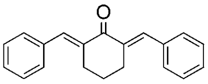
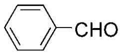
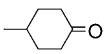
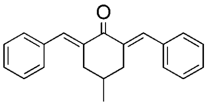
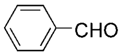
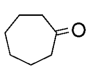
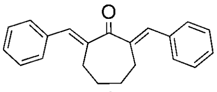
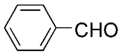
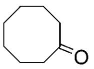
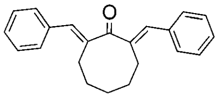
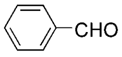
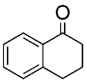
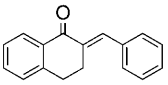
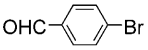
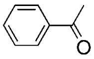
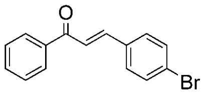
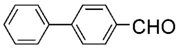
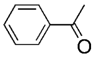
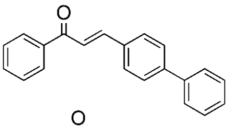
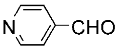
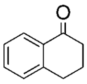
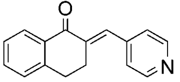
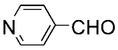
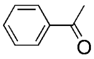
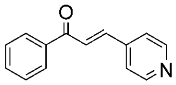
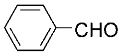
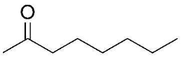
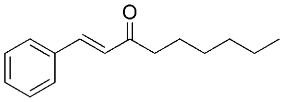
Herein, we have presented a simple and efficient synthetic protocol to synthesize various chalcones using Fe(BTC) as heterogeneous catalysts under mild reaction conditions. Compared to heterogeneous, nonporous iron citrate and homogeneous ferric chloride, Fe(BTC) exhibits a superior performance that derives from a combination of Lewis acid iron ions with one exchangeable coordination position and large porosity in terms of surface area and pore size. Fe(BTC) exhibits a superior performance to that of other related MOFs. We have shown that Fe(BTC) is a general catalyst for a number of ketones and aldehydes that smoothly condense to afford chalcones in good yields. The catalyst could be easily recovered after the reaction and can be reused without any loss in the yield of the product. Considering the easy preparation of Fe(BTC) and the low toxicity of iron, this reaction system is green and can be implemented for the large-scale synthesis of chalcones.

Experimental Section

General Remarks

All reagents and starting materials were obtained commercially from Aldrich and used without any further purification unless otherwise noted. The percentage conversion, purity and relative yields of the final products were determined using Hewlett Packard 5890 series II gas chromatograph with FID detector and high purity helium as carrier gas. The products were identified by GC-MS using a Hewlett Packard 6890 series spectrometer.

Table 2. Synthesis of various chalcones using Fe(BTC).[a]

Entry	Aldehyde	Ketone	Product	Yield [%]
1				80
2				67
3				18
4				74
5				71 (8)[b]
6				75 (8)[b]
7				31 (52)[b]
8				6 (54)[b]
9				90
10				63
11				94
12				41
13				25
14				34

[a] *Reaction conditions*: Aldehyde (1 mmol), ketone (1 mmol), Fe(BTC) = 150 mg, toluene (6 mL), 110 °C, 24 h.

[b] Value in parenthesis represents mono product.

Typical Procedure for Chalcone Synthesis

MOFs were purchased from Sigma–Aldrich and used as received. A 50-mL round-bottomed flask was charged with 150 mg (37.50 mg of iron from ICP analysis) of catalyst in 3 mL of toluene 0.47 mmol of benzaldehyde and 0.47 mmol of acetophenone. The reaction mixture was stirred for the required time and temperature. After 15 h, an additional portion of toluene (3 mL) was charged into the flask and the reaction continued further. After the required reaction time, the reaction mixture was cooled down to room temperature and extracted with dichloromethane (15 mL). The mass balances of the recovered reaction mixture accounted for more than 90% of the initial substrate as confirmed by GC using nitrobenzene as external standard. The products were analyzed by GC and characterized by GC-MS. The yield of the chalcone was determined by mmol of aldehyde and mmol of ketone converted in a given time to form the corresponding chalcone.

A similar procedure was followed for the synthesis of chalcone with other catalysts (iron citrate and $FeCl_3 \cdot 6H_2O$) in the presence of toluene as solvent maintaining the same iron content as for the Fe(BTC) catalyst.

Experimental Procedure for Reusability Tests

The reusability of Fe(BTC) was tested for the synthesis of chalcone. At the end of the reaction, the mixture was filtered and the catalyst was washed with fresh toluene and dried at 70°C for 2 h, then reused without further purification for a second run with fresh benzaldehyde and acetophenone. After the second use, the resulting Fe(BTC) was used for a third consecutive run wherein a minor loss in activity was observed. Crystallinity of the three-times used sample was compared by powder XRD.

Acknowledgements

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A minimal formal correction has been carried out since the first online publication of this article. In Table 2, entry 8, the yield has been corrected to 6 (54) from 31 (54) in the first online publication.

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