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Priority Communication

Metal organic frameworks as efficient heterogeneous catalysts for the oxidation of benzylic compounds with *t*-butylhydroperoxide

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ABSTRACT

Iron and copper metal organic frameworks of 1,3,5-benzenetricarboxylate [Fe(BTC) and $Cu_3(BTC)_2$] are efficient and reusable solid catalysts for the oxidation of benzylic compounds with *t*-butylhydroperoxide as oxidant in acetonitrile with moderate to good yields. The solids were stable under the reaction conditions as confirmed by comparison of the powder XRD of the fresh and reused catalysts. EPR spectroscopy using diphenyl-*N*-*t*-butyl nitrone as spin trap has allowed to detect C-centered radicals as reaction intermediates.

1. Introduction

Metal organic frameworks (MOFs) are crystalline materials whose network is constituted by metal ions or metal clusters connected by multidentate organic linkers [1–3]. MOFs are the less dense and higher surface area materials with potential application in gas storage and liquid phase separations [4,5]. Considering the structural similarity between MOFs and zeolites and that zeolites are the paradigmatic solid catalysts, one field in which MOFs find promising applications is heterogeneous catalysis. In principle, the use of MOFs as solid catalysts could be hampered by the lower framework stability of these materials compared to zeolites and also by the lack of free coordination positions around the metal ions or metal clusters. Nevertheless, there is an increasing number of reports showing that MOFs do show potential in catalysis [6–12].

Transition metal salts and complexes, and particularly those containing iron or copper, are good catalysts for the oxidation of benzylic carbons using hydroperoxides as oxidizing reagents [13–18]. Typically the problem in this case is deactivation arising from complex degradation and metal aggregation as metal oxide particles. Considering that the structure of MOFs consists in isolated metal ions or clusters maintained in framework positions by organic linkers that should avoid aggregation, we anticipated that iron and copper MOFs could possibly act as heterogeneous catalysts for the benzylic oxidation provided that they can coordinate with hydroperoxide and maintain their crystal integrity during the reaction.

In the present study, we will show that large pore size Fe(BTC) and $Cu_3(BTC)_2$ (BTC: 1,3,5-benzenetricarboxylate, about 0.6 nm pore size [19,20]) are efficient and reusable heterogeneous catalysts for the oxidation of benzylic compounds to the corresponding oxidation products in good to high yields. In these two MOFs, metal clusters are coordinated with the carboxylate groups of the ligands. The structure of Fe(BTC) is built up by Fe_3–μ_3O iron octahedra sharing a common vertex μ_3-O linked by the benzene-1,3,5-tricarboxylate moieties in such a way that this leads to two types of mesoporous cages of free apertures of 2.5 and 2.9 nm, accessible through microporous windows of 0.55 and 0.86 nm. The BET surface area of BTC MOFs is over 1000 m^2/g. The catalytic efficiency of these Fe and Cu transition metal MOFs contrasts with the poor activity of $Al_2(BDC)_3$ (BDC: 1,4-benzenedicarboxylate).

2. Experimental

2.1. General procedures

All reagents and starting materials were obtained commercially from Aldrich and used without any further purification unless otherwise noted. Scanning electron microscopic images were obtained on a JEOL JSM – 5410 instrument operated at 20 kV. The percentage conversion, purity and relative yields of the final products were confirmed using Hewlett 5890 series II gas chromatograph with FID detector and high purity helium as carrier gas. The

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products were identified by comparing with authentic samples and with GC–MS Hewlett Packard 6890 series.

2.2. Typical procedure for benzylic oxidation

MOFs were purchased from Sigma–Aldrich and used as received. Fe(BTC) (Cat.: 69,087-2), $Cu_3(BTC)_2$ (CAS: 51937-85-0) and $Al_2(BDC)_3$ (CAS: 654061-20-8). A 50 mL round-bottomed flask was charged with 75 mg (18.75 mg of iron from ICP analysis) of catalyst in 4 mL of acetonitrile, 0.27 mmol of the corresponding benzylic compound and 0.05 mL of 80% TBHP (CAS: 75-91-2). The reaction mixture was stirred for the required time and temperature at 450 rpm. 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 95% of the initial substrate as confirmed by GC using dodecane as external standard. The products were analyzed by GC and GC–MS. Mass balances were determined using dodecane as external standard. Known amounts of dodecane were added to the aliquots of the reaction mixture and the mixture injected in GC. The similar procedure was followed for the oxidation of xanthene with other catalysts (iron citrate and FeY zeolite) in the presence of TBHP. Quenching experiments were also performed in a similar manner with appropriate radical quencher. FeY zeolite was prepared by magnetically stirring 10 g of commercial NaY (Si/Al 2.4) at room temperature for 2 h in 100 mL of 0.2 M aqueous solution of $Fe(NO_3)_3$ at pH 3 acidified using 0.05 M of HNO_3. After the ion exchange, the FeY zeolite was filtered, washed exhaustively with milliQ water and dried at 60 °C in an oven. Before its use, FeY zeolite was dehydrated at 150 °C for 2 h under reduced pressure. Iron citrate is a commercial sample (Aldrich) and was used as received.

2.3. Experimental procedure for reusability tests

The reusability of Fe(BTC) was tested for the oxidation of xanthene. At the end of the reaction, the mixture was centrifuged, the filtrate was decanted, and the catalyst was dried at 60 °C for 2 h, then reused directly without further purification for the second run with fresh xanthene and TBHP. It was used for four consecutive runs with minor loss in activity. The weight of the catalyst recovered in each run starting from runs 1–4 was 77, 74, 71 and 68 mg, respectively.

3. Results and discussion

An optimization of the oxidation of xanthene to xanthone showed that the nature of the oxidant as well as the metal present in the MOF is essential for the oxidation to occur. The results obtained are presented in Table 1. While molecular oxygen and hydrogen peroxide were inefficient to promote xanthene oxidation, *tert*-butylhydroperoxide (TBHP) was a good oxidizing reagent in terms of the percentage yield of xanthone. Using TBHP in the presence of Fe(BTC) at 60 °C, xanthone is obtained as the sole product in 90% yield. The iron content in Fe(BTC) determined by ICP analysis was 25.2 wt%, which is slightly defective (0.75) with respect to the amount of TBHP. Fig. 1 presents a time conversion plot for the oxidation of xanthene in the presence of Fe(BTC) as a solid catalyst.

There is a slight decrease in the yield of the product when the amount of the catalyst is reduced. The oxidation rate decreased with the increase in temperature and on the other hand the reaction was completed when using threefold TBHP excess. Under optimized conditions using only 7.5 mg of catalyst, the maximum TOF estimated for Fe(BTC) at 15% conversion was 12 h^{-1}. This value can be compared favorably with that estimated based on the yield reported in the literature for xanthene oxidation with TBHP using iron chloride as catalyst which is about 10 h^{-1} at 90% conversion. Though the present catalytic system gives higher yield of the oxidized products when an excess TBHP is used, we have restricted the amount of oxidant to 1.5 equiv, which represents a good balance between high product yield and TBHP cost. A blank control established that under these conditions Fe(BTC) is able to completely decompose TBHP even in the absence of xanthone; thus, some spurious decomposition of TBHP is competing with xanthene oxidation which explains the need of some TBHP excess.

Table 1
Oxidation of xanthene with TBHP as oxidant in acetonitrile.[a]

Entry	Catalyst	Temperature (°C)	Yield[b] (%)	Selectivity[b] (%)
1	Silica	60	–	–
2	Fe(BTC)[c]	60	–	–
3	Fe(BTC)[d]	70	9	99
4	Fe(BTC)	60	78	99
5	Fe(BTC)[e]	60	90	99
6	Fe(BTC)[f]	70	72	98
7	Fe(BTC)	80	60	99
8	Fe(BTC)[g]	70	93	>98
9	Fe(BTC)[h]	70	>99	99
10	Fe(BTC)[i]	60	82	99
11	Fe(BTC)[j]	70	13	95
12	Fe(BTC)[k]	70	28	94
13	iron citrate[l]	70	79	>98
14	FeY[m]	70	14	96
15	$Cu_3(BTC)_2$	70	82	85
16	$Al_2(BDC)_3$	70	42	98

[a] *Reaction conditions*: xanthene (50 mg), catalyst (75 mg), TBHP (80%, 0.05 mL), acetonitrile (4 mL), time 24 h. The mass balances of the recovered substrate and xanthone account for more than 95% of the initial amount.

[b] Percentage yield and selectivity are determined by GC and selectivity corresponds to oxidation products.

[c] Without TBHP and bubbling air.

[d] Using H_2O_2 (0.06 ml, 33 wt%) instead of TBHP.

[e] 100 mg of Fe(BTC) is used.

[f] TOF is calculated from the conversion at 1 h.

[g] TBHP (80%, 0.075 mL).

[h] TBHP (80%, 0.1 mL).

[i] Yield after 4th run.

[j] 1.5 equiv. of hydroquinone.

[k] 1.5 equiv. of TEMPO.

[l] 15 mg of iron citrate.

[m] 250 mg of Fe-exchanged Y zeolite.

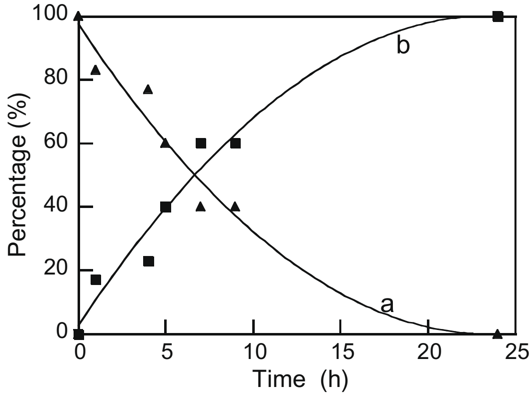


Fig. 1. Conversion of xanthene (a) and percentage of xanthone formed (b) vs. time by TBHP oxidation in acetonitrile using Fe(BTC) as heterogeneous catalyst. For reaction conditions see Table 1.

In addition, the Fe(BTC) catalyst is also examined for reusability and the same catalyst is found to be active for four cycles with a yield of 82% with almost complete selectivity toward xanthone.

Comparison of the SEM images of the fresh and used Fe(BTC) reveals that the MOF solid particles maintain the morphology (see Supplementary material) upon use, suggesting that the solid is acting as a stable heterogeneous catalyst.

To firmly support that the crystal structure of Fe(BTC) has survived the reaction, we performed XRD of the used catalyst and observed that the diffraction pattern was maintained. Fig. 2 shows a comparison of the XRD of fresh and reused Fe(BTC). Thus, the activity decrease upon reuse could be caused by minor structural damage and/or pore blocking by trace amounts of reaction byproducts.

Heterogeneity of the catalysis was ascertained by performing the reaction up to 40% xanthene conversion, filtering the solid while the system was still at the reaction temperature and letting the supernatant react further under the same conditions. No further conversion was observed in the absence of Fe(BTC) solid particles showing that the catalysis takes place in the solid phase. On the other hand, we have also performed adsorption studies of xanthene and triphenylmethane on Fe(BTC) at different time intervals and it indicates that adsorption is very slow as the time progress.

Similar to the Fe^{+III} MOF, $Cu_3(BTC)_2$ was also found to be active for the oxidation of xanthene to xanthone with good selectivity. In contrast, $Al_2(BDC)_3$ MOF was markedly inefficient in promoting this oxidation, indicating the role of the transition metal ion in the catalysis. This lack of activity of $Al_2(BTC)_3$ to promote oxidation with hydroperoxides compared to transition metals is in agreement with the literature where there are many examples on transition metal catalyst [21]. Apparently, the swing between two redox states is necessary in the mechanistic cycle for hydroperoxide activation [21]. Substantial decrease in percentage yield of xanthone in the presence of hydroquinone and TEMPO indicates that some key reaction intermediates behave as radicals. Scavengers that intercept these radicals can quench the reaction.

To address the influence that coordination with framework carboxylate groups plays on the catalysis, we selected iron citrate as model and performed a catalytic test in homogeneous phase for the reaction of TBHP with xanthene. In the solid state, the crystals of iron citrate show a coordination sphere that can be considered similar in many respects to the one present in Fe(BTC). The catalytic results obtained are given in Table 1 (entry 13) and show that at the same substrate/iron ratio, iron citrate exhibits a similar, but lower catalytic activity than Fe(BTC). This result supports the assumption that the iron carboxylate is the active site in Fe(BTC). Even though iron citrate promotes benzylic oxidation with reasonably good yield, Fe(BTC) is superior in terms of reusability. To further address the catalytic activity of Fe sites, we prepared iron-exchanged zeolite Y and performed xanthene oxidation under the general conditions. Remarkably lower activity and selectivity for xanthene oxidation using Fe-exchanged Y zeolite were observed compared to Fe(BTC) (see Table 1), thus providing an additional evidence in support of the beneficial influence of carboxylate coordination on the activity of the iron species.

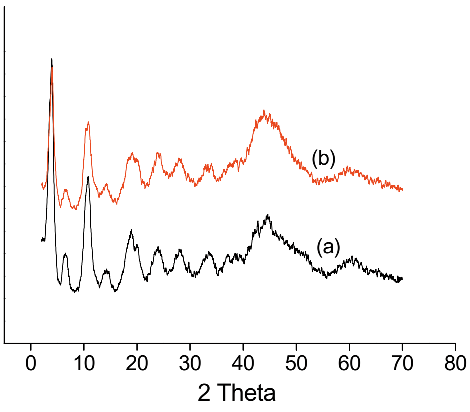


Fig. 2. Powder XRD of fresh (a) and reused Fe(BTC) (b).

The remarkably simple and convenient reaction conditions, easy workup, and high yield for the transformation of xanthene to xanthone prompted us to extend the scope of the Fe(BTC) as heterogeneous catalyst for the oxygenation of other benzylic compounds. The results are summarized in Table 2. Fluorene, indane, and diphenylmethane are oxidized to the corresponding ketones selectively.

The relative yield of the oxidation products under the same conditions suggests that the C–H bond energy of the benzyl positions is one parameter controlling the reactivity [22]. On the other hand 9,10-dihydroanthracene gives a mixture of three oxidation products including anthracene, mono, and diketones. The product distribution does not vary when the oxidation of dihydroanthracene is carried out in the absence of oxygen indicating that anthracene and the quinones are formed exclusively by TBHP through competing pathways. In addition, oxidation of tetralin gives the corresponding ketone as a major product with alcohol and naphthalene being other by-products. Concerning the reaction mechanism, Scheme 1 presents a reasonable proposal based on related precedents [23] on the use of Fe(III) catalyst for hydrocarbon oxidation by TBHP. The first step will involve coordination of TBHP on Fe(III).

As commented earlier, the structure of Fe(BTC) contains Fe_3–μ_3O clusters. These iron aggregates have one of the positions that is not engaged with the framework carboxylate groups and is free to coordinate with the solvent, a substrate, or any other ligand [20]. This non-framework coordination position could act as catalytic site in Fe(BTC) and would be responsible for the binding of TBHP, activating this hydroperoxide for benzylic oxidation. After coordination, *t*-butoxyl radicals will be generated that will abstract a hydrogen atom from the substrate leading to a carbon-centered radical.

This mechanistic proposal was supported by using diphenyl-*N*-*t*-butyl nitrone (PBN) as spin trap and recording EPR spectrum of the treatment of TBHP by Fe(BTC) at 70 °C in the presence of PBN. Under these conditions radicals arising from nitrone trapping were observed (Fig. 3). Controls under same conditions in the absence of TBHP gives a negligible EPR spectrum at least three orders

Table 2
Oxidation of various benzylic and cyclic compounds by TBHP in acetonitrile catalyzed by Fe(BTC).[a]

Entry	Substrate	Time (h)	Yield[b] (%)	Selectivity[b] (%)
1	Fluorene	88	73	99
2	Fluorene	24	38 (35)[c]	99
3	Indane	24	31	87
4	Indane	88	54	94
5	9,10-Dihydroanthracene	27	96	26
6	9,10-Dihydroanthracene[d]	24	85	24
7	Tetralin[e]	24	62	71
8	Triphenylmethane	24	20[f]	25[f]
9	Adamantane	24	29[f]	99[f]
10	Cyclooctane	24	28	75

[a] *Reaction conditions*: Substrate (50 mg), Fe(BTC) (75 mg), TBHP (80%, 0.05 mL), acetonitrile (4 mL), temperature 70 °C.

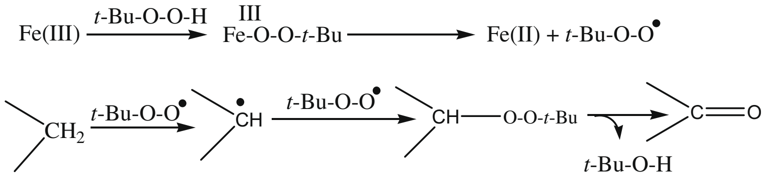
[b] Percentage yield and selectivity determined by GC and selectivity corresponds to ketone. The mass balances of the recovered substrate account for more than 95% of the initial amount.

[c] Yield with $Cu_3(BTC)_2$ under identical conditions.

[d] Reaction is carried out in an inert atmosphere.

[e] Reaction temperature 75 °C.

[f] Percentage yield and selectivity correspond to alcohol.



Scheme 1. Proposed mechanism for the oxidation of benzylic compounds by iron(III) with TBHP.

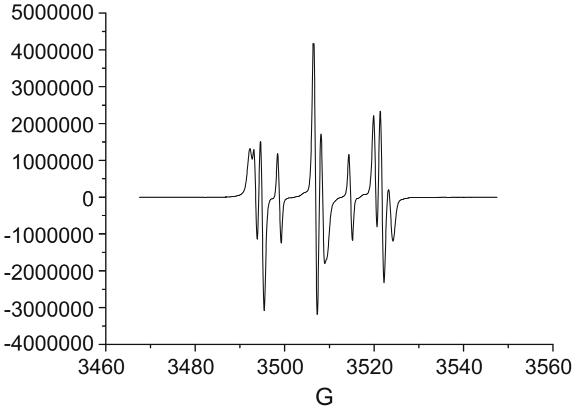


Fig. 3. EPR spectrum recorded for the treatment of TBHP with Fe(BTC) at 70 °C in the presence of PBN (see Supplementary material for simulation).

of magnitude lower than that when catalyst, TBHP, and nitrone are present. After generation of alcoxyl radicals, hydrogen abstraction at the benzylic methylene groups will generate a carbon-centered radical.

The shape selectivity of Fe(BTC) as heterogeneous catalyst was demonstrated using a large molecule that cannot access the interior of the pores. The structure of Fe(BTC) has a pore size of 0.6 nm [19]. It has been previously shown that triphenylmethane (1.1 nm molecular size) is size-excluded from the pores of zeolite Y and the same can be assumed that occurs for Fe(BTC) [24]. Thus, it could be anticipated that triphenylmethane should not undergo oxidation if the reaction takes place inside the MOF micropores in spite of the higher reactivity of C–H in the tertiary benzylic carbon. Not surprisingly, the attempts to oxidize triphenylmethane resulted in the formation of triphenylmethanol with low yield, supporting that the benzyl oxidation takes place predominantly inside the micropores of MOF particles.

Interestingly, oxidation of adamantane gives 1- and 2-adamantanol in a 5:1 ratio and no detectable quantity of the corresponding ketones. The product distribution in adamantane oxidation has been proposed to be a hallmark of a free radical aerobic oxidation when there is low selectivity for the oxidation of the tertiary vs. the secondary carbon and when the 1-/2-adamantanol ratio is low [15]. Thus, the adamantane product distribution together with hydroquine quenching suggests that Fe(BTC)-catalyzed oxidation occurs mainly through the oxidation of free radicals.

4. Conclusions

In summary, we have successfully shown the utility of inexpensive Fe and Cu MOFs as effective catalysts for the aerobic oxidation of xanthene and other benzylic compounds with t-butylhydroperoxide in acetonitrile. For those products that can access the MOF micropore system the reaction takes place with high to moderate yields. The solid catalyst can be easily reused maintaining the particle integrity and with some gradual decay in activity. The availability of MOFs and the simple product isolation make this system quite attractive for academic as well as industry communities.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2009.08.001.

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