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Aerobic Oxidation of Benzylic Alcohols Catalyzed by Metal−Organic Frameworks Assisted by TEMPO

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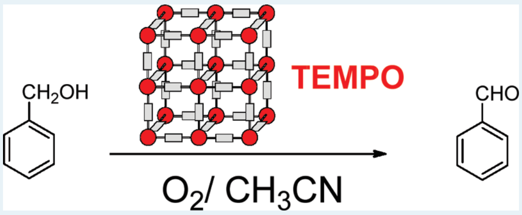
Supporting Information

ABSTRACT: $Cu_3(BTC)_2$ (BTC: 1,3,5-benzenetricarboxylate) combined with TEMPO as cocatalyst is an effective and reusable heterogeneous catalyst to effect the aerobic oxidation of benzylic alcohols in acetonitrile to the corresponding benzaldehydes under mild temperature at atmospheric pressure. The main deactivation process was attributed to the formation of carboxylic acids arising from the overoxidation of the aromatic aldehyde acting as poisons, coordinating to the free Cu(II) sites and blocking the pores. Comparison with copper acetate as a soluble, homogeneous system established that immobilization of the Cu(II) in the rigid crystal structure of $Cu_3(BTC)_2$ does not diminish the intrinsic catalytic activity of this transition metal ion.



KEYWORDS: $Cu_3(BTC)_2$, alcohol oxidation, metal−organic frameworks, TEMPO, copper, aerobic oxidation

INTRODUCTION

Alcohol oxidation is one of the most important transformations in organic chemistry that is also widely used in industry.[1] Typically, stoichiometric oxidants having transition metals are used to effect this oxidation in high yields and selectivities.[2] However, transition metal oxidants generate considerable amounts of metal containing wastes that are undesirable from the environmental point of view.[3] For this reason, there has been a strong move toward the development of catalytic reactions using benign oxidizing reagents such as hydrogen peroxide and organic peroxides, molecular oxygen being the ideal oxidant from the environmental point of view.[3] In recent years, noble metal nanoparticles and particularly supported gold nanoparticles have shown a high activity to effect alcohol oxidation using molecular oxygen under moderate temperatures and pressures.[4] However, considering the high cost of noble metals, it would be still desirable to develop non-noble metal catalysts to effect alcohol oxidation. In the present manuscript, we describe that metal organic frameworks (MOFs) in the presence of piperidinyloxyl as cocatalyst can be an efficient system to promote the aerobic oxidation of benzyl alcohols under mild conditions.

MOFs are crystalline solids in where the structure is built by metal ions or clusters of metal ions held in place by organic di- or multitopical linkers.[5] MOFs are at the top of the list of porous solids and exhibit very large surface area (mostly internal) as well as the lowest framework density.[6] The synthesis of new MOFs and their use for hydrogen storage, CO_2 sequestration, and gas separation is a current research front in chemistry.[7] MOFs contain a large percentage of transition metals that can act as catalytic sites[8,9] provided that they have free coordination positions not compromised in the construction of MOFs. These materials are expected to have many similarities from the structural point of view with zeolites and related microporous solids. Zeolites constitute the best example of successful heterogeneous catalysts.[10] Thus, there is a logical interest in exploiting the possibilities of MOFs as heterogeneous catalysts.[9,11,12] The main drawbacks of MOFs as solid catalysts compared to zeolites are their lower thermal and chemical stability and the fact that for some MOF structures the nodal metal ions or clusters do not have free coordination positions to interact with substrates and reagents. The current state of the art in the use of MOFs as catalysts has been recently reviewed and their advantages, limitations, and general applicability of MOFs as solid catalysts have been commented in detail.[13−16]

In the present work, we have used three commercially available MOFs. The first one is $Cu_3(BTC)_2$ (BTC: 1,3,5-benzenetricarboxylate) whose structure is constituted by a cluster of two copper ions with a paddle wheel shape that has a square planar coordination.[17] The BTC ligand acts as a trigonal planar ligand connecting the diatomic metal clusters defining nanocages of about 2.5 nm with windows of 0.8 nm. $Cu_3(BTC)_2$ has been used widely as a heterogeneous catalyst in acetalization of aldehydes with methanol,[18] quinoline synthesis,[19] α-pinene oxide rearrangement,[8] trimethylsilylazide addition to carbonyl compounds,[20] oxidation of benzylic compounds with *t*-butylhydroperoxide,[21] ring-opening of epoxides with methanol,[22] alkylation of amines with dimethyl carbonate,[23] cyclopropanation of styrenes,[24] and cycloaddition of phenylacetylene with benzyl azide.[25]

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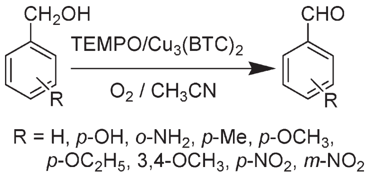
Scheme 1. Aerobic Oxidation of Alcohols Catalyzed by $Cu_3(BTC)_2$ Hosting Piperidinyl Oxyl



R = H, *p*-OH, *o*-NH$_2$, *p*-Me, *p*-OCH$_3$, *p*-OC$_2$H$_5$, 3,4-OCH$_3$, *p*-NO$_2$, *m*-NO$_2$

Recent precedents to this work are the combination of copper salts with piperidinyloxyl radical catalyst to effect aerobic oxidations reported by Sheldon[26,27] and other groups.[28−33] Sheldon and his co-workers have shown that the swing between Cu(II) and Cu(I) combined by oxyl radicals able to initiate the oxidation by hydrogen atom abstraction can promote the transformations of some alcohols into carbonyl compounds.[26] Importantly, in these pioneering works, they were using NaClO as the terminal oxidizing reagent in a biphasic dichloromethane/water system. In our case, oxygen is the oxidizing agent and no chlorinated solvents are used.

Inspired by natural copper-containing enzymes[34] which are involved in electron transfer oxidation reactions, we are interested in studying the catalytic activity of the MOF in combination with oxyl radicals. One advantage of MOFs is that they do not require the addition of an external ligand to form the metal complex to act as the homogeneous catalyst. Hence in the present work, we describe the catalytic oxidation of benzylic alcohols to benzaldehydes using molecular oxygen as the terminal oxidant promoted by $Cu_3(BTC)_2$ under mild conditions as shown in Scheme 1.

RESULTS AND DISCUSSION

The oxidation of benzyl alcohol was chosen as a model substrate to study the catalytic activity of $Cu_3(BTC)_2$ to identify suitable reaction conditions using molecular oxygen as the terminal oxidant. The results are presented in Table 1. Initially, the oxidation of benzyl alcohol was tested with $Cu_3(BTC)_2$ with a catalytic amount of TEMPO as radical initiator. Blank experiments in which one of the components, $Cu_3(BTC)_2$ or TEMPO or sodium carbonate, was missing resulted in no oxidation. Also when oxidation of benzyl alcohol was attempted in the absence of molecular oxygen, negligible yield of benzaldehyde was attained. Additional control experiments were carried out using TEMPO as stoichiometric oxidizing reagent (1 and 2 equiv) and $Cu_3(BTC)_2$ as catalyst under inert atmosphere (Table 1, entries 6 and 7). Although a stoichiometric amount of TEMPO effects the oxidation of benzyl alcohol to benzaldehyde, combining molecular oxygen with a catalytic amount of TEMPO is preferable from the viewpoint of green chemistry since it avoids the formation of stoichiometric amounts of byproducts derived from TEMPO. However, the percentage conversion of benzyl alcohol was affected much when the amount of TEMPO was reduced further (entry 13, Table 1); thus, an optimum substoichiomeric amount of TEMPO that allows promotion of the aerobic oxidation of benzyl alcohol in a reasonable time with adequate selectivity. These controls clearly imply that catalyst, basic medium, and molecular oxygen are required to promote the oxidation reaction. It has been observed that $Cu_3(BTC)_2$ promotes the oxidation in combination with sodium carbonate, substoichiometric amounts of TEMPO, and molecular oxygen in acetonitrile at 75 °C. In addition, the yield of benzaldehyde was decreased as the reaction temperature was reduced. An analogous trend was observed with respect to the decrease of catalyst amount from 0.48 to 0.36 mmol (entries 11 and 12, Table 1). Therefore, $Cu_3(BTC)_2$ is the MOF showing the best catalytic activity for the oxidation of benzyl alcohol to benzaldehyde using molecular oxygen as terminal oxidant. Figure 1 shows the time conversion plot for the aerobic oxidation of benzyl alcohol under optimal conditions catalyzed by $Cu_3(BTC)_2$ and TEMPO.

Table 1. Aerobic Oxidation of Benzyl Alcohol Promoted by MOFs under Various Reaction Conditions[a]

run	catalyst	TEMPO (mg)	Na_2CO_3 (mg)	yield (%)[b]
1			85	1
2		25	85	3
3	$Cu_3(BTC)_2$		85	4
4	$Cu_3(BTC)_2$	25		5
5	$Cu_3(BTC)_2$[c]	25	85	4
6	$Cu_3(BTC)_2$[c]	144[d]	85	70
7	$Cu_3(BTC)_2$[c]	288[e]	85	91
8	$Cu_3(BTC)_2$	25	85	89, 64[f]
9	$Cu_3(BTC)_2$[g]	25	85	75
10	$Cu_3(BTC)_2$[h]	25	85	37
11	$Cu_3(BTC)_2$[i]	25	85	77
12	$Cu_3(BTC)_2$[j]	25	85	26
13	$Cu_3(BTC)_2$	14	85	45
14	$Cu(NO_3)_2 \cdot 3H_2O$		85	5
15	$Cu(NO_3)_2 \cdot 3H_2O$[k]	25	85	78
16	$Cu(CH_3COO)_2 \cdot H_2O$[l]	25	85	85

[a] Reaction conditions: benzyl alcohol (0.925 mmol), catalyst (150 mg, 0.732 mmol), acetonitrile (5 mL), 22 h, 75 °C, oxygen atmosphere. [b] Determined by gas chromatography (GC) with nitrobenzene as internal standard. The selectivity of benzaldehyde was always >98%. [c] Reaction at inert atmosphere. [d] Corresponding to 1 equiv of TEMPO. [e] Corresponding to 2 equiv of TEMPO. [f] Yield in the second use. [g] Reaction at 60 °C. [h] Reaction at 40 °C. [i] With 100 mg (0.48 mmol) of catalyst. TON is 1.5. [j] With 75 (0.36 mmol) mg of catalyst. TON is 0.68. [k] At 3 h. [l] Copper acetate·H_2O (150 mg).

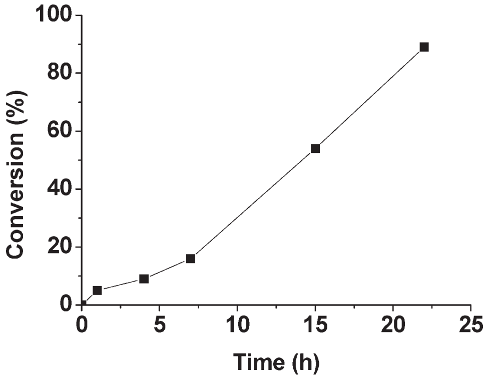


Figure 1. Time conversion plot for the aerobic oxidation of benzyl alcohol to benzaldehyde catalyzed by $Cu_3(BTC)_2$ and TEMPO (reaction conditions: benzyl alcohol (0.925 mmol), catalyst (150 mg, 0.732 mmol), acetonitrile (5 mL), 22 h, 75 °C, oxygen atmosphere).

For the sake of comparison, copper acetate monohydrate and copper nitrate trihydrate were used as homogeneous catalyst for the same reaction. As is shown in Table 1 (entries 14 and 15), the

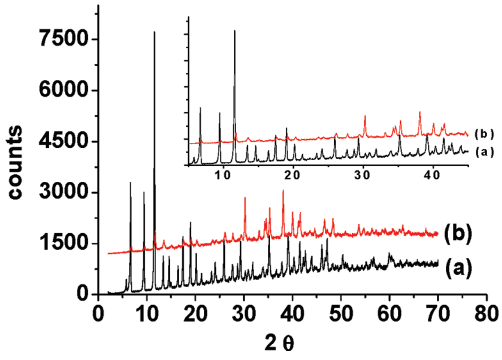


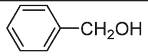
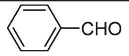
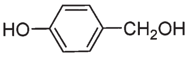
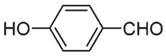
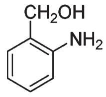
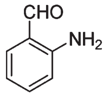
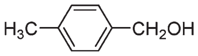
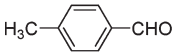
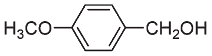
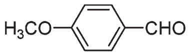
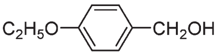
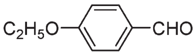
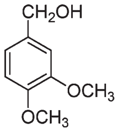
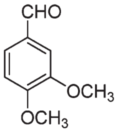
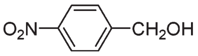
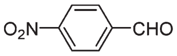
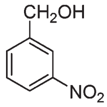
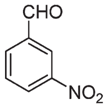
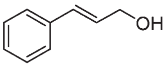
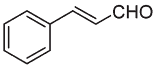
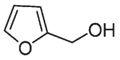
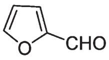
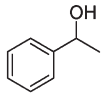
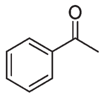
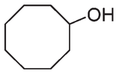
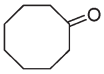
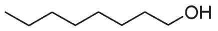
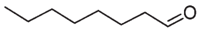
Figure 2. Powder XRD of (a) fresh and (b) $Cu_3(BTC)_2$ used twice. The inset shows an expansion of part of the XRD.

latter catalyst resulted in negligible conversion of benzaldehyde in the absence of TEMPO, while both copper salts in combination with TEMPO yield benzaldehyde with a high selectivity similar to that achieved with $Cu_3(BTC)_2$ as solid catalyst. The activity of copper acetate clearly indicates the intrinsic activity of copper(II) as redox sites to promote oxidation of benzyl alcohol to benzaldehyde assisted by TEMPO. Thus, it appears that the active sites either in solution or in the solid would be incompletely coordinated copper(II) carboxylate and that the intrinsic activity of these copper(II) complexes does not disappear when forming $Cu_3(BTC)_2$. The analogous behavior of $Cu_3(BTC)_2$ as heterogeneous catalyst with copper acetate is comparable with the existence of Lewis acid sites within the micropores of MOFs even though the former catalyst is constituted by the coordination of carboxylate groups.

To verify whether the catalysis of $Cu_3(BTC)_2$ is truly heterogeneous or, on the contrary, is due to some leached copper species present in the liquid phase, the reaction was carried out under the optimized conditions described in Table 1 and the $Cu_3(BTC)_2$ solid catalyst was filtered in hot from the reaction mixture at 18% formation of benzaldehyde. After removal of the $Cu_3(BTC)_2$ catalyst, the solution in the absence of solid was again stirred. After 22 h, no further product formation was observed in the absence of solid. On the other hand, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of the filtrate showed the presence of 1 ppm of the copper in the solution corresponding to 0.07% of the copper present in the catalyst. Hence it can be concluded that although some copper becomes dissolved into the solution, it is catalytically irrelevant and the process is truly heterogeneous.

The reusability of $Cu_3(BTC)_2$ was investigated for the oxidation of benzyl alcohol under identical conditions as described in Table 1. After the required time, the reaction mixture was filtered, dried, and the solid used for a consecutive run without further treatment. It was observed that, after two consecutive uses, the catalyst showed major changes in its crystallinity as evidenced by powder XRD. Comparison of the XRD patterns of the fresh and $Cu_3(BTC)_2$ used twice is provided in Figure 2. As it can be seen, there is a considerable change in the relative intensity of some peaks, particularly at low angle values. Although these XRD changes can be attributed in part to the fact that it can be expected that TEMPO will coordinate with the active sites present in the MOF and will cause some variation of peak intensities, the significant changes observed in the XRD after its use indicate that $Cu_3(BTC)_2$ undergoes some structural variations in the present experimental conditions. We will come later to this point when commenting on the influence of carboxylic acids on the catalytic activity. It should be mentioned that precedents in the literature reporting the use of a Zn-MOF containing Pt nanoparticles (2–5 nm) as catalyst for the solventless, room-temperature aerobic oxidation of benzylic alcohols results in the complete destruction of the MOF framework and leaching of Pt nanoparticles.[35]

Table 2. Oxidation of Susbstituted Benzylic Alcohol and Other Alcohols Using $Cu_3(BTC)_2$ with Oxygen[a]

Run	Substrate	Product	Yield (%)[b]
1			89
2			57
3			52
4			65
5			42
6			33
7			8
8			45
9			10
10			62
11			21, 27,[c] 39[c]
12			14
13			2
14			3

[a] Reaction conditions: alcohol (1 mmol), $Cu_3(BTC)_2$ (150 mg), TEMPO (0.5 equiv), Na_2CO_3 (1 equiv), acetonitrile (5 mL), 22 h, 75 °C, oxygen atmosphere. [b] Determined by GC using nitrobenzene as internal standard. [c] Yield after 32 and 44 h with an additional portion of $Cu_3(BTC)_2$ (150 mg).

Further, adsorption experiments showed a big decrease in the BET surface area from the fresh to the reused catalysts from 1019 to 14.1 m^2/g. This may be due to the presence of some inorganic and organic impurities generated during the course of the reaction that blocks the micropore system. In addition, the catalyst is also contaminated with benzoic acid as evidenced from FT-IR spectra (see the supporting information).

In order to expand the scope of the aerobic oxidation of benzylic alcohol by $Cu_3(BTC)_2$ assisted by TEMPO, we performed the aerobic oxidation of various alcohols. The results obtained are summarized in Table 2. Electron-donating substituents like hydroxy, amino, and methyl groups on the phenyl ring have resulted in good yields to the corresponding benzaldehyde. In addition, methoxy and ethoxy substituted benzyl alcohols were converted into the corresponding aldehydes with moderate yields (Table 2 entries 5 and 6). On the other hand, 3,4-dimethoxybenzyl alcohol resulted in a poor yield even with two electron donating groups. Although, 3,4-dimethoxybenzyl alcohol has a larger kinetic diameter than benzyl alcohol, the most likely reason for the low activity of $Cu_3(BTC)_2$ for this reaction is the influence of the electron-donating substituents. We will come back to this issue when describing the poisoning experiments.

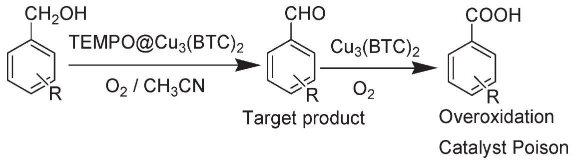
Next, we have studied some electron withdrawing substituents like nitro benzyl alcohols. *p*-Nitrobenzyl alcohol gave much better yield than *m*-nitrobenzyl alcohol under identical conditions. Apparently in the latter case, the negative influence on alcohol oxidation due to the presence of electron withdrawing nitro substituent is overimposed to the larger kinetic dimension of this alcohol due to the meta position.

Aerobic oxidation of cinnamyl alcohol resulted in a moderate yield of cinnamaldehyde without disturbing the C═C double bond. The present protocol was also tested for heterocyclic alcohol. For instance, aerobic oxidation of furfuryl alcohol resulted in furfuraldehyde in low yield.

To understand the reason why oxidation of furfuryl alcohol as well as other alcohols having electron-donating groups does not progress further and as a way to increase the yield of furfuraldehyde, once the reaction stops, an additional portion of fresh $Cu_3(BTC)_2$ catalyst was added to the reaction mixture. It was observed that the oxidation of furfuryl alcohol to furfural was further continued upon addition of fresh catalyst. A second addition of fresh $Cu_3(BTC)_2$ almost doubled the initial yield. These experiments clearly indicate that the reason for low conversion is the lack of catalytic sites in the reaction mixture and deactivation of the catalysts. Furthermore, a control experiment in which the corresponding furoic acid (30 mg) was added on purpose to the initial reaction mixture stopped the reaction. Thus, in the cases in which electron-donating substituents are favored over oxidation of the primary aromatic aldehyde to the corresponding carboxylic acid, the reaction does not proceed to completion. In a way to realize the catalytic activity of $Cu_3(BTC)_2$ and the low reactivity of some benzyl alcohols, we performed two controls on the aerobic oxidation of benzyl alcohol under the same experimental conditions as described in Table 1 except with two amounts of benzoic acid (15 and 30 mg). After the required time, the reactions were stopped, filtered, and the reaction mixture was analyzed. It was observed that benzaldehyde formation was drastically suppressed in the presence of benzoic acid (9% and 5% when adding 15 and 30 mg of benzoic acid, respectively). These experiments clearly demonstrate that the oxidized byproduct namely carboxylic acids may block the active catalytic sites and hence the catalysis is ceased. Thus, the available data suggest that catalysts deactivation by poisoning with carboxylic acid can be the reason for the low conversions achieved in some cases particularly when overoxidation appears to be easy. Scheme 2 summarizes our proposal.

Secondary alcohols like 1-phenylethanol and cyclooctanol were reluctant toward oxidation to the corresponding carbonyl compounds. Similar behavior was noticed with 1-octanol, and the yields were very low. Oxidation of primary aliphatic alcohols to the corresponding aliphatic aldehydes still remains a challenge in aerobic oxidation of alcohols in most of the heterogeneous catalysts reported so far, and thus, the low conversion of 1-octanol is understandable based on its low reactivity.[36] In order to account for the poor reactivity of this substrate, a control experiment was carried out to understand the interaction of the substrate with the active sites. When 1-octanol was oxidized with copper acetate instead of $Cu_3(BTC)_2$ under identical conditions, 43% of 1-octanal was observed. This experiment reveals that the pore accessibility of the substrate in the presence of TEMPO and sodium carbonate in acetonitrile medium may play a vital role in determining the reactivity of the substrates. Since $Cu_2(BTC)_3$ has two pore dimensions, it will be the smallest pore size (0.8 nm); the one that limits diffusion inside the crystallites. Finally, the oxidation of cyclohexanol was tested also using copper acetate and TEMPO under the same identical conditions, and unfortunately, the formation of cyclohexanone was not observed. Hence, we have demonstrated that the coordinatively unsaturated sites present in $Cu_3(BTC)_2$ could be conveniently used in the aerobic oxidation of benzyl alcohols. On the basis of the results reported in the present work, the low reactivity of some alcohols may be due to (i) the inability of substrates/reagents to reach the active sites and (ii) catalyst deactivation by poisoning and/or pore blocking. Our data indicates that $Cu_3(BTC)_2$ or in general an MOF having carboxylate linkers should not be suitable catalysts in those cases where one of the reactants, products, or byproducts is a carboxylic acid.

Scheme 2. Deactivation of $Cu_3(BTC)_2$ by Overoxidation of Benzaldehyde



CONCLUSIONS

To summarize, we have shown that $Cu_3(BTC)_2$ is a general catalyst for the oxidation of a number of benzyl alcohols that smoothly undergoes oxidation with molecular oxygen as oxidant to give benzaldehydes selectively in moderate to good yields. The catalyst could be easily recovered after the reaction and can be reused for consecutive runs with minor decrease in the yield of the product due to the formation of carboxylic acids that act as catalyst poisons. The main advantage of our procedure is that expensive noble metals are not needed in the process. Compared to nonporous copper acetate, $Cu_3(BTC)_2$ exhibits a similar behavior that is derived from a combination of Lewis acidity of copper ions with coordinatively unsaturated vacant position and large porosity in terms of surface area and pore size. Although there are several precedents of the use of copper for the aerobic oxidation of alcohols and we have found limitations in the $Cu_2(BTC)_3$/TEMPO system in terms of scope and catalyst stability, the use of MOFs offer the possibility to design specifically a MOF with enhanced performance with regard to $Cu_2(BTC)_3$. In particular, deactivation could be minimized with using linkers other than polycarboxylates. In addition to the results reported here, analogous systems to the one reported here could also be applicable for other aerobic oxidations, such as the benzylic oxidation of hydrocarbons and cycloalkanes.

EXPERIMENTAL SECTION

Materials. Basolite C 300 [$Cu_3(BTC)_2$] and the benzyl alcohols used in the present study were purchased from Sigma Aldrich and used as received. Solvents were used in high purity without any further pretreatment.

Characterization Techniques. The percentage conversion, purity and relative yields of the final products were determined using Hewlett-Packard 5890 series II gas chromatograph with an flame ionization detector (FID) and high purity helium as the carrier gas. The products were identified by comparing their retention times in GC with authentic samples and by their mass spectra recorded with GC-MS Hewlett-Packard 6890 series. Powder XRD diffraction patterns were recorded in a Philips X'Pert diffractometer using the Cu K_α radiation ($\lambda = 1.54178$ Å) as the incident beam, PW3050/60 (2 theta) as goniometer, PW 1774 spinner as sample stage, and PW 3011 as detector, with the incident mask fixed with 10 mm. PW3123/10 for Cu was used as a monochromator. PW3373/00 Cu LFF was used as X-ray tube with power scanning of 45 kV and 40 mA current. The sample powder was loaded into a holder and leveled with a glass slide before mounting it on the sample chamber. The specimens were scanned between 2 and 70° with the scan rate of 0.02/s. Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2000 volumetric adsorption analyzer. Before the measurements, the samples were outgassed for 4 h at 473 K. The specific surface area was calculated by applying the BET model to the nitrogen adsorption data. Chemical composition was determined by atomic absorption in a Varian SpectrAA-10 Plus, and elemental analysis was performed in a Fisons EA1108CHN-S. IR spectra were recorded within KBr pellets in a Nicolet 710 FT spectrophotometer.

Typical Procedure for Alcohol Oxidation. A 50 mL round-bottomed flask was charged with the required amount of catalyst, TEMPO, and sodium carbonate. To this mixture, 5 mL of acetonitrile was added followed by the appropriate quantity of alcohol. The reaction mixture was stirred vigorously under oxygen atmosphere for the required time and temperature. At the end of the reaction, the heterogeneous mixture was cooled down to room temperature and extracted with acetonitrile (10 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 internal standard. This may be explained by the adsorption of some reactants/products on $Cu_3(BTC)_2$. A similar procedure was followed for copper acetate maintaining the same copper content as for the $Cu_3(BTC)_2$ catalyst.

Experimental Procedure for Reusability Tests. The reusability of $Cu_3(BTC)_2$ was tested for the oxidation of benzyl alcohol. At the end of the reaction, the heterogeneous mixture was diluted with acetonitrile, filtered and dried at 70 °C. The recovered catalyst was reused without further purification for the second run with fresh benzyl alcohol.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** FTIR spectra of the fresh and reused $Cu_3(BTC)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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