

# Deactivation of Cu<sub>3</sub>(BTC)<sub>2</sub> in the Synthesis of 2-Phenylquinoxaline

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**Abstract**  $Cu_3(BTC)_2$  deactivates by deterioration of its crystal structure during the use of this metal organic framework as catalyst in the synthesis of 2-phenylquinoxaline from phenacylbromide and *o*-phenylenediamine at room temperature. The material resulting from the use of  $Cu_3(BTC)_2$  as catalyst was characterized by powder XRD, UV–Vis diffuse reflectance spectra and EPR showing that the crystal structure collapses and  $Cu^{2+}$  becomes reduced under the reaction conditions.

Graphical Abstract



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#### **1** Introduction

Metal–organic frameworks (MOFs) are crystalline materials in which the lattice is constituted by metal nodes held in place by rigid linkers [1, 2]. The high metal content, the possibility of having some coordinatively unsaturated sites around the metal atoms, their large surface area and porosity have made MOFs as one of the most promising materials for heterogeneous catalysis [3–9]. There is by now a considerable number of examples showing that MOFs can exhibit very high catalytic activity to promote a large variety of organic reactions of interest in the synthesis of fine chemicals [10] among other processes.

One of the main advantages of MOFs as heterogeneous catalysts is their easy and reliable synthesis from readily available precursors. In this context, a convenient and facile procedure for the room-temperature synthesis of HKUST-1 from copper(II) hydroxide in aqueous ethanolic solution has been reported [11]. One of the major concerns to be addressed when using MOFs as catalysts is stability under reaction conditions [12]. There are examples showing that some MOFs are initially active as catalysts but, however, deactivate during the course of the reaction due to the incompatibility of MOF structure with solvents or reagents under the conditions required for the catalysis [12]. Specifically, one MOF with large interest as heterogeneous catalyst, but that has been found to become destroyed in some reactions is  $Cu_3(BTC)_2$  (BTC: 1,3,5-benzenetricarboxylate) [13]. This MOF is amply used as heterogeneous catalysts in many different types of reactions including cyanosilylation [14], epoxide rearrangement [15], ring opening of epoxide [16], acetalization of aldehydes [17],

oxidation of xanthene [18] and Knoevenagel condensations [19]. However, in several cases, it has been observed that  $Cu_3(BTC)_2$  is not stable enough to survive the reaction conditions, as for instance in the case of the aerobic oxidation of thiols to disulfides [20] and aerobic oxidation of benzyl alcohol to benzaldehyde [21]. Considering the catalytic properties of  $Cu_3(BTC)_2$ , it is important to delineate further for which type of reactions this commercially available MOF can stand the reaction conditions and also to provide information on those other cases in which  $Cu_3(BTC)_2$  is not stable as solid catalysts.

Recently, MOFs are being used as one of the convenient heterogeneous catalysts for various organic transformations with very high activity compared to other porous solids [9, 22]. In particular,  $Cu_3(BTC)_2$  has been reported as heterogeneous solid acid catalyst for the synthesis of quinoline derivatives in high yields under solvent-free reaction conditions. The reaction between 2-aminobenzophenone and acetylacetone in the presence of  $Cu_3(BTC)_2$  resulted in 80 % of 3-acetyl-2-methyl-4-phenylquinoline in 1 h and the reaction was completed in 2 h [23]. It was also shown that Cu<sub>3</sub>(BTC)<sub>2</sub> can be recovered without any significant structural changes. The advantage of using MOFs as solid acid catalysts is that it shows higher activity compared with homogeneous catalysts. Furthermore, it can be reused in consecutive cycles. Quinoxaline is one of the nitrogen containing heterocycles that has been synthesised using many homogeneous Lewis acid [24] catalysts, Brönsted acid [25] catalysts and heterogeneous solid catalysts [26–28].

In this context, our aim is to use  $Cu_3(BTC)_2$  as heterogeneous catalyst for the synthesis of 2-phenylquinoxaline from phenacyl bromide and *o*-phenylenediamine (OPD) at room temperature. Unfortunately, it was observed that the catalyst is not stable under these mild conditions, resulting structural deterioration. Structural analysis of the material resulting after the use of  $Cu_3(BTC)_2$  as catalyst show that OPD interacts with  $Cu^{2+}$  ions in  $Cu_3(BTC)_2$  leading to transformation of the lattice and reduction of  $Cu^{2+}$  ions.

## 2 Results and Discussion

In our continuous effort of using MOFs as heterogeneous solid catalysts, we were interested in studying the catalytic activity of  $Cu_3(BTC)_2$  for the synthesis of 2-phenylquinoxaline by condensation of phenacyl bromide and OPD in ethanol at room temperature (Scheme 1). It was observed that under the present reaction conditions  $Cu_3(BTC)_2$  promotes the reaction towards the formation of the desired product in 57 % yield after 3 h. However,  $Cu_3(BTC)_2$  becomes deactivated as noticed by the change in the colour from blue to yellow and the fact that the reaction did not progress further.



Scheme 1 Condensation of OPD and phenacyl bromide to form 2-phenylquinoxaline

It has been already shown unambiguously that Cu<sub>3</sub> (BTC)<sub>2</sub> possesses Lewis acid sites which are responsible in promoting chemical transformations. This could be achieved by the removal of coordinated solvent molecules from Cu nodes, thus, creating coordinated unsaturated sites or Lewis acid sites. Under the present experimental conditions, OPD reacts with phenacyl bromide and interacts simultaneously with the Lewis acid sites in  $Cu_3(BTC)_2$ , thus, leading to the reduction of  $Cu^{2+}$  to the lower oxidation state or metallic Cu. This reduction process collapses the crystal structure by leaching of  $Cu^{2+}$  and trimesic acid to the solution (Scheme 2). Analysis of the reaction mixture by GC-MS clearly indicates the presence of trimesic acid, proving the breakdown of metal-ligand coordination bond present in MOF. It is interesting to mention here that care must be given to maintain catalyst stability as well as to select the reactants which should not disturb the crystalline nature of the catalyst. It is relevant to mention here that the collapse of MOFs crystal structures is mainly due to the nature of reagent and temperature. In the present case, OPD interacts with Cu<sup>2+</sup> possibly through a strong coordinative bond competing that responsible for the crystal structure of  $Cu_3(BTC)_2$ .  $Cu^{2+}$  is known to form strong bonds with diamines [29-31]. There are precedents in which amines as reagents produce the collapse of the structure of the MOF acting as catalyst. For instance, methylation of n-hexyl amine by dimethyl carbonate has been reported using with Al(OH)(BDC) (BDC: 1,4-benzenedicarboxylate) at 170 °C observing together with methylated and carbamoylated products the presence of dimethyl terephthalate [32]. Formation of dimethyl terephthalate was interpreted as indicating that the coordinative bond between Al<sup>3+</sup> and BDC linker is distroyed by the amine liberating free carboxylate groups that later undergo methylation by dimethyl carbonate. In another precedent, the crystal structure of Cu<sub>3</sub>(BTC)<sub>2</sub> was collapsed during the aerobic oxidation of thiophenol at 70 °C in acetonitrile medium after 10 min due to the strong Cu<sup>2+</sup>thiol bond [13]. We note, however, that in the present case, the experimental conditions are milder, since the reaction is performed at room temperature and the reaction times are comparatively shorter. It appears that OPD interacts strongly with  $Cu^{2+}$ , resulting in the collapse of the crystal structure. It seems that the effect of OPD should be general for other MOFs whose lattice is based on Cu<sup>2+</sup>-carboxylate interactions.

Scheme 2 Decoordination of  $Cu_3(BTC)_2$  to trimesic acid and  $Cu^{2+}$  by OPD. L: ligands that can be coordinating species present in the medium including other OPD,  $Br^-$  or solvent molecules



Currently, there is a need to delineate the stability of MOFs compared with zeolites and other related metal oxides with the aim to clarify if MOFs could be used as industrial heterogeneous catalysts. We have already demonstrated that Cu<sub>3</sub>(BTC)<sub>2</sub> undergoes major changes in its crystal structure by forming Cu nanoparticles when reacted with aliphatic/aromatic thiols [13]. Similarly, destruction of Cu<sub>3</sub>(BTC)<sub>2</sub> framework was observed in the oxidation of CO [33]. In another precedent, the structure of Pt-doped HKUST-1 collapsed in the presence of dissociated hydrogen due to the higher reduction potential of Cu compared with H, the instability of the divalent copper in HKUST-1 increasing with temperature. Unlike HKUST-1, MIL-53 and ZIF-8 maintained their structures in processes that involve both dihydrogen and dissociated hydrogen at temperatures up to 150 °C [34]. Also,  $Cu_3(BTC)_2$  with an incorporated Keggin polyoxometalate has been shown to be stable under steaming conditions up to 210 °C, while the isostructural HKUST-1 degrades and transforms into  $[Cu_2OH(BTC)(H_2O)]_n \cdot 2nH_2O$ from 70 °C onwards [35]. Hence, it is of interest to determine in more detail the cause of Cu<sub>3</sub>(BTC)<sub>2</sub> deactivation in the quinoxaline synthesis. In the present study, we provide spectroscopic information showing that by interaction with OPD, Cu<sub>3</sub>(BTC)<sub>2</sub> undergoes a transformation in its crystal structure.

Thus, after the reaction, the solid material derived from  $Cu_3(BTC)_2$  used as catalysts was washed with excess ethanol and it was characterized by powder XRD, UV–Vis diffuse reflectance spectroscopy (DRS) and EPR. This study shows that  $Cu_3(BTC)_2$  stability must be surveyed when any catalytic reaction involves the use of OPD as reactant.

Figure 1 shows the powder XRD patterns of fresh  $Cu_3(BTC)_2$  and the solid material derived from  $Cu_3(BTC)_2$  used as catalysts after the treatment with phenacyl bromide and OPD. As it can be seen there, the characteristic peak pattern and peak intensity of  $Cu_3(BTC)_2$  changes completely and decreases much in its intensity when treating  $Cu_3(BTC)_2$  with these reactants. Also, Fig. 1 shows a new peak at low angle which is absent in the fresh material indicating that there is a structural change of the solid material derived from  $Cu_3(BTC)_2$  used as catalysts. It can



Fig. 1 Powder XRD patterns of **a** fresh  $Cu_3(BTC)_2$ , **b**  $Cu_3(BTC)_2$  treated with 100 mg of OPD, **c**  $Cu_3(BTC)_2$  treated with 175 mg of OPD and **d** the solid material derived from  $Cu_3(BTC)_2$  used as catalysts after the reaction. Note that diffractrogram "a" and "d" are totally different

be seen in Fig. 1 that the stability of the crystal structure is mainly dependent on the concentration of OPD that is the reagent causing damage of the Cu<sub>3</sub>(BTC)<sub>2</sub> crystallinity. XRD indicates that the crystal structure of Cu<sub>3</sub>(BTC)<sub>2</sub> is relatively unaffected when the concentration of OPD is low (100 or 175 mg) that correspond to less than one OPD equivalent per  $Cu^{2+}$  in  $Cu_3(BTC)_2$ . When the OPD (250 mg) concentration exceeds with Cu<sup>2+</sup> amount (OPD: $Cu^{2+}$  mol ratio 1.12), the crystal structure of  $Cu_3$ (BTC)<sub>2</sub> undergoes major changes in its diffraction pattern (Fig. 1). In contrast to the behaviour of  $Cu_3(BTC)_2$  in the presence of OPD, XRD and the colour of Cu<sub>3</sub>(BTC)<sub>2</sub> was maintained when the MOF was treated with phenacyl bromide under identical reaction conditions. In any case, the crystal structure was completely collapsed when Cu<sub>3</sub>(BTC)<sub>2</sub> was used as catalyst for the synthesis of 2-phenylquinoxaline from phenacyl bromide and OPD at room temperature. Thus, XRD clearly establishes that most of the characteristic peaks in the fresh catalyst have decreased/disappeared in the solid material derived from  $Cu_3(BTC)_2$  used as catalysts supporting our claim based on literature precedents of the possible interaction of OPD substrate with the dimeric Cu nodes in the MOFs structure,

transforming it into another crystal structure and leading to deactivation. Overall, XRD shows that  $Cu_3(BTC)_2$  undergoes structural transformation in the presence of OPD by destroying its crystal structure probably into another inactive form.

Figure 2 provides DRS of fresh and deactivated Cu<sub>3</sub> (BTC)<sub>2</sub> after the condensation reaction leading to 2-phenylquinoxaline formation. The fresh  $Cu_3(BTC)_2$  exhibits two absorption bands around 284 and 700 nm. The first absorption band corresponds to the aromatic ligand and the latter one is due to the d-d transition of  $Cu^{2+}$ . Interestingly, the d-d band completely diminishes in the solid material derived from Cu<sub>3</sub>(BTC)<sub>2</sub> used as catalysts after the catalytic reaction. It is interesting to note that the decrease in the intensity of d-d band was dependent on the concentration of OPD. When the concentration of OPD increased gradually, the intensity of d-d band diminished completely even at room temperature. However, the solid material derived from Cu<sub>3</sub>(BTC)<sub>2</sub> used as catalysts still shows the absorption band corresponding to the ligand due to the existence of ligand even after the structural change. Furthermore, Fig. 2 also shows that the absorption between 200 and 300 nm characteristic of aromatic linkers has reduced considerably its intensity in the solid material derived from Cu<sub>3</sub>(BTC)<sub>2</sub> used as catalysts. The residual absorption in this UV region probably indicates that some linker is still present in the solid material derived from Cu<sub>3</sub>(BTC)<sub>2</sub> used as catalysts. From powder XRD it was concluded that the structure of Cu<sub>3</sub>(BTC)<sub>2</sub> has completely changed and DRS shows the gradual disappearance of  $Cu^{2+}$  as a function of OPD concentration.

EPR spectra were measured for  $Cu_3(BTC)_2$  and the solid material derived from  $Cu_3(BTC)_2$  used as catalysts after the reaction. The observed results are presented in Fig. 3. The fresh catalyst  $Cu_3(BTC)_2$  shows the EPR spectrum



corresponding to the presence of  $Cu^{2+}$ . In contrast, the solid material derived from  $Cu_3(BTC)_2$  used as catalysts showed a decrease in its intensity and a change in the coupling constant of the EPR signal indicating a decrease in the population of EPR active copper species ( $Cu^{2+}$ ). This decrease in the intensity of  $Cu^{2+}$  agrees well with the results from DRS and must be related to the collapse of the crystal structure observed by powder XRD. Furthermore, literature data showing that  $Cu^{2+}$  promotes spontaneous oxidation of OPD can explain why  $Cu^{2+}$  becomes reduced under the reaction conditions [36].

Thus, in view of the moderate strength of the  $Cu^{2+}$ carboxylate interaction responsible for MOF structure, and the high affinity of Cu ions for thiols and amines, it can be anticipated that  $Cu_3(BTC)_2$  should not be considered an appropriate solid catalyst for those reactions that involve the type of reagents with high affinity as Cu ions ligands.

Interestingly, the synthesis of 2-phenylquinoxaline has been reported by the oxidative cyclization of  $\alpha$ -hydroxyketone and OPD using Cu(BDC) as heterogeneous catalyst in quantitative yield at 100 °C in toluene under air atmosphere in 3 h [37]. Furthermore, the reaction using Cu<sub>2</sub>(BDC)<sub>2</sub>(DABCO) as catalyst resulted in 87 % conversion, while MOF-118 was found to be even more active by giving 92 % conversion after 3 h. On the other hand, Cu<sub>3</sub>(BTC)<sub>2</sub> encapsulated heteropolyacid exhibited 84 % conversion. A slightly lower yield was achieved with MOF-199 as catalyst under identical conditions. These previous results are in good agreement with the present work and can be interpreted as derived from the instability of MOF-199 whose structure is similar to Cu<sub>3</sub>(BTC)<sub>2</sub>. A very interesting point from this precedent is that among the various Cu-based catalysts tested for the synthesis of 2-phenylquinoxaline, the crystal structure of Cu(BDC) was not damaged. Interestingly, Cu(BDC) exhibited 97 % conversion even after eight runs and powder XRD of the recovered Cu(BDC) after its use as catalyst revealed that its





Fig. 2 DRS of fresh  $Cu_3(BTC)_2$  (*black line*),  $Cu_3(BTC)_2$  treated with 100 mg of OPD (*blue line*),  $Cu_3(BTC)_2$  treated with 175 mg of OPD (*red line*) and the solid material derived from  $Cu_3(BTC)_2$  used as catalysts (*green line*)

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Fig. 3 EPR spectra of fresh  $Cu_3(BTC)_2$  (solid line) and the solid material derived from  $Cu_3(BTC)_2$  used as catalysts (dotted line)



Scheme 3 Contrasting frame work stability of various Cu MOFs in the synthesis of 2-phenylquinoxalines

crystallinity was maintained with slight difference in the diffractogram. This stability was proposed to derive from the flexibility of Cu(BDC) structure and the non-isotropy during fresh sample preparation. Scheme 3 compares the herein observed data for  $Cu_3(BTC)_2$  with those of related precedents.

Comparing the present data with that of the results reported in the literature [37] it can be concluded that the catalyst stability must be surveyed after any catalytic reaction. Furthermore, the observed results are applicable only to the crystal structure of  $Cu_3(BTC)_2$  under a combination of reagents and conditions and it cannot be generalized to other Cu-based MOFs. Based on the results from DRS and EPR, it can be assumed that Cu exists in the metallic state either as Cu nanoparticles or in the form of Cu (I)-complexes. Further studies are required to identify in detail the composition of the solid material derived from  $Cu_3(BTC)_2$  used as catalysts.

# **3** Conclusions

The present work highlights that  $Cu_3(BTC)_2$  undergoes structural deactivation in the presence of OPD which results in drastic structural changes. The observed results indicate that Cu<sub>3</sub>(BTC)<sub>2</sub> as heterogeneous solid catalyst is not stable in reactions that involve OPD as one of the reagents. This may be due to the strong coordination of OPD groups with the coordinatively unsaturated  $Cu^{2+}$  sites which subsequently decomposes the crystal structure even at room temperature and can promote  $Cu^{2+}$  reduction. This study illustrates that the active sites are decomposed or changed into another inactive material as evidenced by powder XRD, DRS and EPR and contrasts with related precedents. Hence, it can be concluded that the catalyst stability mainly depends on the reaction temperature, nature of reagents, contact time of catalyst with reagents and solvent and predictions on MOF stability can be misleading.

## **4** Experimental Section

#### 4.1 Materials

 $Cu_3(BTC)_2$  also commercially known as Basolite C 300 MOF, OPD and phenacyl bromide used in the present study was purchased from Sigma Aldrich and used as received. Solvents used in the present study were purchased from Sigma Aldrich.

# 4.2 Characterization Techniques

Powder XRD diffraction patterns were measured in the refraction mode using a Philips X'Pert diffractometer using the CuK<sub> $\alpha$ </sub> radiation ( $\lambda = 1.54178$  Å) as the incident beam, PW3050/60 (2 theta) as Goniometer, PW 1774 spinner as sample stage, PW 3011 as detector, 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 levelled with a glass slide before mounting it on the sample chamber. The specimens were scanned between  $2^{\circ}$  and  $70^{\circ}$ with the scan rate of 0.02°/s. UV-Vis diffuse reflectance spectra were measured using a Cary 100 G UV-Vis-NIR spectrophotometer using an integrating sphere accesory. EPR spectra were recorded using a Bruker EMX, with the typical settings: frequency 9.80 GHz, sweep width 30.6 G, time constant 80 ms, modulation frequency 100 kHz, modulation width 0.2 G, microwave power 200 mW.

## 4.3 Experimental Procedure

To a stirred solution of 0.250 mg of OPD and 480 mg of phenacyl bromide in 20 mL of ethanol, 350 mg of Cu<sub>3</sub> (BTC)<sub>2</sub> (activation at 150 °C for 3 h) was charged and the mixture was stirred at room temperature under air at atmospheric pressure. As the reaction progresses, the colour of the heterogeneous mixture turned from blue to yellow.

After 2 h, the pale yellow solid was filtered, washed with ethanol (50 mL) in two portions, dried.

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