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Reusable Cu^{II} Based Metal Organic Framework as Catalyst for the Oxidation of Olefins

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Abstract

The metal organic framework $[Cu_2(bipy)_2(btec)]_\infty$, was used as an heterogeneous catalyst in the liquid phase oxidation of styrene and cyclohexene, with *tert*-butylhydroperoxide (TBHP) as oxidant either in water/dicholoroethane or n-decane medium. Four catalytic systems were tested and compared after 6 hours of reaction time. The oxidation of styrene using $[Cu_2(bipy)_2(btec)]_\infty$ showed a competitive conversion, as compared with some Cu^{II} heterogeneous catalysts and MOF catalysts. Conversion between 61-45% in dichloroethane:TBHP:water at 75 °C was obtained, using molar ratios of substrate:catalyst from 200 to 2400. When the solvent was replaced by n-decane, the conversion remained similar, that is, between 57-46%, for the same mole ratio range of substrate:catalyst. For styrene oxidation in dichloroethane:TBHP:water $[Cu_2(bipy)_2(btec)]_\infty$ is not selective; the products being benzaldehyde, styrene epoxide and 1-phenylacetaldehyde in 37%, 35% and 29% yields, respectively. The oxidation of cyclohexene showed a conversion of 34-16%, for the same experimental conditions in dichloroethane:TBHP:water at 75 °C; the catalytic reaction presenting a higher selectivity in the formation of 2-cyclohexene-1-one as product. When n-decane was used, the total conversion in cyclohexene oxidation decreased approximately by 10%, as compared to the dichloroethane:TBHP:water system. The activities reported for the Cu-MOF showed a very high selectivity for the allylic oxidation product. Leaching during the catalytic reaction was found to be negligible, and the structure was maintained during the four catalytic runs, as confirmed by powder X-ray diffraction analysis of the reused catalyst.

Key-words: Cu-MOF; heterogeneous catalysis; olefin oxidation, epoxidation olefin

Introduction

Allylic oxidation products and epoxides of alkenes have wide applications in organic synthesis, and in the manufacture of perfumery, pharmaceutical products, dyestuff and agrochemicals [1-4]. The use of heterogeneous catalysts in the oxidation reaction of these olefins has become an area of growing interest, since they can be easily isolated from the reaction products, and thus they present the possibility of reusability [5-8]. Much attention has been paid in the use of heterogeneous catalysts in oxidation reactions since these catalysts reduce waste, thus promoting environmentally benign chemical processes.

Homogeneous catalysts possess higher efficiency and are suitable for the study of the reaction mechanisms, but their higher susceptibility to drastic reaction conditions and the difficulties associated with their isolation from the product mixture restrict their reusability. These disadvantages have been overcome by immobilizing metal complexes on suitable supports. Many of the mentioned heterogeneous catalysts are solid inorganic species or transition metal complexes immobilized in mesoporous matrixes or grafted on surfaces [9,10]. The anchoring of metal species on solid supports not only exhibits improved catalyst stability and selectivity of the product, but it also enables easy recovery and reuse of the catalyst [11,12]. Since the preparation of heterogeneous catalysts without the need of an organic or inorganic support is still of great need and remains of immense interest, another group of catalysts has been being investigated in recent years; metal organic frameworks (MOFs) [13]. Their covalently bonded structures make them even better candidates for heterogeneous catalysis, since leaching is less frequent in these frameworks as compared with the supported catalysts.

MOFs are crystalline materials whose structures are related to those of zeolites and other inorganic porous solids. The interest in MOFs has increased exponentially in the past years, due to their intriguing structural properties and potential applications in various fields, including gas adsorption, storage, and catalysis [14-19]. Considering the high metal content present in MOFs, and their similarity with zeolites, these materials are nowadays attracting an increasing interest as heterogeneous catalysts. In this respect, the reported $[Cu(bipy)H_2btec)]_\infty$ [20] is an excellent example of a MOF with application in the heterogeneous catalysis area. Our group found that this Cu-MOF presented catalytic activity and selectivity for the oxidation of cyclohexene and styrene in only 6 h time reaction. Corma et al. have reported aerobic oxidation of tetralin, cumene and ethylbenzene using Cu-MOFs as catalysts; the studied MOFs are reported with activities between 87%-95% [21-22]. On other hands titanium- and cobalt-monosubstituted Keggin heteropolyanions $[PW_{11}CoO_{39}]^{5-}$ and $[PW_{11}TiO_{40}]^5$ were supported on a chromuim terephthalate polymer matrix MIL-101, and used in heterogeneous oxidation of α-pinene with a reported conversion of around 50%[23]. Recently, Juan-Alcañiz et al. [24] have developed a versatile post-functionalization for metal incorporation in MIL-101(Cr) with oxamate as ligand. This resulted in catalytic centers of metal–organic complexes or in controlled formation of metal nanoparticles. These heterogeneous catalysts containing oxamate based Cu-MOF showed high activities in the oxidation of benzyl alcohol and phenyl acetylene in only 4 h of reaction.

Other studies using MOFs, based on molybdenum/vanadium phosphate and lanthanide, as catalysts reported the epoxidation or oxidation of styrene. These catalysts present over 90% conversion for styrene oxidation, but the selectivity of the epoxidation of styrene was low [25-28]. Based on the role of the reported copper(II) metal organic framework $[Cu(bipy)H_2btec)]_\infty$ as catalyst for olefin oxidation, we now report the catalytic properties of another Cu-MOF, $[Cu_2(bipy)_2(btec)]_{\infty,}$ which was also studied as a catalyst under mild reaction conditions in the oxidation of olefinic substrates. A comparison of both catalytic systems is made for the same reaction.

Experimental

Synthesis

$[Cu_2(bipy)_2(btec)]_{\infty}$, previously synthesized by Hao et al. [29] was obtained by the hydrothermal technique using $Cu(CH_3COO)_2 \cdot 2H_2O$ (0.1997 g), 1,2,4,5-benzenetetracarboxylic acid (H_4btec, 0.1270 g), 2,2´-bipyridine (bipy, 0.1567 g), and NaOH (0.080 g). (Yield: 0.3276 g, 95 %; Elemental analysis (Calc.%) C: 52.5; H: 2.6; N: 8.1%. (Exp.%) C: 52.3; H: 3.0; N: 8.5%.

X-Ray Diffraction

A Siemens D 5000 diffractometer was used to record all the powder diffractograms. In order to characterize the chemical identity of the synthesized Cu-MOF**,** the powder X-ray diffraction pattern of the obtained product was compared with the diffractogram generated with the data previously reported by Hao et al. [29] (Fig. 1). This technique was also used to corroborate that no significant structural changes occur when the catalyst was reused.

Figure 1 here

ICP spectroscopy

The solutions obtained after catalytic reactions were analyzed by optical ICP spectroscopy, using a Perkin Elmer Optima 2000 DV model spectrometer. The free copper concentrations were determined, using standards of different concentration.

N_2 Sorptometry

The surface area of $[Cu_2(bipy)_2(btec)]_\infty$ was measured using the Braunuer-Emmet-Teller (BET) method on a Micromeritics ASAP 2010 equipment, after degassing the sample. The results of the physical characterization of the catalyst by N_2 sorptometry show that the specific area is approximately 11 m^2g^{-1} and the pore volume is 0.060 cm^3g^{-1}, being the adsorption isotherm of type III, according to the IUPAC classification.

Catalytic Studies

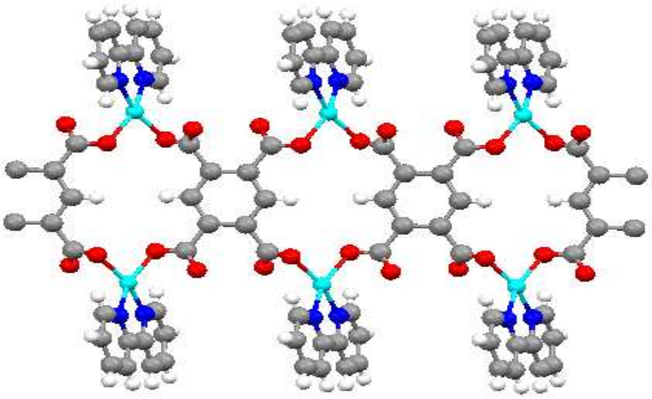
For the heterogeneous oxidation of styrene and cyclohexene, reactions were performed in a magnetically stirred two necked round-bottom 25 mL flask fitted with a condenser, and placed in a temperature controlled oil bath. All the reactions were carried out under nitrogen atmosphere. Experiments were done at 75ºC, using the following reaction conditions: the catalyst (variable mass) was added in the reactor together with 1,2-dichloroethane (DCE) or n-decane (10 mL as solvent); when the reaction temperature was reached the substrate, styrene (4,6 mL; 40 mmol) or cyclohexene (4,1mL; 40 mmol), and the oxidant were added. The oxidant TBHP was incorporated to the reaction mixture, using TBHP 70% in water (3,9 mL; 40 mmol) or TBHP 5M in decane (7,3 mL; 40 mmol). The studied molar ratios of substrate:TBHP:catalyst were: 200:200:1, 400:400:1, 800:800:1, 1200:1200:1 and 2400:2400:1. Aliquots of the solution (10 μL) were removed at different reaction times, and analyzed by gas chromatography (GC) [30].

Gas chromatographic analyses were carried out with a Hewlett Packard 5890 GC, equipped with a flame ionization detector (FID), and a Carbowax 20M capillary column (25 m x 0.2 mm x 0.2 μm), using nitrogen as carrier gas. The oxidation products were identified by spiking, using standard compounds, and by MS-GC.

Results and Discussion

Structure Description

The compound $[Cu_2(bipy)_2(btec)]_\infty$ was obtained according with the literature procedure [29] and is shown in scheme 1.



Scheme 1. $[Cu_2(bipy)_2(btec)]_\infty$

Catalytic Studies

Even though the BET surface for the Cu-MOF was small (~11 m^2g^{-1}; see Fig 2), at the cryogenic temperature of liquid nitrogen, a selective sorption occurs through a size-exclusion, as is the case of many narrow-pore systems. These results indicate a non-porous structure. The selective sorption of MOFs [30] depend strongly on the type of substance adsorbed and the temperature. Therefore, the area determined by the BET method may become different under catalytic condition, since the adsorbed amount will depend on the interactions between the adsorbed molecules and adsorbent surface.

Figure 2 here

The catalyst showed considerable activity for the studied olefinic substrates (styrene and cyclohexene) in two different reaction media (dichloroethane/water and n-decane).

The conversion increased only by 10% after 24 h (average for all the used substrate:catalyst ratios) compared with the results obtained for 6 h. The selectivity for long periods of time was also maintained, only with small variations for both solvents. Therefore the results informed in this paper correspond to data obtained for 6 hours. Figure 3 shows the conversion of styrene and cyclohexene for the 400:1 mole ratio.

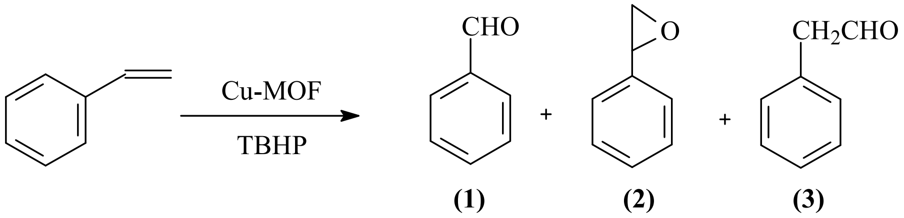
Figure 3 here

Table 1 and table 2 show the effect of different oxidants in the oxidation of cyclohexene and styrene, for substrate/catalyst ratio 400:1. For both organic substrates the best oxidant is terbutylhydroperoxide. When the reaction was made using oxygen as oxidant the conversion is only 15% and 5% for cyclohexene oxidation, and no conversion was observed in styrene oxidation. Moreover when the study was made using hydrogen peroxide as oxidant the catalytic reaction took place in homogeneous condition. The oxidant dissolved almost completely the catalyst, and the free metal concentration, determined by ICP spectroscopy was 62% of copper. On other hand based on studies made for us, the optimal temperature for the reaction is 75°C; under this temperature the conversion is low and over 75° C the selectivity of the reaction is poor, since the oxidant terbutylhydroperoxide decompounds easily [20].

Table 1 and Table2

Aqueous Dichloroethane System for Styrene Oxidation

The obtained products for the catalyzed oxidation reaction of styrene in dichloroethane, using aqueous TBHP as oxidant, were benzaldehyde (**1**) styrene epoxide (**2**), and 1-phenylacetaldehyde (**3**) (Scheme 2).



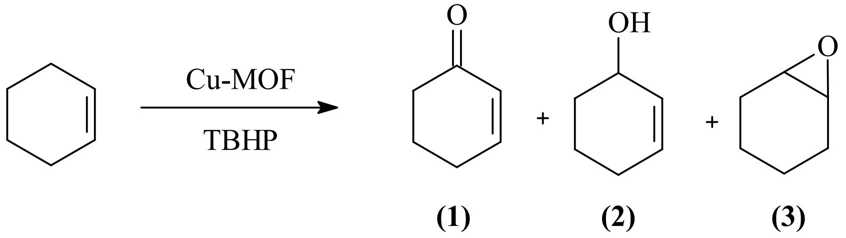
Scheme 2. Oxidation Products of Styrene.

The total conversion of styrene at the different molar ratios, is reported at 6 h of reaction time and 75 °C, with values between 61 - 45% (Table 3)**.** The average yield of products (**1**), (**2)** and **(3)** was approximately 24, 34 and 42% respectively for substrate/catalyst mole ratios from 200:1 to 2400:1.

Table 3 here

Aqueous-Dichloroethane System for Cyclohexene Oxidation

The obtained products for the catalyzed oxidation reaction of cyclohexene in dichloroethane, using aqueous TBHP as oxidant, were 2-cyclohexene-1-one (**1**), 2-cyclohexene-1-ol (**2**); cyclohexene epoxide was not obtained (**3**) (Scheme 3). A small quantity of other unidentified products (**4**) was also present.



Scheme 3. Oxidation Products of Cyclohexene.

$[Cu_2(bipy)_2(btec)]_\infty$ MOF showed moderate catalytic activity for cyclohexene oxidation. The total conversion of cyclohexene oxidation is also reported for 6 h of reaction at 75 °C, with values between 16% and 34%, depending on the substrate:catalyst ratio (Table 4); the reaction being selective towards 2-

cyclohexene-1-one (**1**) (ca.74%). Thus, under the used experimental conditions, the allylic hydrogen is more reactive than the double bond of the cyclic fragment.

Table 4 here

The conversions in the cyclohexene oxidation reaction were lower than those for styrene oxidation, which is in agreement with what is reported in the literature [31], that is, that the former olefin is more difficult to oxidize (Fig. 3).
The conversion increases only ca. 10% when the reaction time is increased to 24 h; the yields being very similar to those observed for 6 h. The higher selectivity towards the 2-cyclohexene-1-one is maintained for all substrate/catalyst ratios (from 200:1 to 2400:1; average value of 74%).

Effect of Solvent

Non- Aqueous n-Decane System for Styrene or Cyclohexene Oxidation

Table 5 and Table 6 show the catalytic activity and selectivity of $[Cu_2(bipy)_2(btec)]_\infty$, using the n-decane/TBHP system. Styrene oxidation in n-decane does not produce important differences in the catalytic behaviour of the $[Cu_2(bipy)_2(btec)]_\infty$ MOF (Table 5). The same is observed for the catalytic reaction of the oxidation of cyclohexene, as can be seen in Table 6. it is important to remark that a small amount of cyclohexene epoxide is observed in the non-aqueous system, contrary to what is obtained for the dichloroethane/aqueous system, where the epoxide was not detected. While Ghiaci et al. [32] observed an enhancement in the allylic oxidation of cyclohexene when a mixed chlorinated solvent/aqueous system was used as compared to n-decane, in the case of the $[Cu_2(bipy)_2(btec)]_\infty$ MOF the observed selectivity is similar for both solvent systems. When the catalytic activities in dichloroethane/H_2O and n-decane were compared became evident that the dichloroethane/ H_2O is a better catalytic system than that of n-decane, probably due to the greater polarity of the solvent (dichloroethane/H_2O), which facilitates the interactions between the polar surface of the catalyst, oxidant and substrate.

Table 5 and Table 6 here

Possible Mechanisms

Literature reports high activities in the oxidation of styrene and cyclohexene using immobilized copper complexes or Cu-MOF. For example, our group reported the epoxidation of styrene and cyclohexene using the Cu-MOF, $[Cu(bipy)(H_2btec)]_\infty$ [20]; this catalyst showing high selectivity for epoxide formation among the products. Jana et al. reported a copper(II) Schiff base complex anchored on a MCM-41 matrix, which catalyzes the oxidation of styrene at 80°C, with an unprecedently high conversion of 97%, and epoxide selectivity of 89% [33]. On the other hand, Baca et al. [34] and Mukherjee et al. [35] reported the catalytic oxidation of cyclohexene, using a Cu-MOF catalyst and a copper(II) complex immobilized on a modified silica surface; these heterogeneous catalysts showing 100% and 63 % conversion respectively, with a major yield for 2-cyclohexen-1-one. In all these studies the common factor is a copper centre with different coordinated ligands, showing that copper is the active site of the catalytic reaction. We herein are reporting the oxidation of styrene and cyclohexene using a Cu-MOF catalyst, $[Cu_2(bipy)_2(btec)]_\infty$, which presents 45 to 61% conversion for styrene oxidation, and 16 to 34% for cyclohexene oxidation. When we compare the results obtained by us with those reported in literature [35], it is possible to conclude that the studied Cu-MOF shows interesting activities in the oxidation of styrene and cyclohexene for short reaction times, together with a good reusability.

The different reported results permit to infer that the symmetry of the metal center, the coordinated ligands, pore volume, diffusion of substrate and TBHP activation play an important role in the obtained conversion and selectivity. Different types of ligands, superficial properties and metal center properties are known to have influence in the active intermediates formed during the oxidation of olefins; the most common intermediates in the catalytic oxidations being peroxometal, oxometal or free radicals. These species have strong influence on the selectivity of the studied oxidation reaction. For example, the metal centers in $[Cu(bipy)(H_2btec)]_\infty$ are quasi planar, and the catalyst presents high selectivity for styrene and cyclohexene epoxide as products, while $[Cu_2(bipy)_2(btec)]_\infty$ has copper(II) centers in distorted tetrahedral geometry and shows low yields for styrene and cyclohexene epoxide. This fact suggests that the geometry around the metal center is important in the catalytic selectivity of the Cu-MOF, since the lack of free coordination positions around the metal ions in $[Cu_2(bipy)_2(btec)]_\infty$, as compared with $[Cu(bipy)H_2btec)]_\infty$ [20] is affecting the oxidation mechanism [36].

Transition metal complexes in homogeneous and heterogeneous media are reported to catalyze oxidation of styrene into a variety of products such as epoxide, carbonyl compounds, and diols, and to produce oxidative C-C cleavage products [37-41]. In homogeneous or heterogeneous medium the transition metal activate TBHP, forming different types of intermediates. Normally the generated $(CH_3)_3CO^\bullet$ and $(CH_3)_3COO^\bullet$ have less selectivity in the oxidation process than the peroxometal and oxometal species [20,42].

Fernandes et al. and Silva et al. [43,44] reported recently the mechanism for the oxidation of styrene, using different transition metal catalysts and TBHP as oxidant. However, Silva proposed an oxo-intermediate for the Mn catalyst which cannot be produced in the case of Cu-MOF catalyst, since a two-electron oxidation process has to be considered for the metal center in order to generate the oxo-intermediate. Therefore, even though the products obtained by us during the styrene oxidation are all confirmed by the cited mechanism given by Silva, a different mechanism has to be proposed. Recently, Ryan et al. [36] reported a theoretical study for the decomposition of TBHP using metal-organic frameworks during the oxidation reaction of olefins. The mechanism using $(CH_3)_3CO^\bullet$ and $(CH_3)_3COO^\bullet$ species as intermediates in the oxidation of olefins was used in the calculations. However, the authors concluded that the direct bonding of TBHP to the metal centers was not possible, due to the steric effects around the metal centers in the MOF framework, and a Haber-Weiss type cycle was not probable. The theoretical study also concluded that the sites inside the MOFs have to be less active for the catalytic oxidation reaction, proposing that the major activation of TBHP occurs on the external surface of the MOFs, where unsaturation of some of the copper(II) coordination spheres is probable.

The present study of the oxidation of styrene showed that the yields for styrene oxide, benzaldehyde and 1-phenylacetaldehyde are similar. Ghosh et al. [45] proposed a mechanism for the oxidation reaction using TBHP. A similar mechanism is used to explain the obtained products in the present study (Fig. 4). The $(CH_3)_3OO^\bullet$ or $(CH_3)_3O^\cdot$ radicals may react with styrene, producing styrene oxide. On other hand, the styrene oxide may be obtained by the catalytic peroxometal mechanism using copper compounds [46]. Finally, the product 1-phenylacetadehyde is formed by the isomerisation of styrene oxide. [42,43]. On the other hand, benzaldehyde is formed by a two steps mechanism, starting with the attack of $(CH_3)_3OO^\bullet$ on styrene [44].

Figure 4 here

The mechanism for cyclohexene oxidation using heterogeneous Cu catalysts has been reported several times in the literature [18,36,42,44,46], and the products detected for this reaction are epoxide, ketones and diols. The results obtained by us for cyclohexene oxidation showed a low yield in epoxide when n-decane was used, and a null yield in the aqueous dichloroethane system. On the other hand, a high yield towards the ketone production, and the complete absence of diols in the oxidation process was observed. Probably the TBHP activation occurs on the external surface of the Cu-MOF, by a similar radical mechanism given for styrene oxidation [47,48]. Therefore it is possible to propose a similar radical mechanism (Fig. 5) for the cyclohexene oxidation as that for styrene.

The cyclohexene epoxide may be formed by two different paths. The first one is a free radical mechanism and the second one is a direct interaction with the Cu-MOF. The cyclohexene-1-ol and 2-cyclohexene-1-one are produced by a free radical mechanism as shown in figure 4.

Figure 5 here

Figure 6 and Figure 7 show the Turnover Number (TON) for the oxidation of the studied olefins, using the studied $[Cu_2(bipy)_2(btec)]_\infty$. The TON values increase from 264 to 1397, as the mole ratio is increased from 200:1 to 2400:1 for styrene oxidation, while the TON values for cyclohexene oxidation increase from 42 to 480, for the same substrate to catalyst ratios. When the TON values are analysized, it is possible to observe that the catalyst is very stable in a large range of substrate: catalyst molar ratios. During the time of reaction of 6h the cycles of catalytic reaction improve significantly, suggesting that the nature of the catalyst does not change significantly during the catalytic process. This fact is very important, considering that the catalytic compound is reusable.

The catalytic activities for styrene oxidation showed turnover frequencies (TOF) between 19 h^{-1} and 200 h^{-1}(see table 3). The values increase when the substrate:catalyst mole ratio is increased. Similar behaviour was observed for the studied cyclohexene oxidation, with turnover frequencies between 11 h and 80 h^{-1}, as the substrate:catalysts ratio increased (see table 4). The higher TOF for styrene may be attributed to the structure of the former substrate, which is favourable for oxidation. However, the conversions are similar for all the experiments, this fact being very surprising considering that this reaction has been reported to have a reaction order of one in substrate concentration [48]. The most likely explanation for this behaviour is that the substrate has diffusion problems on the Cu-MOF surface when the concentration is increased. On the other hand, the high reported TON values show that the catalyst is very stable for a large mole ratio substrate:catalyst.

Figure 6 and Figure 7

Reusability of the Catalyst

When the reusability of $[Cu_2(bipy)_2(btec)]_\infty$ for the oxidation reaction was investigated, it was possible to observe that the catalyst remained active during at least four cycles: first cycle: 60 %; second cycle: 58 %; third cycle: 57 %; fourth cycle: 54 % (further catalytic cycles were not studied). After each catalytic cycle the catalyst was separated by filtration from the reaction mixture, was washed with water and 1,2-dichloroethane and dried under vacuum. The studies show a small decrease in the activity after four catalytic cycles (6%).

However, the catalyst was not activated by thermal treatment, due to the fact that MOFs are not stable under these conditions.

Besides, the filtered solution was tested and did not present any catalytic activity, due to desorbed copper (II) species. When the reaction solutions were analyzed by ICP spectroscopy after finishing the catalytic reaction, the concentration of free copper was only 0.3% y 0.2% in 1,2-dichoroethane and n-decane respectively. These results confirm that the reaction takes place in heterogeneous conditions. Homogeneous conditions were only observed when the reaction was made with hydrogen peroxide as oxidant (around 62%) of free copper).

The re-used catalyst was not significantly altered in its structure, as shown by the recorded diffractograms (Fig. 8). The catalytic process was observed to proceed without an important variation, as stated above.

Figure 8

Conclusions

The $[Cu_2(bipy)_2(btec)]_\infty$ is an active catalyst in the oxidation reaction of styrene and cyclohexene.

The oxidation process for styrene and cyclohexene shows TOF values of 200 h^{-1} and 80 h^{-1} after 6 h of reaction, respectively. The highest TOF values were obtained for the substrate/catalyst ratio of 2400:1.

The increase in the TON values permits to assess the high stability of the $[Cu_2(bipy)_2(btec)]_\infty$ catalyst in the oxidation reaction of styrene and cyclohexene, as the conversion remains almost invariable with the increase of the molar ratio of substrate to catalyst.

The different solvent systems used in the catalytic study do not produce significant changes in the observed activity and selectivity of the reaction; with only a small difference of 6 % in the yields of the oxidation products for styrene and cyclohexene.

The results suggest that TBHP is activated by the Cu-MOF through the radical mechanism, with the $RO^\bullet$ and $ROO^\bullet$ species being generated on the external surface of the MOF, producing low selectivity in the catalytic oxidation of styrene. The results reported for the cyclohexene oxidation also permit to infer that the mechanism is primarily via radicals, since allylic oxidation of the substrate is mainly observed.

During the oxidation reactions diol formation was not detected for the studied systems.

The $[Cu_2(bipy)_2(btec)]_\infty$ is reusable with minor differences of about 6% in the catalytic behavior between cycles.

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