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$[Cu(H_2btec)(bipy)]_\infty$: Reusable Metal Organic Polymer Catalyst for Epoxidation Reactions

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Summary: The search of new inorganic materials with better catalytic properties is an important field of research. Reusability, efficiency and atom economy correspond to the main parameters to characterize a catalyst. In this work, we inform the effectiveness of $[Cu(H_2btec)(bipy)]_\infty$ ($H_4btec = 1,2,4,5$-benzenetetracarboxylic acid) as an heterogeneous coordination polymer catalyst for the oxidation of olefins. The catalyst exhibits good atom economy, high turnover numbers and good selectivity for a ratio of 4000/1 substrate/catalyst for cyclohexene and styrene oxidation. Furthermore, the catalyst was recycled and reused for seven consecutive cycles, retaining the structural integrity and effectiveness as catalyst in all the performed experiments.

Keywords: catalysis; metal-polymer complex; olefin epoxidation; reusable catalyst

Introduction

The use of the coordination complexes as building blocks to obtain more sophisticated architectures -including cages, helices, grids and networks- has undergone an explosive growth over the past decade, mainly because of their potential applications as functional materials. Research efforts on the synthesis and characterization of metal-organic coordination polymers has led to significant advances in the search for novel electronic, optical, magnetic, and catalytic properties. The modification of the properties of the inorganic polymers is based on the incorporation of different transition metal centers with different specific coordination environment.[1–3]

The term metal–organic framework (MOF) describes a class of materials in which polyfunctional organic ligands form coordination bonds with multiple metal atoms to form extended polymeric structures in one, two, and three dimensions.[4] The variation of the ligand character, functionality, spacer length, metal atom, and synthetic conditions has given rise to the formation of a large number of porous compounds with a correspondingly large variety of properties and applications.[5] Research groups have used copper for the construction of MOFs; for example by incorporating triethylenediamine as a spacer larger porosities are obtained.[6] In this field mixed-ligand networks have recently become more important.[7] Multi-carboxylate ligands, especially benzoic acid-based ligands,[8] and 1,2,4-triazole derivatives[9] are frequent choices for metal–organic networks due to their planar and rigid structure.[10–11] Benzene-1,3,5-tricarboxylate is also a rigid, planar molecule and has been extensively used in the form of its three anions $H_nbtc^{(3-n)-}$ ($n = 0, 1, 2$).

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In the catalysis area, the major problems encountered in homogeneous catalysis are the poor recycling efficiencies of the catalysts and the separation of the product(s) from the reaction mixture. Since, a reusable catalyst should be characterized by its easy separation (one of the most desirable properties in an industrial process), during the last few decades the attention in this area has been focused on the preparation and use of heterogeneous catalysts for different catalytic processes. Selective heterogeneous catalysis of organic transformations has been seen as one of the most promising potential applications of MOFs ever since 1990 s.[12–15]

Epoxides are very useful and versatile intermediates for the synthesis of many commodities and fine chemicals, and studies on epoxidation of the C=C bond have received attention.[16] Many catalytic epoxidation methods, including asymmetric epoxidation have been developed,[17] but selective epoxidation of alkenes using heterogeneous catalysts and clean oxidants under mild conditions is still a challenge.[18] On the other hand, intense research activity has been directed towards the assembly of coordination polymers due to their potential application in gas adsorption, optoelectronic devices and catalysis.[19–27] The key step in the design of these coordination polymers is to select suitable multidentate bridging ligands and spacers. For this reason, our attempts have been centred in the development of new catalytic MOF systems with copper as the main metal center present in the solid catalyst. Accordingly, 1,2,4,5-benzenetetracarboxylic acid (H_4btec) has been used to form bridges between metallic centres, generating varied and sometimes surprising molecular architectures.[28–33]

Heterogeneous catalysts based on metal organic frameworks of copper(II) complexes with bipyridine and carboxylate ligands have only been reported as catalysts for the epoxidation of cyclohexene and styrene by our group,[34] and the results for this reaction are better than the reported for other copper(II) compounds. These reported copper(II) heterogeneous catalysts, correspond mostly to complexes containing Schiff base ligands, which are supported or encapsulated in mesoporous materials, such as alumina or layered silicates.[35–36]

Our research activity has been focused mostly on the design and the synthesis by hydrothermal method of novel coordination polymers and clusters, by using neutral donor ligands (i.e., 2,2′-bipyridine, 4,4′-bipyridine, ethylenediamine), strictly anionic ligands (i.e., aromatic carboxylates), and their combination for the preparation of useful catalysts for the epoxidation of alkenes. In this work, we are reporting the reusability, structural integrity and effectiveness of the inorganic polymer $[Cu(H_2btec)(bipy)]_\infty$ as catalyst in the oxidation of olefins.

Experimental Part

The catalyst $[Cu(H_2btec)(bipy)]_\infty$ **(1)** was synthesized and characterized as previously described by our group.[34] The catalytic activity of **1** for the oxidation of olefins was investigated using cyclohexene and styrene as substrates, and tert-butylhydroperoxide (TBHP) as the oxidant. In the oxidation reactions, the catalyst could be recovered by simple filtration, and reused several times without significant loss of the activity in the process.

Physical Measurements

IR spectra were recorded on a Bruker 66 V instrument. Phase identification was carried out with X-ray powder diffraction technique on a D5000 Siemens diffractometer, using CuKα1 radiation ($\lambda = 1.54056$ Å). Gas chromatographic analysis was carried out with a Perkin Elmer 8500P instrument equipped with FID, using an Equity^{TM}-1 column and nitrogen as carrier gas.

The nitrogen adsorption isotherms were measured at 77 K on a Micromeritics Gemini-2370 Analyzer (Norcross, Atlanta, U.S.A.). The volume of adsorbed N_2 was normalised to the standard temperature and pressure. The BET surface area (Sg) was calculated applying the BET equation, and the microporous volumen (Vo) was calculated applying the Dubinin-Radushkevich equation.

Catalytic Procedure

In a typical experiment, an amount of the catalyst (0.01 mmol) was placed in a sealed atmosphere (N_2) glass reactor together with the olefin (40 mmol) and TBHP (40 mmol) in 1,2-dichloroethane as solvent (10 mL). At the end of the each cycle of the heterogeneous reaction (each cycle = 24 hours of reaction time and 75 °C), the catalyst was separated, thoroughly washed with solvent and reused under similar conditions. The recycled catalyst was analyzed by powder X-ray diffractograms, showing that the crystallinity of the solid is retained for seven cycles. IR spectra of the recycled sample are identical to that of the starting material.

In order to verify whether the observed catalytic activity is derived from the activity of the solid catalyst or from leached copper species, the reacting solutions were analyzed in search of residual copper(II) ions. The emission spectroscopy analysis showed a neglegible concentration of copper species in solution. Besides, when the reaction was carried out with the filtrate under the same conditions, no further oxidation reaction was observed. These results can rule out any contribution to the observed catalysis from copper species that could be leached into the reaction solution, and therefore the observed catalysis is intrinsically heterogeneous.

Result and Discussion

In order to obtain the effective surface of this reported MOF we used the adsorption isotherms to determine the amount of N_2 molecules adsorbed to the surface.

The recorded adsorption isotherm presents a similar shape to the type III isotherm in the IUPAC classification. The MOF $[Cu(H_2btec)(bipy)]_\infty$ with the adsorbed N_2 has a similar affinity as the initial surface before the adsorption process. For this reason, once it has adsorbed N_2 molecules, it also acts as a free site for another molecule to adsorb. This leads to an uneven coating with clean areas, and regions covered with monolayers and multilayers (Figure 1).

The MOF $[Cu(H_2btec)(bipy)]_\infty$ has a surface area, $S_g = 138\,m^2\,g^{-1}$, microporous volumen $V_0 = 0.03\,cm^3\,g^{-1}$, and a mesoporous volume $V_m = 0.28\,cm^3\,g^{-1}$. The surface

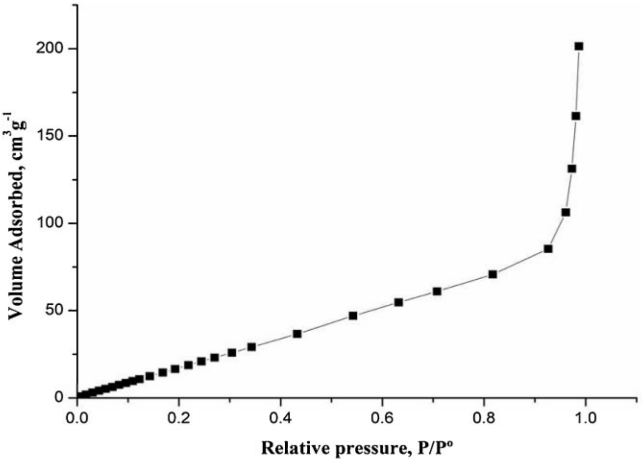

Figure 1.
Adsorption isotherm BeT of $[Cu(H_2btec)(bipy)]_\infty$.

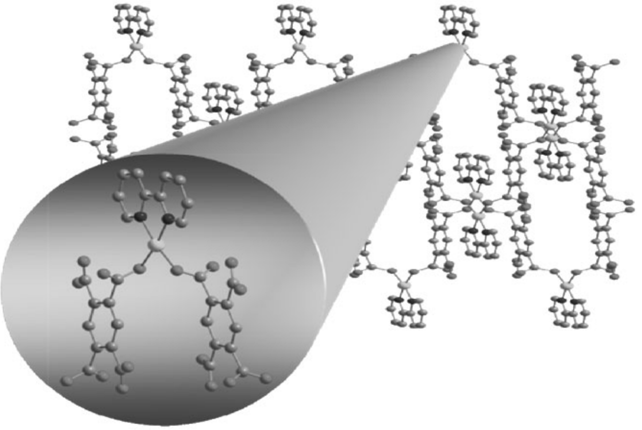

Figure 2.
Interlinking of carboxylate ligands in $[Cu(H_2btec)(bipy)]_\infty$.

area reported for the catalyst $[Cu(H_2btec)(bipy)]_\infty$ is particularly high, when compared with other inorganic materials.[37,38] This fact can be explained by analyzing the structure of the catalyst $[Cu(H_2btec)(bipy)]_\infty$, where it is possible to observe the interlinking of the carboxylate ligands between copper(II) atoms of two contiguous chains (Figure 2). This characteristic makes the lattice less compact, and should permit a more efficient approach of the oxidant and the substrate to the metallic site.

Figure 3 shows the different diffractograms obtained for the isolated catalyst after each catalytic cycle. The analysis of the data shows that compound **1** possesses good stability up to the seventh studied cycle, maintaining the crystallinity after several oxidation reactions.

The results for several cycles of the epoxidation of cyclohexene and styrene are summarized in Table 1 and 2. The cyclohexene oxidation catalyzed by **1** yielded mainly the following products: cyclohexene epoxide, 2-cyclohexenone and cyclohexanone, where the epoxide corresponds to the principal product. The results clearly show that $[Cu(H_2btec)(bipy)]_\infty$ allows obtaining a conversion of 62% of the substrate in the first catalytic cycle, with a selectivity towards the formation of cyclohexene epoxide of 68%. For the side products such as 2-cyclohexenone and cyclohexanone, the chemoselectivity for the first cycle is only 12% and 13%, respectively. After the first cycle, this activity decreases gradually until it reaches in the seventh cycle a conversion of 54%, and a selectivity for cyclohexene epoxide of 49%. (Table 1). It is important to remark that during the consecutive studied cycles the concentration of 2-cyclohexenone remains constant, with an increase in the concentration of cyclohexanone.

The oxidation reaction of styrene with TBHP yielded only benzaldehyde and styrene epoxide as products with a lower conversion. The catalytic system gave a higher selectivity towards epoxide production than the one observed for cyclohexene. The catalytic reaction shows a similar trend obtained for cyclohexene, that is, the conversion of the substrate decreases from 27% (first cycle) to 19% (seventh cycle). In the case of the epoxidation of styrene, the concentration of the obtained epoxide shows a slight decrease with the recycling of the catalyst (Table 2).

Therefore, it is important to remark that the $[Cu(H_2btec)(bipy)]_\infty$ catalyst presents a high chemoselectivity towards the epoxide formation, even after several cycles. The stability of the heterogeneous catalyst, and its catalytic efficiency are remarkably high for both substrates. For the first cycle, cyclohexene epoxide and styrene epoxide

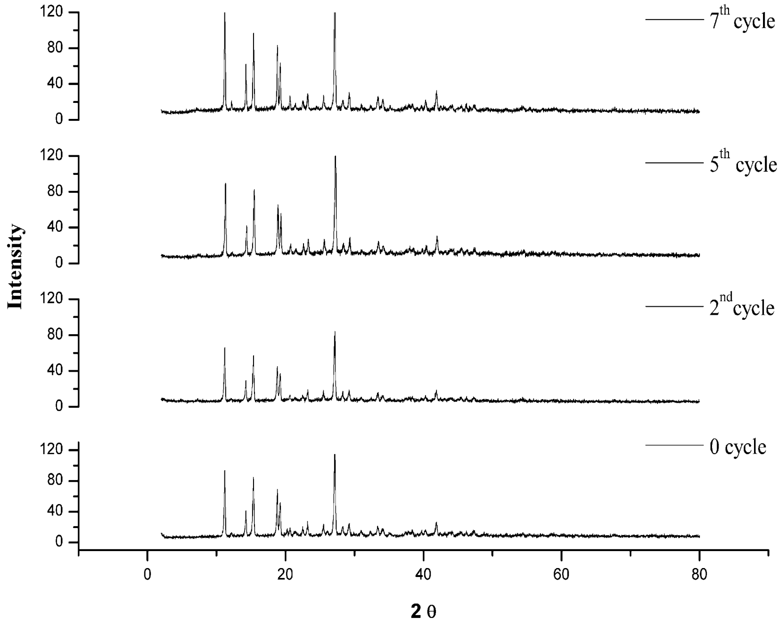

Figure 3.
X-ray powder diffraction patterns of $[Cu(H_2btec)(bipy)]_\infty$ for different catalytic cycles.

gave a TON value of 1690 and 755, respectively. The TOF obtained for the same reaction conditions also gave high values, 70 h^{-1} for cyclohexene epoxide and 32 h^{-1} for styrene epoxide for the first cycle of 24 h.

As mentioned above, the TON and TOF values also decreased in all cases over several runs. For cyclohexene epoxide and styrene epoxide a TON value of 1054 and 471 respectively, was observed for the seventh cycle. The obtained TOF values for the same reaction conditions gave 44 h^{-1} for cyclohexene epoxide and 20 h^{-1} for styrene epoxide, for the last studied cycle.

Several reusable supported heterogeneous catalysts for epoxidation of styrene have been reported in the literature. Solid catalysts such as Ti/SiO_2, Ti/MCM,

Table 1.
Effect of the catalytic activity of **1** for different cycles of the epoxidation of cyclohexene[a]

Run	TON	TOF (h^{-1})	Conversion	Chemoselectivity (%)		
				epoxide	-one	-enone
1°	1690	70	61.8	68.4	12.7	11.9
2°	1455	61	60.6	60.0	13.2	10.2
3°	1294	54	60.9	53.1	17.6	9.6
4°	1177	49	57.6	51.1	20.6	12.8
5°	1082	45	52.0	52.0	24.0	14.0
6°	1105	46	53.7	51.5	23.3	11.4
7°	1054	44	54.0	48.8	23.6	11.6

[a] Reaction conditions: Catalyst $[Cu(2,2\text{-}bipy)(H_2btec)]_\infty$ 0.01 mmol; cyclohexene, 40 mmol; TBHP 40 mmol; Cyclohexene/TBHP/Catalyst 4000:4000:1; 1,2-dichloroethane 10 mL; Temperature 75 °C; Reaction time 24 h. TON: turnover number; TOF: turnover frequency.

Table 2.
Effect of the catalytic activity of **1** for different cycles of the epoxidation of styrene[a]

Run	TON	TOF (h^{-1})	Conversion	Chemoselectivity (%)	
				epoxide	-enone
1°	755	32	26.9	70.2	29.0
2°	688	29	25.3	68.0	29.0
3°	596	25	22.0	67.7	32.2
4°	687	29	25.9	66.3	34.1
5°	561	23	21.9	64.0	35.4
6°	522	22	20.8	62.7	33.3
7°	471	20	18.9	62.3	31.7

[a] Reaction conditions: Catalyst $[Cu(2,2\text{-}bipy)(H_2btec)]_\infty$ 0.01 mmol; styrene, 40 mmol; TBHP 40 mmol; Styrene/TBHP/Catalyst 4000:4000:1, 1,2-dichloroethane 10 mL; Temperature 75 °C; Reaction time 24 h. TON: turnover number; TOF: turnover frequency.

Fe, V/SiO_2, titanoborosilicate (TBS-2), or titanosilicate (TS-2) supported gold nanoparticles, BaO, and BaO/Ga_2O_3 can be mentioned.[39–45] However, the first reusable copper(II) catalyst of this type (CuO/SiO_2) for styrene epoxidation by aqueous TBHP, was only reported in 2007 by Choudhary et al.[46] This study is difficult to compare with the present report, since the data shown in our study correspond to reaction time of 24 h, while the previous data were obtained for a reaction time of 5 h. Besides, Choudhary et al. inform an observed small decrease in the styrene oxide concentration for longer reaction times, which is due to the isomerization of this product to phenyl acetalaldehyde. This decrease is not observed for the studied catalyst $[Cu(H_2btec)(bipy)]_\infty$.

With respect to copper(II) organic polymers, the catalytic system $[Cu_2L(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)(\mu_{1,1,1}\text{-}N_3)]$ where L = 4-methyl-2,6-bis(phenylmethyliminomethyl)phenol, supported on SiO_2 can be mentioned.[47] This metal organic polymer was used for the oxidation of cyclohexene and styrene in acetonitrile, and was shown to be a good catalyst with a high total conversion for 24 h of reaction (76 and 88% respectively) and an excellent chemoselectivity (84 and 90% respectively). The reusability of this catalyst was only demonstrated for three cycles.

Therefore, to our knowledge, $[Cu(H_2btec)(bipy)]_\infty$ catalyst is the first copper(II) based MOF system to be reported, presenting a good activity and excellent reusability in the epoxidation of cyclohexene and styrene. Furthermore, this catalyst will be studied in other oxidation reactions.

Conclusion

In summary, $[Cu(H_2btec)(bipy)]_\infty$ MOF system presents a very good efficiency as an heterogeneous catalyst for the epoxidation of cyclohexene, and a moderate efficiency for the epoxidation of styrene. Besides, the catalytic system can be recycled and reused for several oxidation reactions. In the case of styrene the high selectivity for the epoxide product is retained even after the seven studied cycles, while for cyclohexene the chemoselectivity is slightly reduced.

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