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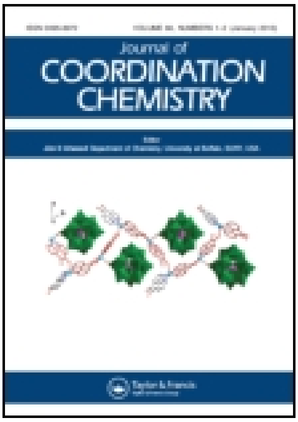

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Heterogeneous catalytic epoxidation of olefin over a hydrothermally synthesized 3D phosphate bridged copper(II) framework

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A 3D copper phosphate, $[Cu_2(PO_4)(OH)]_n$ (**1**), has been synthesized hydrothermally and characterized by single-crystal X-ray diffraction analysis. In $[Cu_2(PO_4)(OH)]_n$, there are two types of copper centers having distorted trigonal bipyramidal geometry and distorted octahedral geometry that are connected by the μ_2-bridging of each phosphate oxygen ultimately forming a η^8-PO_4 bridged 3D network. The compound exhibited excellent catalytic performance in olefin epoxidation. Epoxidation of styrene and substituted styrenes, as well as bulky olefins like cycloalkenes and long-chain alkenes, is efficiently catalyzed by $[Cu_2(PO_4)(OH)]_n$ using *tert*-butylhydroperoxide in acetonitrile. The results obtained in the heterogeneous catalytic reactions show that the olefins are converted to the respective epoxides in good yield with high selectivity. $[Cu_2(PO_4)(OH)]_n$ was catalytically more active and selective in comparison to simple copper(II) phosphate salt in heterogeneous medium. The catalyst can be recycled and reused several times without significant loss of activity.

Keywords: Metal-inorganic framework; Copper(II) phosphate; Heterogeneous catalysis; *tert*-Butylhydroperoxide; Olefin epoxidation

1. Introduction

Transition metal coordination polymers attract attention because of interesting molecular topologies and applications in catalysis, magnetism, gas adsorption, etc. [1–3]. Hydrothermal process is an efficient method for synthesizing such materials by incorporating desired metal ions with polydentate-bridging ligands. This method has been extensively used for preparation of zeolites and mesoporous silica [4] and is now being used as an effective technique for synthesizing coordination polymers. Copper phosphates and organophosphonates are a large class of compounds which have been studied in depth [5, 6]. The literature shows only limited work on purely inorganic phosphates including some work on phosphate ester hydrolysis [7], transition metal phosphonates [8], and amine-templated metal-inorganic framework solids [9].

There have been extensive studies on selective catalytic oxidation reactions of alkenes, aromatics, alcohols, etc. catalyzed by copper compounds in heterogeneous or homogeneous

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*Corresponding author. Email: rupamsen@ua.pt medium [10]. Transition metal complexes have been used as catalysts for epoxidation of alkenes [11]. Amongst the oxidants used in catalytic reaction, alkyl-hydroperoxides are receiving increased attention. *tert*-Butylhydroperoxide is used on a large scale in industrial epoxidation, for example, in Halcon-Arco and Sumitomo processes [12]. Recycling of co-products (e.g. *tert*-BuOH) has been realized in the Sumitomo process. The recycling of catalysts is of great economic and environmental importance in chemical and pharmaceutical industries, especially when expensive and/or toxic heavy metal complexes are employed. Many attempts have been made, such as intercalating or encapsulating the metal complex into layered compounds or within the cavities of a porous solid (e.g. zeolites) [13], binding the metal complex into the polymeric matrix [14] and employing the steric hindrance [15] to design recyclable catalysts.

Olefin epoxidation reactions by copper complexes under homogeneous condition are well known [16]. Recently, application of copper(II) complexes in heterogeneous catalysis has received attention [4, 17, 18]. Koner *et al.* explored the catalytic epoxidation of alkenes over copper-Schiff-base complexes immobilized into MCM-41 matrix [18]. Nevertheless, copper-based metal-organic/inorganic framework compounds have scarcely been used as catalyst in olefin epoxidation reactions [19].

Here, we report the catalytic efficiency of hydrothermally synthesized 3D framework, $[Cu_2(PO_4)(OH)]_n$ (**1**), towards epoxidation of alkenes in heterogeneous medium.

2. Experimental

2.1. *Materials and methods*

$Cu(NO_3)_2 \cdot 3H_2O$, cyclooctene, cyclododecene, 1-hexene, 1-octene, styrene, 3-methyl styrene, 4-methyl styrene, *trans*-stilbene, and *tert*-butylhydroperoxide (70 wt.% aq.) were purchased from Aldrich and used as received. Ortho-phosphoric acid (ca. 85%, density = 1.7), cesium hydroxide, and solvents were purchased from Merck (India).

Single-crystal X-ray diffraction (XRD) data were collected at 293(2) K on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Fourier-transform infrared spectra of KBr pellets were measured on a Perkin–Elmer RX I FT-IR spectrometer. The metal content of the sample was estimated on a Varian Techtron AA-ABQ atomic absorption spectrometer. TG analysis was made using a Perkin Elmer (SINGAPORE) Pyris Diamond TGA unit. The heating rate was programmed at $5\,^{\circ}C\,min^{-1}$ with a protecting stream of N_2 flowing at a rate of $20\,mL\,min^{-1}$. Powder XRD patterns of the samples were recorded with a Scintag XDS-2000 diffractometer using CuK_{α} radiation. N_2 sorption measurements were performed on an Autosorb iQ (Quantachorme Inc., USA) gas sorption system at 77 K. The products of the catalytic reactions were identified and quantified by a Varian CP-3800 Gas Chromatograph using a CP-Sil 8 CB capillary column.

2.2. *Synthesis of $[Cu_2(PO_4)(OH)]_n$ (1)*

The structure of $[Cu_2(PO_4)(OH)]_n$ was reported previously [20]. The phase-pure compound was synthesized by hydrothermal treatment of copper nitrate (0.241 g, 1 mM) with excess ortho-phosphoric acid (15 mM) in the presence of cesium hydroxide

(0.90 g, 6 mM) dissolved in 10 mL milliQ water in a 25 mL Teflon-lined autoclave for three days at 170 °C, followed by cooling to room temperature. Green block-shaped crystals (yield 50%) were separated out during hydrothermal treatment. The crystals were filtered off by suction, washed with copious amounts of distilled water, and dried in air. AAS analysis shows that $[Cu_2(PO_4)(OH)]_n$ contains 52.98% of copper (calcd 53.16%). The FT-IR spectrum of $[Cu_2(PO_4)(OH)]_n$ shows two strong absorptions at 1151 and 961 cm^{-1} assigned to v(P–O) and an absorption at 3460 cm^{-1} from v(O–H).

2.3. *Catalytic reactions*

The catalytic reactions were carried out in a glass batch reactor according to the following procedure. Substrate (1 g), solvent (8 mL), and catalysts (2 mg) were first mixed. The mixture was then equilibrated to 65 °C in an oil bath. After addition of *tert*-butylhydroperoxide (1.5 mL), the reaction mixture was stirred continuously. Reactions were performed in air. The products of the epoxidation reactions were collected at different time intervals, and identified and quantified by gas chromatography. Compound was dried under vacuum (100 °C, 12 h) prior to reuse as catalyst.

3. Results and discussion

3.1. *X-ray structure of $[Cu_2(PO_4)(OH)]_n$ (1)*

Compound **1** possesses a densely packed 3D framework consisting of two metal centers, Cu(1) and Cu(2), where Cu(1) centers are distorted trigonal bipyrimidal and Cu(2) centers are distorted octahedral (figure S1). The phosphate anion assembles eight copper centers by μ_2-bridging of each phosphate oxygen, forming a η^8-PO_4 bridged network (figure S2). The basal plane of the Cu(1) centers is formed by three oxygens of phosphates (Cu1–O2, O2*, and O3; $* = 1/2+x$, $1/2-y$, and $-1/2+z$) and the two axial position are occupied by two other phosphate oxygens (O3 and O1). Cu(2) is bound by six oxygens from phosphates. The basal plane is formed by O1, O1*, O2, and O1, and the two axial positions are O1 and O1*. Cu(1) ions are bridged by μ_2–O3 forming a consistent dimeric unit and the Cu(2) centers are bridged by μ_2–O1 forming another dimeric unit. The Cu(1) dimeric units are perpendicular to each other in alternation within a layer, but the Cu(2) dimeric units share the edge of the octahedron (figure S3). The Cu(2) ions are in the basal plane, with a deviation of 2.44 Å. In the dimeric units with Cu(1) centers, the copper ions are separated by 3.059 Å and for Cu(2) dimers, the centers are situated at 2.94 Å. Cu(1) and Cu(2) centers are bridged by O2 and O1 oxygens. PO_4 groups can be described as distorted tetrahedra. The P–O distances, with a mean value of 1.54 Å, range from 1.524(2) to 1.552(2) Å and the O–P–O angles are 107.82(9)°–111.44(9)° (mean value 109(2)°). The PO_4 groups are connected to the copper trigonal bipyramidal and octahedron by four oxygen vertices, O(1), O(2), O(2)*, and O(3) ($*=x, y, z$). All oxygens are bridged bidentate interacting with eight copper centers.

The bond valence sum (S) for Cu(1) and Cu(2) centers in $[Cu_3(PO_4)_2]_n$ (**1**) was calculated according to equation (1) [21]:

$$S = \exp[(r_0 - r)/B] \qquad (1)$$

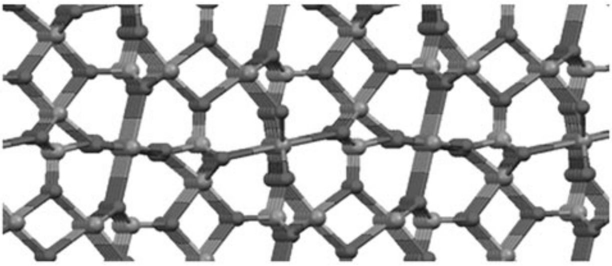


Figure 1. 3-D framework structure of **1**.

where r is the observed bond distance, r_0 and B are empirically determined parameters, r_0 (Cu–O) = 1.679(2) Å, and B is 0.37. The calculated values of S, 1.95 for Cu(1) and 2.12 for Cu(2), are in agreement with the expected value of 2 for Cu(II) [21]. The Cu (1) TBP and Cu(2) octahedra are cross-linked by phosphate anions forming the 3D network (figure 1).

3.2. *Thermogravimetric analysis*

To ascertain thermal stability of $[Cu_2(PO_4)(OH)]_n$, thermogravimetric (TG) analysis was undertaken. TG analysis reveals that the framework is thermally stable to 380 °C in air; above this temperature, the framework starts to decompose, which completes at 990 °C (see Supplementary material; figure S4). The complete decomposition of the compound proceeds in one step, resulting in CuO, as shown by powder XRD measurements. The calculated weight loss for the whole process (66.7%) is in agreement with the experimental value of 66.4%.

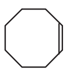
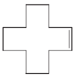
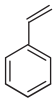
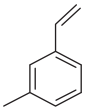
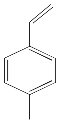
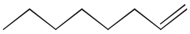
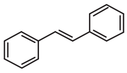
3.3. *Nitrogen sorption study*

Nitrogen sorption measurements of $[Cu_2(PO_4)(OH)]_n$ were undertaken to verify the porous nature of the compound as well as to calculate the surface area of the catalyst (see Supplementary material; figure S5). Brunauer–Emmett–Teller (BET) [22] surface area of the compound was calculated from N_2 adsorption isotherms. The adsorption of N_2 follows a type II isotherm and the BET surface area is estimated as $24\,m^2/g$, indicating that there are no micropores or mesopores. The structure of $[Cu_2(PO_4)(OH)]_n$ is very densely packed. This can be easily seen with a space-filling representation of the structure and it is supported by PLATON [23] calculations. Careful examination of the crystal structure ensures that there are no pores or cavities of any appreciable size whatsoever. Also, there are neither guest nor coordinated solvent molecules, which could give a void after activation. Secondly, the surface area is very low for truly microporous metal-inorganic frameworks. It can simply indicate the external surface, rather than the surface of the microporous structure.

3.4. *Catalytic epoxidation reactions*

Olefin epoxidation catalyzed by various MOF/MIF-based heterogeneous catalysts is well documented in the literature by using H_2O_2 [24] or TBHP [25]. Compound **1** catalyzes alkenes from terminal linear to cyclic, styrene, and also stilbene. Results of the catalytic epoxidation of different substrates are given in table 1. A graphical representation of relative efficacy of $[Cu_2(PO_4)(OH)]_n$ for epoxidation of various alkenes in acetonitrile with time is given in figure 2. The compound is active towards epoxidation of styrene and its derivatives, 3-Me styrene, and 4-Me styrene. Styrene and the substituted styrenes were converted above 90% with the highest selectivity of 70%, along with the benzaldehyde/substituted benzaldehyde as the usual side product. Epoxidation of styrene with *tert*-BuOOH over a variety of catalysts under heterogeneous conditions has been studied [18]. Xiao *et al.* reported styrene epoxidation with a similar $[Cu_2(PO_4)(OH)]$ complex [26], where selectivity reached 67% with the limited conversion of 44%. Seelan *et al.* studied epoxidation of styrene over copper phthalocyanine immobilized NaY catalyst,

Table 1. Epoxidation of olefins catalyzed by $[Cu_2(PO_4)(OH)]_n$ and copper phosphate salt in acetonitrile at 65 °C[a].

			% Selectivity of products		
Substrate	Reaction time (h)	Conversion [wt.%]	Epoxide	Others	TON[g]
	24	(a) 92 (b) 66	100 100	– –	499 380
	24	(a) 81 (b) 27	86 44	14[b] 56[b]	291 103
	24	(a) 96 (b) 67	60 30	40[c] 70[c]	551 408
	24	(a) 96 (b) 90	70 9	30[d] 91[d]	485 483
	24	(a) 92 (b) 97	59 4	41[e] 96[e]	465 520
	24	(a) 100 (b) 74	100 89	– 11	709 558
	24	(a) 85 (b) 19	100 52	– 48	452 107
	24	(a) 80 (b) 21	85 38	15[f] 62[f]	337 94
	24	(a) 89 (b) 62	94 83	6 17	295 218

[a]Reaction conditions: alkenes (1 g); catalyst (2 mg); *tert*-BuOOH (1.5 mL); and solvent (8 mL). The products of the epoxidation reactions were collected at different time intervals, and were identified and quantified by Varian CP-3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column. (a) and (b) correspond to the catalytic performance of $[Cu_2(PO_4)(OH)]_n$ and copper phosphate salt, respectively. [b]Cyclododecanol, [c]benzaldehyde, [d]3-methyl benzaldehyde, [e]4-methyl benzaldehyde, [f]2-decanone, and [g]TON = moles converted/moles of active site.

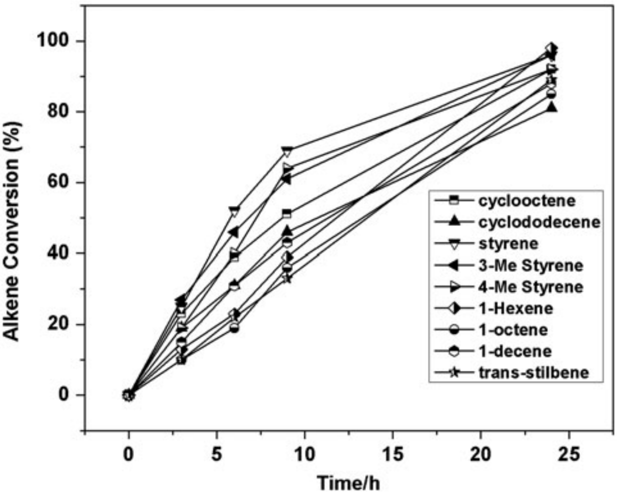


Figure 2. Reaction profiles for epoxidation of olefins with *tert*-BuOOH catalyzed by $[Cu_2(PO_4)(OH)]_n$.

which shows over 95% conversion with epoxide selectivity of 24% [27]. In our earlier study, we employed vanadium dihydrogen phosphate, where the conversion was 100% but the oxide selectivity was limited to 44% [28]. Selectivity of the epoxide was improved (53%) when copper-perchloro-phthalocyanine had been anchored onto MCM-41; however, conversion remains at 47% [17]. In fact, in the epoxidation of styrene with *tert*-BuOOH over copper/copper complex immobilized zeolite or molecular-sieves catalysts, epoxide selectivity rarely goes above 40% [29]. A high selectivity of 78% was obtained by Maurya and his group, where styrene was converted up to 60.2% with high turnover number (TON) [30]. In a recent attempt, Koner *et al.* have improved the formation of styrene oxide up to 86% using copper(II) Schiff-base anchored MCM-41 catalyst [18].

Cyclic olefins such as cyclooctene and cyclododecene were converted with good yield (conversion 92 and 81%) to their corresponding oxides, with good product selectivity (100 and 86%, respectively). Product selectivity for cyclooctene rarely goes high in homogeneously catalyzed reaction because cyclooctane-1,2-diol is the commonly generated

Table 2. Epoxidation of alkenes with *tert*-BuOOH catalyzed by a variety of catalysts[a].

Catalyst	Conversion (wt.%)	Epoxide (wt.%)	TON	Refs.
Styrene				
$[VO(H_2PO4)_2]_n$[b]	100	44	1249	[28]
[Cu(acpy-oap)Cl]-Y[b]	60.2	78.0	1464	[30]
CuO	40	8	76	This work
$CuCl_2$	48	5	155	This work
Copper phosphate salt	67	41	404	This work
Compound **1**	96	60	551	This work
Cyclooctene				
$[VO(H_2PO4)_2]_n$[b]	90	80	1064	[28]
VOL[5b]	66.87	100	669	[31]
VOL[5b]	86.40	100	864	[31]
Compound **1**	92	100	499	This work

[a]Reaction conditions were the same as given in footnote of table 1.[b]Compound detail and reaction condition are in the references.

byproduct. In earlier study, we converted cyclooctene with 80% epoxide yield [28]. In a recent study, Behzad *et al.* got an impressive selectivity of 100% [31]. Catalytic activities and selectivity in styrene and cyclooctene epoxidation by *tert*-BuOOH over various catalysts are presented in table 2.

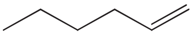
Although terminal alkenes need higher activation energy, we got a fair conversion of 80–100%. Longer alkene, 1-decene, shows 80% conversion with 85% epoxide selectivity while 1-octene and 1-hexene show epoxide conversion of 85 and 100%, respectively, with 100% oxide selectivity. Selectivity and conversion become less when the bulkiness or chain length of the substrates is increased, which may be explained on the basis of steric hindrance caused by the substrates.

The overall catalytic efficiency of $[Cu_2(PO_4)(OH)]_n$ in epoxidation reactions was significant, reflected in the high TONs (table 1). The copper(II) binds the peroxo-group on treatment with peroxides [32] to form the pre-catalyst containing LxCu–OOH (where L = ligand), which are capable of transferring the oxo-functionality to the organic substrates to produce the oxidized products [33]. We assume that in our case, a similar kind of mechanism is operative. X-ray crystal structure analysis shows the presence of five-coordinated Cu(II) in $[Cu_2(PO_4)(OH)]_n$. So, the coordination environment around copper(II) is easily accessible for an external ligand, and as a result, *tert*-butylhydroperoxide gets enough space to bind copper in the intermediate stages of the catalytic cycle.

To optimize the catalytic reaction, we studied some control experiments by varying the oxidants, solvents, and the ratio of the oxidant. Different oxidants like *tert*-BuOOH, H_2O_2, and NaOCl have been used in cyclooctene and 1-hexene epoxidation. The results of this study are given in table 3. *tert*-BuOOH is most efficient amongst them for higher conversion and selectivity. Solvent polarity also plays an important role for epoxidation. The best performance of the catalysts was observed in acetonitrile (see Supplementary material; table S1). The optimum polarity of acetonitrile to dissolve both olefin and *tert*-BuOOH might be facilitating the epoxidation. A graphical representation of the relative efficacy of the $[Cu_2(PO_4)(OH)]_n$ catalyst for the epoxidation of various alkenes in different solvents has been given in figure 3. The efficiency of catalyst, in general, followed the order: acetonitrile > acetone > chloroform ∼ THF > dichloromethane. To determine the optimum reaction temperature, we studied the reactions by varying the temperature from room temperature to 75 °C for different olefins in acetonitrile (figure 4 and see Supplementary material; table S2). The reaction profile clearly indicates that a desired temperature of 65–70 °C is needed to activate the catalyst.

It is occasionally assumed that TBHP acts as an initiator but not a true oxidant, therefore the reaction was also performed in inert atmosphere by varying the amount of

Table 3. Epoxidation of cyclooctene and 1-hexene with various oxidants over $[Cu_2(PO_4)(OH)]_n$[a].

Substrate	Oxidant	Conversion (wt.%)	% Yield of epoxide
	None	Not traceable	–
	H_2O_2	68	62
	tert-BuOOH	92	92
	NaOCl	28	10
	None	Not traceable	–
	H_2O_2	65	65
	tert-BuOOH	100	100
	NaOCl	22	12

[a]Reaction condition was the same as given in footnote of table 1.

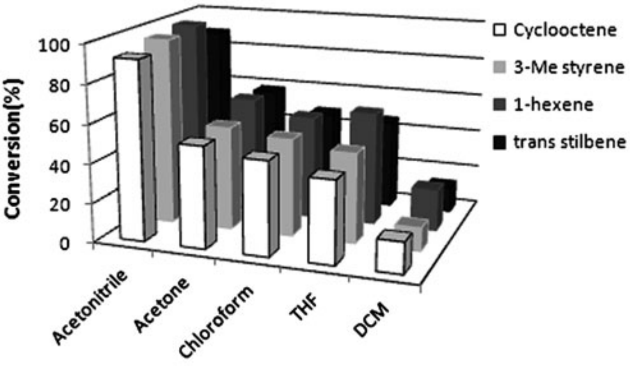


Figure 3. Comparison of catalytic efficacy of **1** in different solvents.

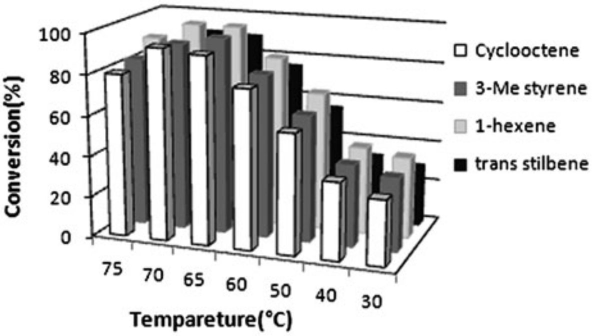


Figure 4. Comparison of catalytic efficacy of $[Cu_2(PO_4)(OH)]_n$ at different temperatures.

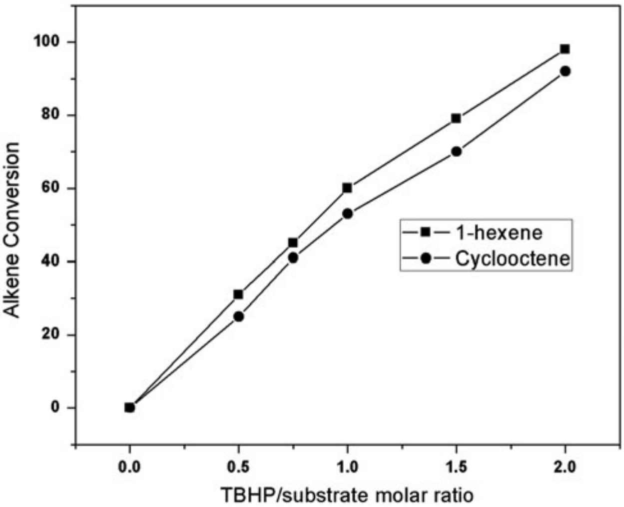


Figure 5. Plot showing performance of the catalysts in epoxidation of 1-hexene and cyclooctene with varied amount of *tert*-BuOOH.

Table 4. Catalytic efficacy of the recovered compound ($[Cu_2(PO_4)(OH)]_n$) in successive runs for 1-hexene and cycloctene epoxidation[a].

Compounds	Cycles	Conversion (wt.%)	Selectivity of product (wt.%)	TON
1-hexene	1	100	100	709
	2	100	100	709
	3	100	100	709
	4	98	100	695
	5	98	100	695
cyclooctene	1	91	100	493
	2	90	100	488
	3	90	100	488
	4	88	100	477
	5	90	100	488

[a]Reaction condition was the same as given in footnote of table 1.

the TBHP and the results prove the vital role of TBHP. When the amount of TBHP was increased, the conversion gradually goes to completion (figure 5). The optimum amount of *tert*-BuOOH needed for completion of catalytic reaction was 1 : 1.5–2 M equivalent (substrate: *tert*-BuOOH). In epoxidation, oxidant requirement is generally of this order [34, 35]. No induction period was observed in any of the reactions.

Simple copper phosphate salt was compared with **1** to see the structural effect (table 1). Although, in some cases, conversion (e.g. 3-Me styrene and 4-Me styrene) was impressive (90 and 97%, respectively) catalyzed by copper phosphate salt, they showed only poor selectivity. For linear chain olefins, e.g. 1-octene, 1-decene, and bulkier cyclododecene, conversion was very poor for copper phosphate salt in comparison with $[Cu_2(PO_4)(OH)]_n$. However, epoxidation of cyclooctene with copper phosphate salt showed 66% conversion with 100% selectivity. So, the overall performance of copper phosphate salt in catalytic reactions is poorer than **1**.

3.5. *Separation, catalyst reuse, and heterogeneity test*

The major advantages of the use of heterogeneous catalysts are recovery of the catalyst from the reaction mixtures and its possible reuse. To test if metal is leached from the solid catalyst during reaction, the liquid phase of the reaction mixture was collected by filtration at the reaction temperature after 30% of the epoxidation reaction was completed for 1-hexene, and the residual activity of the supernatant solution after separation of the catalysts was studied. Atomic absorption spectrometric analysis (sensitivity up to 0.001 ppm) of the supernatant solution of the reaction mixture thus collected by filtration confirms the absence of copper ions in the liquid phase. The filtrate mixture did not show any catalytic activity towards epoxidation (figure S6). These experiments clearly demonstrate that metal is not leaching from the solid catalyst during epoxidation. In order to check the stability of the catalysts, we characterized the solids after completion of reactions. After the catalytic reactions were over, solid catalyst was recovered by centrifugation, washed with fresh acetonitrile several times, and dried in air oven. The recovered catalyst was then subjected for X-ray powder diffraction analysis and IR spectral analysis. Comparison of IR spectra and XRD patterns of the pristine complexes and recovered catalysts convincingly demonstrate that the structural integrity of $[Cu_2(PO_4)(OH)]_n$ is unaltered after epoxidation (see Supplementary figures S7 and S8). Notably, the recovered catalyst can be reused in epoxidation reactions for several times with no significant loss of activity (table 4). The kinetic profiles of the epoxidation reaction of 1-hexene and cyclooctene using virgin and recovered catalysts are virtually the same (figure S9).

4. Conclusion

$[Cu_2(PO_4)(OH)]_n$ demonstrates good catalytic activities in epoxidation towards various industrially important olefinic substrates. Low surface area obtained in the nitrogen sorption measurement indicates that $[Cu_2(PO_4)(OH)]_n$ is not porous to accept guest molecules in the bulk of the solid. Therefore, epoxidation reactions take place on the surface of the catalysts. The use of different solvent and temperature influences the catalytic reactions. Maximum conversion is observed in acetonitrile at 65–70 °C. No decomposition or leaching of the metal centers during the catalytic reactions proved the heterogeneous nature of the catalyst. The catalyst is recyclable up to five cycles without significant loss in their catalytic activity.

Supplementary material

Tables S1 and S2 and figures S1–S9 are available free of charge via the Internet. Supplementary data associated with this article can be found in the online version.

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