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Synthesis and characterization of porous organic polymer containing tailored AB_3 metalloporphyrin: highly active and reusable catalyst for oxidation of benzyl alcohol

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Abstract

In this work, a modern and attractive Cu(II) porphyrin-based polymer network with high surface area was synthesized. This strategy prepares an easy approach to produce highly stable Cu-Porphyrin-based polymer network. The organization of this catalyst was certified by spectroscopic (ultraviolet–visible, Fourier transform infrared, powder X-ray diffraction, thermal gravimetric analysis, energy dispersive spectroscopy and scanning electron microscopy). Catalytic activity of Cu-Porphyrin-based polymer network has been investigated for oxidation of benzyl alcohols to the benzaldehydes. The results indicated that this catalyst displayed high catalytic activity and recycling efficiency in oxidation of benzyl alcohols.

Keywords Porphyrin · Polymer network · Benzyl alcohol · Metalloporphyrin

Introduction

Metalloporphyrins have engrossed significant attention because of their diverse physicochemical properties and their extensive scope of applications such as photodynamic therapy, engineered molecular building blocks, nonlinear optical materials, solar energy storage devices, bio- and optical sensors and metal adsorption [1–8]. Also, they have been perusaled in these systems as biomimetic catalysts of enzymes such as the monooxygenases [9, 10]. Metalloporphyrins are present extracting major regard because they have capability to catalyze a diversity of oxidation reactions imitating P450 with O_2. However, the utilization of them as a catalyst in homogeneous oxidation processes has multiple drawbacks [11]. For case in point: (1) they do display low selectivity and (2) it is hard to separate metalloporphyrins from the reaction mixture, which make homogeneous catalysis a costly method in mercantile

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processes. Also, deactivation of acting sites is caused by association of porphyrin loops by π–π interaction as the reaction proceeds [12]. The above-said problems could be unraveled by fixing them on the surface of solid materials. Since immobilized porphyrins catalysts have the fewer of the disadvantages of homogeneous catalysts, such as the problems in regeneration and recovery. However, a versatility of polymeric supports have been reported; some of them toil from one or more faults in their attributes or synthetic ways, including multiplex steps for synthesis, long reaction times, rude reaction status, the utilization of costly catalysts and solvability in different solvents and low chemical and/or thermal stability. In view of the easiness of provision and the unique properties of the network polycalix[4] resorcinarene (PC4RA), such as multifaceted chemical rectification, good dispersion of active sites, its outspoken functionalization way via post-functionalization without undergoing copolymerization or further post-polymerization, porous surface and high chemical and thermal stability, it would be rational to consider this polymeric structure as a promising starting substance for the synthesis of a new and effective porous organic polymer [13–26]. To the best of our scholarship, in spite of many progresses in the plan, synthesis and usage of functionalized C4RA, there have been no reports on its functionalization through covalently anchored metalloporphyrin onto the overhead rim of C4RA. With the above mentioned, as part of our persistent endeavors to expand high efficiency and environmentally favorable ways for varied substantial reactions and conversions and due to our new fondness in the usage of the PC4RA for the provision of carbonyl compounds. Here, we report the functionalization of PC4RA through a covalently anchored metalloporphyrin and the examination of its performance as a heterogeneous and solid catalyst for the synthesis of benzaldehyde compounds.

Experimental

Characterization

FTIR, EDX, XRD, NMR, SEM, ICP and UV–VIS were performed to determine the as-prepared Cu-Porphyrin@ polymer samples. The empirical details about the utilization of these characterization techniques are given in Supporting Information.

Procurement of 5-(4-carboxyphenyl)-10, 15, 20-triphenylporphyrin (1b)

4-(methoxycarbonyl)phenyltriphenylporphyrin (1a) was prepared according to Lindsay's method [27, 28]. 2.0 mmol (p-methoxycarbonylbenzaldehyde), 6.0 mmol (Benzaldehyde) and 0.1 ml ($BF_3 \cdot OEt_2$) were added to a 500 ml chloroform solution and stirred for an hour. Then, 300 ml chloroform solution of pyrrole (0.56 ml; 8.0 mmol) was added. After the solution color became violet, chloranil (2.2 g; 9.0 mmol) and triethylamine (0.2 ml; 1.43 mmol) were added to the solution, and then, the solution under nitrogen gas, it was heated to 80 °C for one hour. After purification and vaporization of the solvent, the compressed solution was drawn out with n-hexane/ethyl acetate (14:1, v/v). The final products were exposed to column chromatography on silica gel to produce.

In the subsequent step, to a purple solution of 1a (0.121 g) in 40 mL of trifluoroacetic acid (TFA), hydrochloric acid solution (35%; 25 ml) was added. Then, the reaction was heated at 90 °C for 36 h. The reaction blend was drawn out with ethyl acetate and water. An ethyl acetate layer was dried with Na_2SO_4 to produce (1b) [29, 30] (Scheme 1).

5-[4-(N-(3-triethoxysilylpropylbenzamido))]-10, 15, 20-triphenylporphyrin (1d)

After dissolving 1b in 5 ml of chloroform, thionyl chloride (500 µL, 6.884 mmol) was added; then, the solution for 3 h was heated at 65 °C. After cooling the reaction mix to ambient temperature, excess thionyl chloride and the chloroform were eliminated under reduced compression (1c). The solid green remnant was dissolved in waterless dichloromethane; then, (3-aminopropyl) triethoxysilane(80 µL) and triethylamine (160 µL) were added and refluxed for 24 h, and then, the mixture was cooled to ambient temperature. All excess materials were eliminated under reduced compression, and the raw product by silica gel column chromatography was purified (1c) [30, 31] (Scheme 1).

5-[4-(N-(3-triethoxysilylpropylbenzamido))]-10, 15, 20-triphenylporphinatocopper (II) (1e)

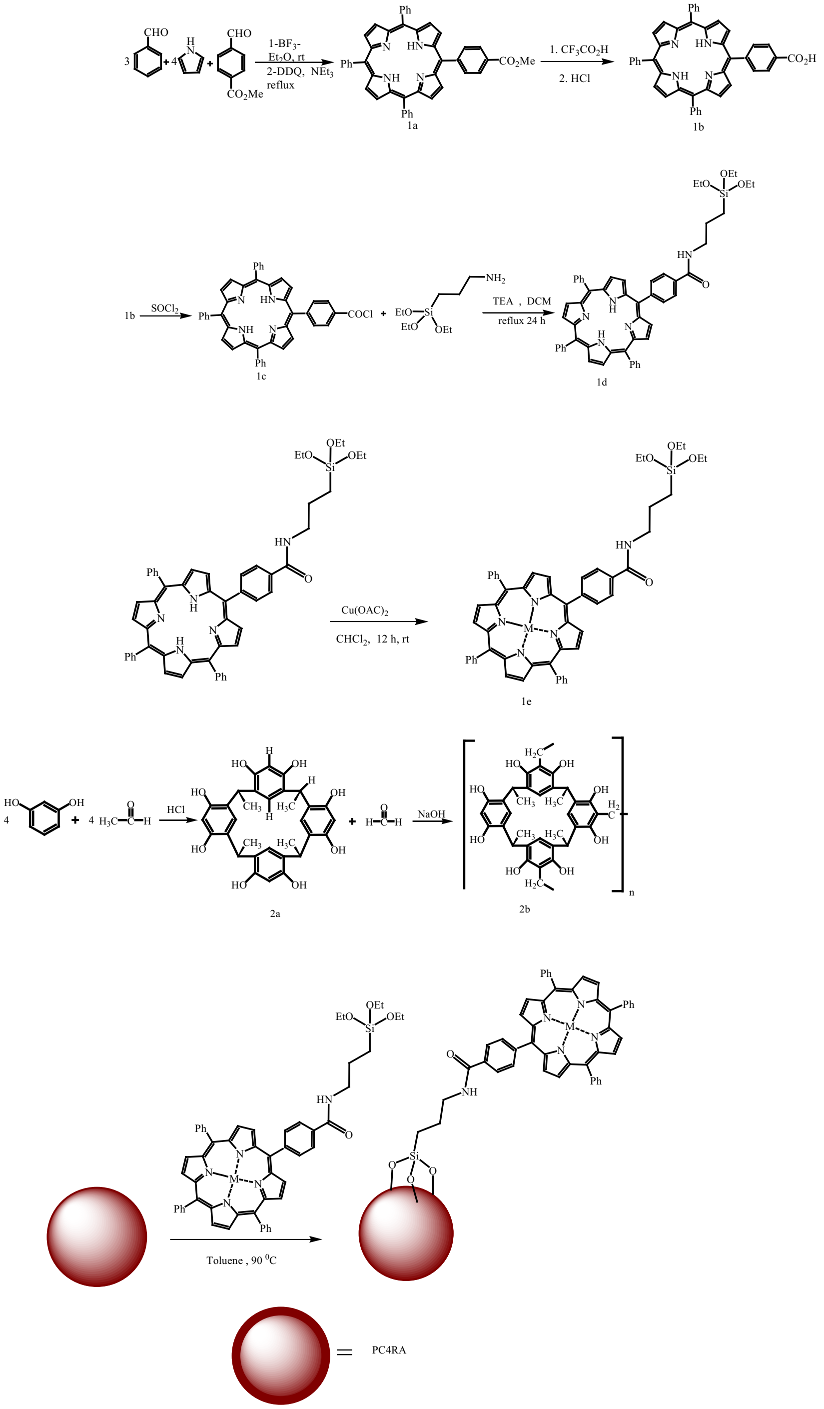
After dissolving 1c (0.058 mmol) in methylene chloride (20 mL), copper (II) acetate (1.156 mmol) was added. For 12 h, the reaction blend was stirred at ambient temperature. Then, the solvent of reaction was eliminated under reduced compression. The remnant was purged by column chromatography on silica gel with hexane/ethyl acetate as eluent [32] (Scheme 1).

Synthesis of calix [4] resorcinarene (C4RA) (2a)

(2a) was readied according to a formerly reported method [33] (Scheme 1).

Synthesis of network polycalix [4] resorcinarene (PC4RA) (2b)

To 14 mmol of previously synthesized C4RA in 40 cm^3 NaOH solution (10%), 42 mmol of formaldehyde was added dropwise at ambient temperature. After finalization of formaldehyde addition, for 20 h the blend was heated at 90 °C. The surplus alkali was washed out from the outcome gel with cold water. Next, the gel became acidic in treatment with 0.1 M HCl solution. Lastly, the solid outcome was dried at 100 °C for 10 h[34] (Scheme 1).



Scheme 1 Synthesis of Cu-porphyrin@ PC4RA

Synthesis of Cu-Porphyrin immobilized on network PC4RA

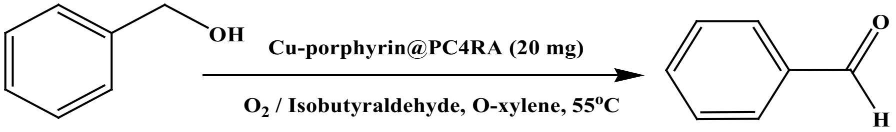
In a round-bottom flask containing 10 mL toluene, 10 mg of PC4RA and 5 mg of (1e) were added at ambient temperature. After heating reaction mixture to 90 °C for 24 h, the resulting solid for several times washed with deionized water and then dried at 70 °C[30] (Scheme 1).

Typical method for oxidation of benzyl alcohol

2 mmol of benzyl alcohol, 6 mmol of isobutyraldehyde, 10 ml of O-Xylol as solvent and 20 mg of catalyst were added in a 25 mL two-neck flask and heated at 55 °C. The mixture was stirred with the oxygen gas pumping into the system. After the reactions, the catalyst was filtered for several times, washed with methanol and then dried under vacuum before being devoted to the next catalytic cycle (Scheme 2). Also the product was analyzed by gas chromatograph (GC) to characterize the product and reactant concentrations.

Results and discussion

As reported before, in modern chemistry, one of the most agitating challenges is the probe for more effective catalytic systems that might blend the privileges of both homogeneous and heterogeneous catalysis. In light of this fact, we prepared Cu-Porphyrin@ PC4RA as a novel catalyst to produce of carbonyl compounds. In the first stride, the reaction of resorcinol and acetaldehyde resulted in C4RA formation which in the next step, under polycondensation with formaldehyde produced the polymeric network (Scheme 1) [33, 34]. Formation of compounds 2a and 2b was corroborated through a series of spectroscopic analysis (see ESI) [35]. In the second step, the porphyrin ligand was synthesized according to previous reports [28–30, 36]. In the following, the porphyrin complex was reacted with 3-aminopropyltriethoxysilane (APTES) [30, 31]. Then, the porphyrin ligand was metalated (1e). Subsequently, metalloporphyrin immobilized on PC4RA (2b) was produced as the outcome of the reaction between compound (2b) and compound (1e) (Scheme 1). In order to characterize the catalyst, and to corroborate the covalent interactions between metalloporphyrin and PC4RA in metallporphyrin@ PC4RA, FTIR was recorded (Fig. 1). The IR spectrum of the functionalized Cu-Porphyrin@ PC4RA appearance a new peak at 1552 cm^{-1} is due to C–N stretching and N–H bending vibrations confirmed the bond of the



Scheme 2 The oxidation benzyl alcohol by Cu-porphyrin@ PC4RA and molecular oxygen

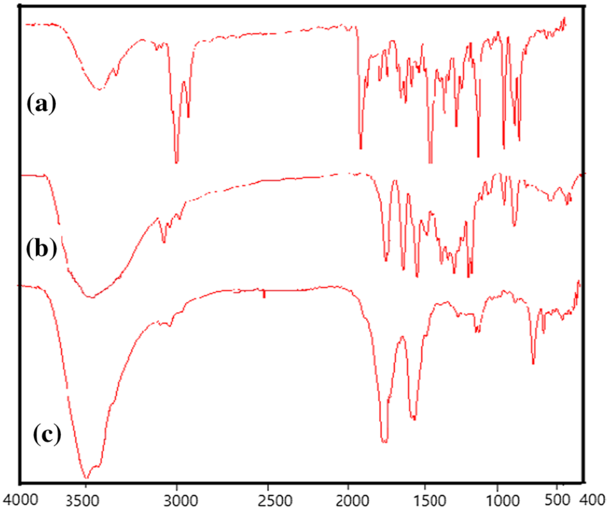


Fig. 1 FTIR spectra of (**a**) synthesized porphyrin (**b**) PC4RA (**C**) Cu-Porphyrin@ PC4RA

amide group and a wide peak at 1109 cm^{-1}, which is showman of Si–O bonds. On the other hand, a wide peak at 3210–3555 cm^{-1} displayed that all of the OH groups of PC4RA (2b) are not totally functionalized due to steric impediment. So, the FTIR data qualitatively corroborated the prosperous grafting of Si groups onto the surface of the polymer (Fig. 1). In addition to FTIR spectrum, other techniques were considered for better catalyst verification (UV–VIS, SEM, XRD, EDX and TGA). Furthermore, the UV–Vis spectrum of porphyrin displays peaks at 413 (Soret band), 513, 547, 590 and 645 nm (Q bands). Upon copper ion concatenation, the pyrrole nitrogen's of porphyrin are coordinated to the copper ion to form Cu-Porphyrin complex. As a result, the intensity of Q peaks is reduced, and the Soret peak displays slight red shift (from 413 to 425 nm) that is characteristic of the creation of Cu-Porphyrin complex (Fig. 2). The EDS analysis was applied to assess the catalyst, which corroborates the presence of N, Si and Cu in the mentioned precatalyst (Fig. 3). In order to achieve an intuition into the morphology of the synthesized catalyst, SEM was used (Fig. 4). Since the catalyst

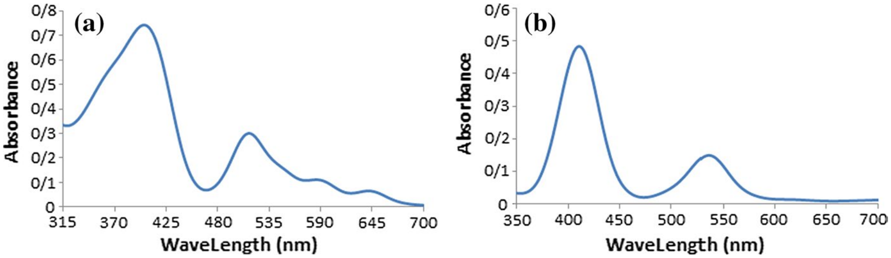


Fig. 2 UV–Vis spectrums of porphyrin (**a**) and Cu-Porphyrin@ PC4RA (**b**)

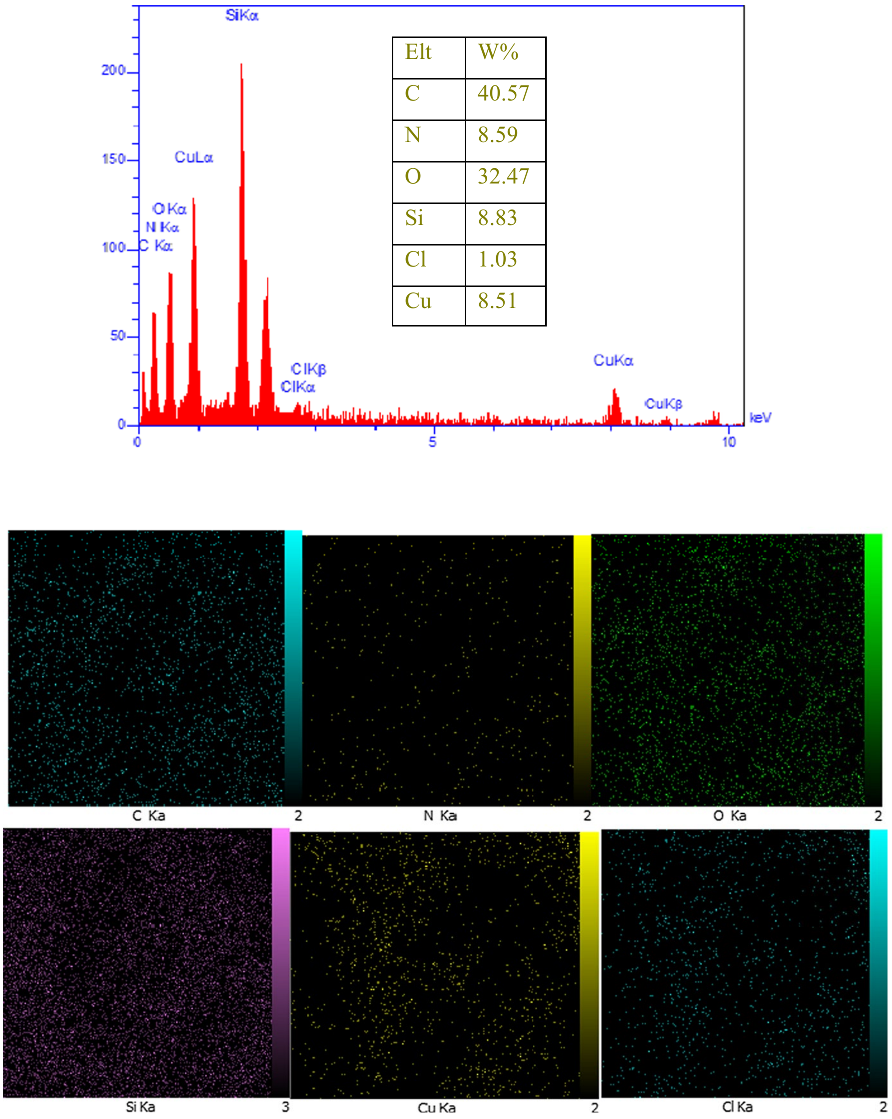


Fig. 3 EDS result for Cu-Porphyrin@ PC4RA

shows smaller pores than PC4RA (see ESI†), it can be derived that the Cu-Porphyrin are successfully fixed onto the polymeric spines. The pattern of XRD is confirmed the Cu-Porphyrin@ PC4RA structure (Fig. 5). The thermal stability of Cu-Porphyrin@ PC4RA was investigated by TGA analysis. The primary negligible weight loss happens before 145 °C, which can be imputed to the vaporization of water or extant solvent. The second loss weight is happened at 145–400 °C, which attributed to the dissociation of Cu-Porphyrin. Thus, TGA analysis shows the high thermal constancy of Cu-Porphyrin@ PC4RA. The third loss weight is

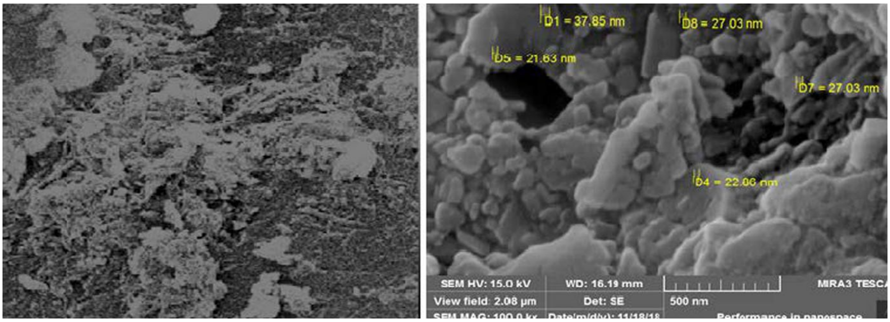


Fig. 4 The SEM image of Cu-Porphyrin@ PC4RA

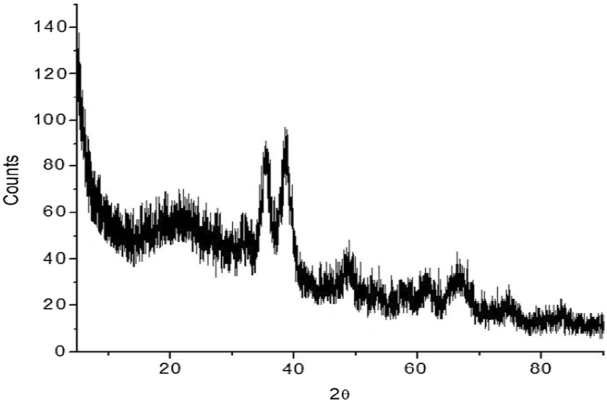


Fig. 5 XRD patterns of Cu-Porphyrin@ PC4RA

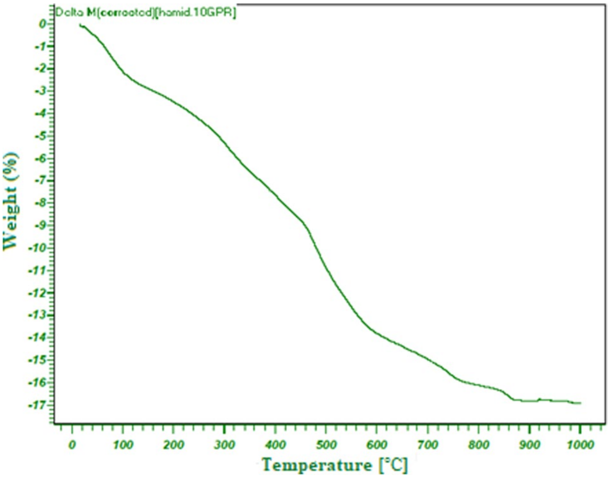


Fig. 6 TGA curves of Cu-Porphyrin@ PC4RA

attributed to dissociation of PC4RA at ~ 460 °C (Fig. 6). To evaluate the catalytic activity of Cu-Porphyrin@ PC4RA in the oxidation reactions, the reaction of benzyl alcohol was chosen as a model system to get efficient results. We studied various conditions, including amount of catalyst, solvents, temperature and isobutyraldehyde, the outcomes of which are tabloid in Table 1. From Table 1, the best result was obtained when the reaction was done in the presence of 20 mg of Cu-Porphyrin@ PC4RA. To investigate the effect of solvent, the reactions with different solvent were conducted. It seemed that the solvent played a key role in the oxidation system. As shown in Table 1, O-Xylene solvent was suitable to the oxidation reaction, which gave high yield of benzaldehyde (entry 3). However, when water, acetonitrile, ethanol and chloroform were used instead, trace product could be obtained (entries 9–12). The benzyl alcohol oxidation catalyzed by metalloporphyrin should involve radical species. So, O-Xylene as solvent is mostly the election for radical reactions because of its disinclination to undergo radical addition. Also the temperature effect was studied on oxidation of benzyl alcohol. With increase temperature from 40 to 55 °C, it was indicated that the conversion efficiency increased. It is remarkable, when temperature was raised benzoic acid could detect (entry 8). The effect of isobutyraldehyde as co-catalyst played a significant role in the oxidation reaction (Table 2). It should be noted that in the lack of co-catalyst, these oxidation reactions require longer time. Also, the catalyst (Cu-Porphyrin@ PC4RA) shows high activity compared to free metalloporphyrin (Table 2). In this reaction method, a wide range of benzyl alcohols have been oxidized that different substitutions including electron-withdrawing or electron-donating groups had good and excellent outputs (Table 3) without any by-products. It seems that the performance of oxidation in these catalytic systems

Table 1 The effect of solvent on the oxidation of benzyl alcohol by O_2 in the presence of Cu-Porphyrin@ PC4RA

Entry	Amount of catalyst(mg)	Temperature °C	Solvent	Time (h)	Yield%
1	5	55	O-Xylene	6	55
2	10	55	O-Xylene	6	75
3	20	55	O-Xylene	6	94
4	30	55	O-Xylene	6	95
5	20	25	O-Xylene	6	30
6	20	40	O-Xylene	6	60
7	20	55	O-Xylene	6	94
8	20	70	O-Xylene	6	85
9	20	reflux	Water	6	30
10	20	reflux	Ethanol	6	25
11	20	reflux	Acetonitrile	6	50
12	20	reflux	Chloroform	6	40

Reaction condition: Benzyl alcohol (2 mmol), isobutyraldehyde (6 mmol), catalyst (20 mg), O-Xylene (10 ml), O_2 (1 atm), 55 °C

Table 2 Comparison between Cu-Porphyrin@ PC4RA and Cu-Porphyrin in the presence of isobutyraldehyde

Entry	Cu-Porphyrin@ PC4RA(mg)	Cu-Porphyrin(mg)	Isobutyraldehyde(mmol)	Time(h)	Yield%
1	20	–	–	6	40
2	20	–	2	6	60
3	20	–	4	6	85
4	20	–	6	6	94
5	–	20	6	6	55
6	–	–	6	6	25

Reaction condition: Benzyl alcohol (2 mmol), O-Xylene (10 ml), O_2 (1 atm), 55 °C

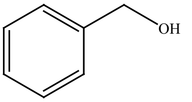
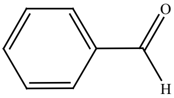
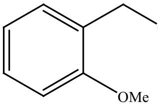
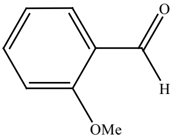
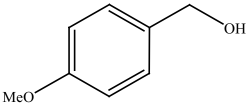
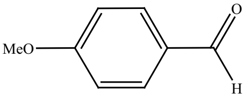
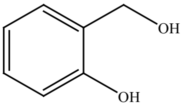
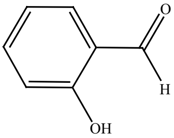
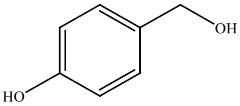
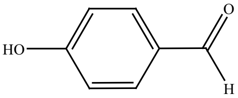
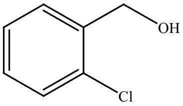
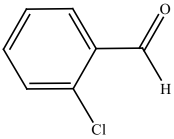
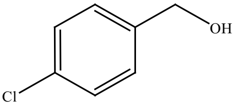
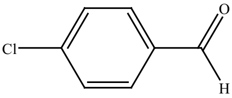
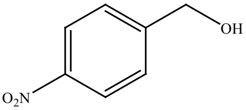
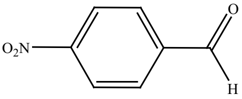
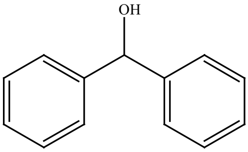
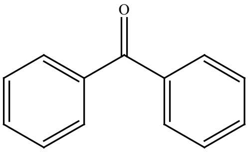
is much related to the electronic and space needs of the substrate (Table 3). The recovery capability from the reaction medium and activity is considered as one of the most important characteristics of the solid catalyst. Thus, we checked the possibility of recovering Cu-Porphyrin@ PC4RA in the oxidation reactions. So, after the each reaction completion, Cu-Porphyrin@ PC4RA was recovered from the reaction mix by easy purification, washed with methanol and hot water, and after drying it was ready to be utilized anew in the following analogous cycle and then reusing the catalyst up to five times without significance loss of activity (Fig. 7). The amount of Cu in the sample was confirmed with ICP technique. Respectively, the weight percentage of copper in fresh and reused catalyst (after five times) was 20.2wt% and 20.17wt%. On these results, we can conclude that there is no considerable difference in weight percentage of copper in reused and fresh catalyst that was used in the primary time in the reaction. Also, this verification showed that Cu linked with porphyrin ring and these linkages are firm. In addition, no leaching occurs in reaction medium.

Conclusions

In this research, at first, 4-(methoxycarbonyl)phenyltriphenylporphyrin was prepared according to Lindsay's method. Then, 4-(methoxycarbonyl)phenyltriphenylporphyrin immobilized on network PC4RA, as an eco-friendly solid-supported catalyst, was successfully prepared and characterized by FTIR, TGA, SEM, XRD, ICP and EDS. This catalytic activity was investigated in the oxidation of alcohols in present O_2. This way renders significant benefits including simple work-up method, short reaction times, good consistency, operational simplicities, clean reaction profiles, cost-effective method, ease of separation and recyclability of the solid catalyst.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11164-021-04563-y.

Table 3 The oxidation of benzyl alcohols in present O_2 and Cu-Porphyrin@ PC4RA

Entry	Alcohol	Product	Time(h)	Conversion%
1			6	94
2			6	88
3			6	90
4			6	85
5			6	90
6			8	90
7			8	75
8			8	60
9			8	94

Reaction condition: Benzyl alcohol (2 mmol), isobutyraldehyde (6 mmol), catalyst (20 mg), O-Xylene (10 ml), O_2 (1 atm), 55 °C

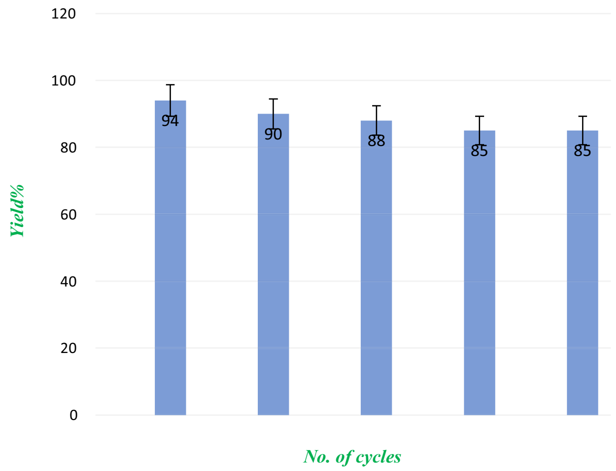


Fig. 7 Recyclability of catalyst

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