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Highly selective aqueous heterogeneous oxygenation of hydrocarbons catalyzed by recyclable hydrophobic copper (II) phthalocyanine nanoparticles

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ABSTRACT

A novel aqueous catalytic method for selective epoxidation of olefins and oxidation of saturated hydrocarbons to ketones using aqueous solution of tetra-n-butylammonium peroxomonosulfate (TBAOX) containing water-insoluble copper (II) phthalocyanine nanoparticles has been developed. No surfactants, additives, toxic reagents or solvents were involved. The impressive turnover numbers obtained for CuPc in this oxidation system displayed the high catalytic activity and relative stability of catalyst. The effective dispersity of CuPc in aqueous solution of TBAOX which yielded particles with average size of 30 nm, was the most important factor to affect the reaction rate. The catalyst could easily be recovered and reused without loss of activity and the reduced form of starting oxidant (n-Bu_4NHSO_4) could also be recycled.

1. Introduction

Phthalocyanine transition metal complexes as important industrial pigments have been considered as potential oxidation catalysts because of their rather cheap and facile preparation in a large scale and in particularly their chemical and thermal stability. However, the low solubility of metallophthalocyanines is perhaps the most significant limitation in their application as catalysts. It may be overcome by sulfonation and carboxylation at the periphery of the molecule to give rise to water-soluble derivatives [1]. Nevertheless, the separation of water-soluble catalysts from the aqueous phase is a time consuming process making them out of recycled materials.

Oxone® ($2KHSO_5{\bullet}KHSO_4{\bullet}K_2SO_4$) has drawn considerable attention as a mild and efficient reagent for various organic transformations in recent years [2]. Despite, the promising employment of Oxone® and their organic salts (n-Bu_4NHSO_5, Ph_4PHSO_5) in the oxygenation of hydrocarbons in the presence of metalloporphyrins [3–5], attempts at using this versatile oxygen source in association with phthalocyanine catalysts were virtually unsuccessful [6,7].

Our ongoing research on the development of new application of tetra-n-butylammonium Oxone® (n-Bu_4NHSO_5, TBAOX) in the oxidation of organic compounds [5,8–12], led to an innovative heterogeneous strategy for clean and selective aqueous oxygenation of hydrocarbons [13] and alcohols [14] catalyzed by water-insoluble Fe(III) and Mn (III) porphyrin complexes. Very recently efficient oxidation of alcohols and sulfides in water catalyzed by hydrophobic copper (II) phthalocyanine (CuPc) as a cheap heterogeneous catalyst has also been developed [15]. Now, we would like to describe the catalytic potential of CuPc in the epoxidation of olefins and oxygenation of saturated C—H bonds using TBAOX in an aqueous media lacking of any organic co-solvents and surfactants (Scheme 1). Some evidences for formation of CuPc nanoparticles in aqueous solution of TBAOX which demonstrate the high oxidation activity of hydrophobic catalyst have also been presented. The catalyst and the reduced form of oxidant (n-Bu_4NHSO_4, $TBAHSO_4$) were easily recovered and reused in the procedure.

2. Experimental

2.1. General remarks

Purity determinations of the products were accomplished by GC on a Shimadzu GC-16A instrument using a 25 m CBP1-S25 (0.32 mm ID, 0.5 μm coating) capillary column. IR spectra were recorded on a Perkin Elmer 780 instrument. UV–vis spectra were recorded on a 160 Shimadzu spectrophotometer. NMR spectra were recorded in $CDCl_3$ solutions with a Brucker Avance DPX FT-NMR 250 MHz instrument. The residual $CHCl_3$ in conventional 99.8 atom% $CDCl_3$

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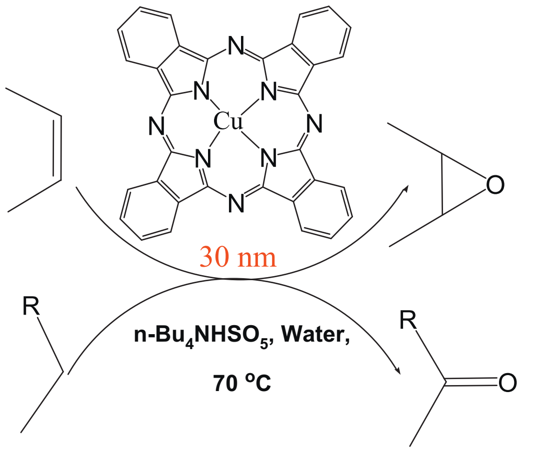


Scheme 1. Oxygenation of hydrocarbons using TBAOX catalyzed by CuPc nanoparticles in water.

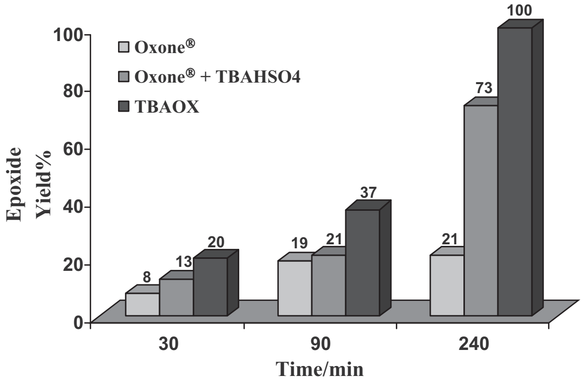


Fig. 1. The comparison of oxidative activity of Oxone®, Oxone®/TBAHSO$_4$ and TBAOX in the epoxidation of cyclooctene catalyzed by CuPc in water at 25 °C.

gives a signal at $\delta = 7.26$ ppm, which was used for calibration of the chemical shift scale. Mass spectra were recorded on a Shimadzu GC–MS-QP5050A. MPcs were synthesized according to the literature [16]. The freshly prepared n-Bu$_4$NHSO$_5$ [5] was a much stronger oxidant than commercially available samples.

2.2. General procedure for epoxidation of olefin

To a mixture of 110 mg of cyclooctene (1 mmol) and 2.8 mg of CuPc (0.005 mmol) in 2 ml bidistilled water was added 0.7 g (2 mmol) of freshly prepared TBAOX. The reaction mixture was stirred under air at 70 °C for 15 min which was monitored by GC and TLC. After completion of the reaction, the mixture was washed with ethyl acetate (3 × 2 ml), and the organic phase was separated and evaporated. If necessary, further purification was performed by silica chromatography eluted with n-hexane/ethyl acetate (10:1).

2.3. General procedure for oxygenation of saturated hydrocarbons

To a mixture of 106 mg of ethylbenzene (1 mmol) and 2.8 mg of CuPc (0.005 mmol) in 2 ml bidistilled water was added 0.7 g (2 mmol) of freshly prepared TBAOX (1.4 g for others). The reaction mixture was stirred under air at 70 °C for 100 min, which was monitored by GC and TLC. After completion of the reaction, the mixture was washed with ethyl acetate (3 × 2 ml), and the organic phase was separated and evaporated. If necessary, further purification was performed by silica chromatography eluted with n-hexane/ethyl acetate (10:3).

2.4. Recycling procedure

After completion of the epoxidation of cyclooctene, the product was isolated by ethyl acetate (3 × 2 ml) and the reaction mixture was centrifuged and the solid catalyst was separated, washed with ethyl acetate (3 ml), dried and reused for the similar reaction. The aqueous phase was lyophilized to obtain TBAHSO$_4$ which can be reused in the preparation of TBAOX.

3. Results and discussion

3.1. Preliminary studies

Knowing that Oxone® has not ability to trigger the epoxidation reaction in blank condition, preliminary catalytic experiments were addressed to the oxidation of cyclooctene (0.2 mmol) with Oxone® (0.4 mmol) in the presence of a few amount of cheap commercially available CuPc (0.5 mol%) in bidistilled water at 25 °C under air. Only 21% cyclooctene oxide was achieved after 4 h. When an equimolar amount of TBAHSO$_4$ was accompanied with Oxone®, the oxidation rate enhanced and 73% epoxide was obtained at the same time. It should be noted that pure KHSO$_5$·H$_2$O in the absence (20%/90 min) and in the presence of TBAHSO$_4$ (17%/90 min) did not improve the olefin conversion. Nevertheless, using TBAOX (0.07 g) the reaction proceeded smoothly and gave 33 and 100% epoxide yield after 1 and 4 h, respectively (Fig. 1). To increase the conversion rate, different factors that may affect the cyclooctene oxidation were probed. The use of different amount of TBAOX in the oxidation of cyclooctene demonstrated that the reaction required 2 equivalent of oxidant for full conversion of substrate at 4 h (33 and 51% epoxide yield by using 0.5 and 1 equivalent of TBAOX, respectively). However, the reaction rate did not changed by using more amount of oxidant. Also the same conversions and epoxide yields were observed by using standard buffered solutions, water-soluble sulfonated catalyst (CuPcS), common nitrogen donors (imidazole and pyridine) and also sodium dodecyl sulfate at CMC condition (0.008 mol/L).

Next, the effect of catalyst content has been examined. The system displayed a low catalyst loading of 0.5 mol% for complete conversion of cyclooctene (38 and 60% epoxide yield by using 0.1 and 0.2 mol% of catalyst, respectively). Nevertheless, an increase in the catalyst content up to 5 mol% did not enhance noticeably the reaction rate. In addition, compared with other common Pc complexes, CuPc was proven to have the higher catalytic activity in the oxidation of olefins. When the catalyst was replaced to FePc and CoPc with the same catalytic amount, cyclooctene oxide was achieved in 71 and 86%, respectively within 4 h.

Finally, our investigation showed that the catalytic activity of CuPc enhanced significantly with increasing reaction temperature (Fig. 2). Full conversion of cyclooctene was achieved within 15 min

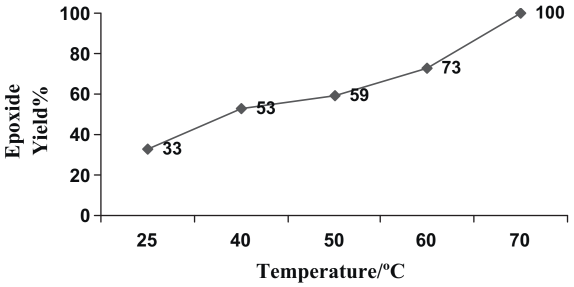


Fig. 2. The influence of temperature on the epoxidation of cyclooctene using TBAOX catalyzed by CuPc in water after 15 min.

Table 1
The effect of different oxidants in the oxidation of cyclooctene catalyzed by CuPc in water.[a]

Oxidant	Cyclooctene oxide%[b]	
	25 °C	70 °C
H_2O_2	0	0
UHP	2	35
TBHP	1.5	36
$NaIO_4$	0	0
n-Bu_4NIO_4	21	50
Oxone®	11	13
TBAOX	33	100

[a] The reactions were run under air for 1 h by molar ratio of 200:400:1 for cyclooctene/oxidant/catalyst.
[b] GC yield.

at 70 °C. Under these conditions cyclooctene oxide was secured in 95% yield after a simple extraction with ethyl acetate.

The effect of other common oxidants including H_2O_2, UHP, *t*-BuOOH, $NaIO_4$ and n-Bu_4NIO_4 was examined for epoxidation of cyclooctene under the catalytic influence of CuPc in water and found them inactive or less reactive than that of TBAOX at different temperatures (Table 1).

3.2. *Catalytic oxidation of olefins and saturated hydrocarbons*

To establish the general applicability of the method, various olefins were subjected to the oxidation protocol using TBAOX under the catalytic influence of the CuPc at 70 °C (Table 2). As summarized in Table 2, different alkenes are generally excellent substrates for this catalyst (entries 1–13). It led to complete conversion of cyclohexenes, cyclooctene and norbornene with the formation of the corresponding epoxides as sole products (entries 1–4). The epoxidation of the least reactive 1-octene as a terminal olefin proceeded with moderate yield and excellent selectivity (entry 5). However, the selectivity tends to decrease when the terminal olefin becomes conjugated with phenyl group so that the lower epoxide yields were obtained for styrenes (entries 6–8). Nevertheless, excellent epoxide selectivities were observed for α-methylstyrne and indene (entries 9 and 10).

The chemoselectivity of the procedure was notable. While, the primary alcohols containing C—C double bonds (allylic and homoallylic alcohols) oxidized completely to the corresponding epoxides under the influence of this catalytic system (entries 11 and 12), secondary one converted to the related α, β-unsaturated ketone as sole product (entry 13).

These results were further supported by performing some competitive reactions between cyclooctene and both benzyl alcohol as an active primary alcohol, and also less reactive cyclohexanol (Table 3). Inspection of the results in Table 3 indicates excellent chemoselectivity for CuPc in the olefin epoxidation rather than oxidation of primary hydroxyl group (entry 1, >98% cyclooctene oxide vs. 1.5% benzaldehyde). However, cyclohexanone was formed as sole product in the oxidation of mixture of cyclohexanol and cyclooctene (entry 2). It is worthy to mention that lower epoxidation selectivity was observed for FePc and CoPc than that of CuPc in the oxidation of cyclooctene in association with benzyl alcohol (entries 3 and 4; 88 and 80% epoxide selectivity, respectively). These results once again confirm the superiority of CuPc as oxidation catalyst in the present system.

Then, we applied this oxidation system in the oxygenation of saturated C—H bonds. It was observed that complete conversion of ethyl benzene took 100 min and gave acetophenone as sole product (96% isolated yield) under the same experimental conditions used for olefin epoxidation (200:400:1, for substrate/TBAOX/CuPc, 70 °C). Nevertheless, oxidation of tetralin and indan required higher amounts of oxidant and gave the related ketones in moderate to high yields at the same time (48, 79% respectively).

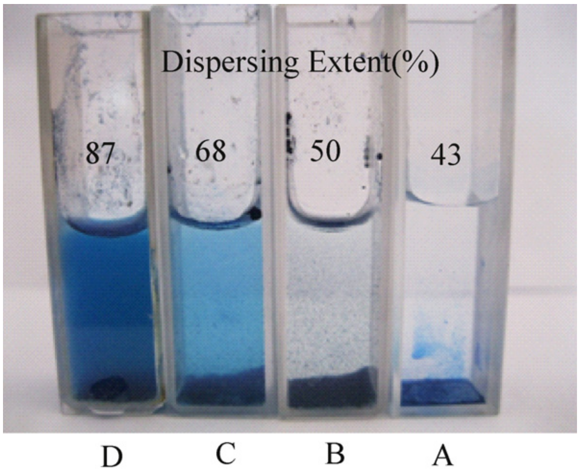


Fig. 3. Photographs of 2.8 mg of CuPc in 2 ml bidistilled water at 70 °C (A), after addition of $TBAHSO_4$ and Oxone® (B), after addition of TBAOX (C), sonicated C (D).

It seems that the attachment of TBAOX to the metal centre giving a six coordinate adduct [PcCu—O—$OHSO_3$] enhances the electrophilicity of Cu-coordinated oxygen atom of the oxidant. Easy oxidation of sulfides to sulfones was achieved by using this species [12,15]. Nevertheless, oxidation of alcohols [15], olefins and saturated hydrocarbons required higher temperature [17]. Presumably a high valent $[Cu{=}O]^+$ active species should be involved under this condition. [17,18] Epoxidation of olefins and oxidation of secondary C—H bonds accomplished efficiently in the presence of this intermediate. Since ketones were produced as main products in the oxidation of saturated hydrocarbons, secondary C—H bonds are more sensitive to this oxidation system. Accordingly, secondary alcohols oxidized selectively in the presence of C—C double bond. Nevertheless, oxidation of primary C—H bonds in both benzylic and aliphatic alcohols proceeded sluggishly under this condition [15].

3.3. *Reactivity and stability of catalyst*

The high/excellent yields of oxidation products obtained using this novel oxidation method in desired times display the high catalytic activity and relative stability of CuPc in association with aqueous solution of TBAOX. It was further supported by the impressive turnover frequency (TOF) obtained for CuPc in the oxidation of cyclooctene (8900/h) and tetraline (5100/h) using 10,000:20,000:1 molar ratio for substrate/TBAOX/catalyst indicating well the high efficiency and stability of the present catalytic system.

The effective dispersity of CuPc catalyst in aqueous solution of TBAOX seems to be the most important factor to affect the reaction rate. We studied dispersing extent (D.E. $\% = (1 - T) \times 100$) of title pigment in water medium (Fig. 3). Without TBAOX virtually CuPc particles were so unstable and hydrophobic, not wetted by water, that they could not be dispersed at all in water at 70 °C even with extensive sonication (Fig. 3A). The addition of $TBAHSO_4$ in the absence and in the presence of Oxone® did not improve noticeably the D. E. (50%; Fig. 3B). Nevertheless, the effect of adding of TBAOX on the dispersibility was quite strong as demonstrated in Fig. 3C (68%). As expected, the catalyst agglomerates break-up during the sonication process improved the D. E. (87%; Fig. 3D).

Transmission electron microscopy (TEM) analysis confirmed the strong dispersing effect of TBAOX on CuPc particles. Fig. 4A shows that CuPc particles are single crystalline with flat edges. Their shapes are polyhedral and look like elongated cylinders

Table 2
Oxygenation of hydrocarbons using TBAOX catalyzed by CuPc in water.[a]

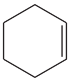
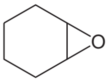
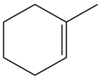
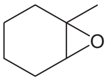
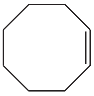
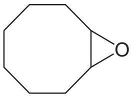
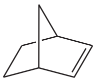
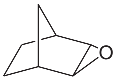
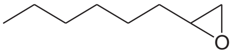
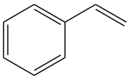
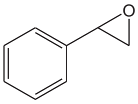
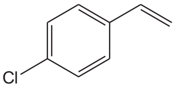
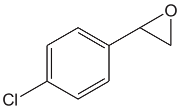
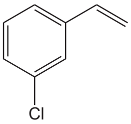
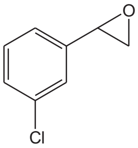
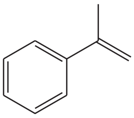
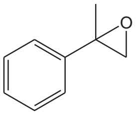
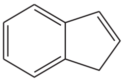
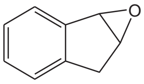
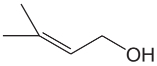
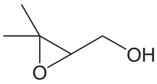
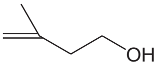
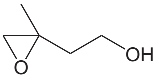
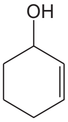
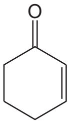
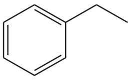
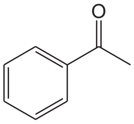
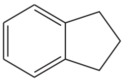
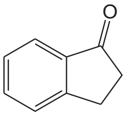
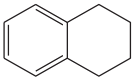
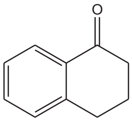
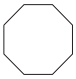
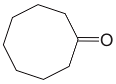
Entry	Substrate	Yield%[b]	Product	^{1}H NMR $\delta_{(ppm)}$	Selectivity %[b]
1		94		3.1[c]	100
2		91		2.9[c]	100
3		95		2.9[c]	100
4		96		2.9[c]	100
5		65		2.5–2.9[c]	100
6		63		2.7–3.8[c]	68[d]
7		86		2.7–3.6[c]	92[d]
8		78		2.7–3.7[c]	81[d]
9		96		2.8–3[c]	100
10		92		4.1–4.3[c]	100
11		90		2.7[c]	100
12		85		2.5[c]	100
13		94		2–2.4, 6, 7.1	100
14		96		2.6, 7.3–7.6, 7.9	100
15		79		7.4–7.7, 3.1, 2.7	100

Table 2 (*Continued*)

Entry	Substrate	Yield%[b]	Product	^{1}H NMR $\delta_{(ppm)}$	Selectivity %[b]
16		48		8, 7.2–7.5 2.6–2.9, 2.1	100
17		8		1.2–1.9, 2.4	100

[a] The oxidation of olefins were run under air at 70 °C for 15 min (entries 1–13) and saturated hydrocarbons for 100 min (entries 14–17). The molar ratio of substrate:TBAOX:catalyst was 200:400:1 except for entries 15–17 which was 200:800:1.

[b] Yields of isolated products. Selectivities were determined by GC and ^{1}H NMR.

[c] $\delta_{(ppm)}$ of C—H oxiran ring.

[d] The remainders are related benzaldehydes; δ_{COH} are 10.1, 9.98 and 9.96 ppm for entries 6–8, respectively.

Table 3

The competitive reactions between olefin and alcohols using TBAOX catalyzed by MPc in water.[a]

Entry	Catalyst	Substrates	Products (yield%)[b]
1	CuPc	Cyclooctene + benzyl alcohol	Cycloocten oxide (>98), benzaldehyde (1.5)
2	CuPc	Cyclooctene + cyclohexanol	Cycloocten oxide (0), cyclohexanone (100)
3	FePc	Cyclooctene + benzyl alcohol	Cycloocten oxide (77), benzaldehyde (10)
4	CoPc	Cyclooctene + benzyl alcohol	Cycloocten oxide (80), benzaldehyde (20)

[a] The reactions were run under air at 70 °C for 15 min and the molar ratio of olefin:alcohol:TBAOX:catalyst was 200:200:400:1.

[b] GC yields.

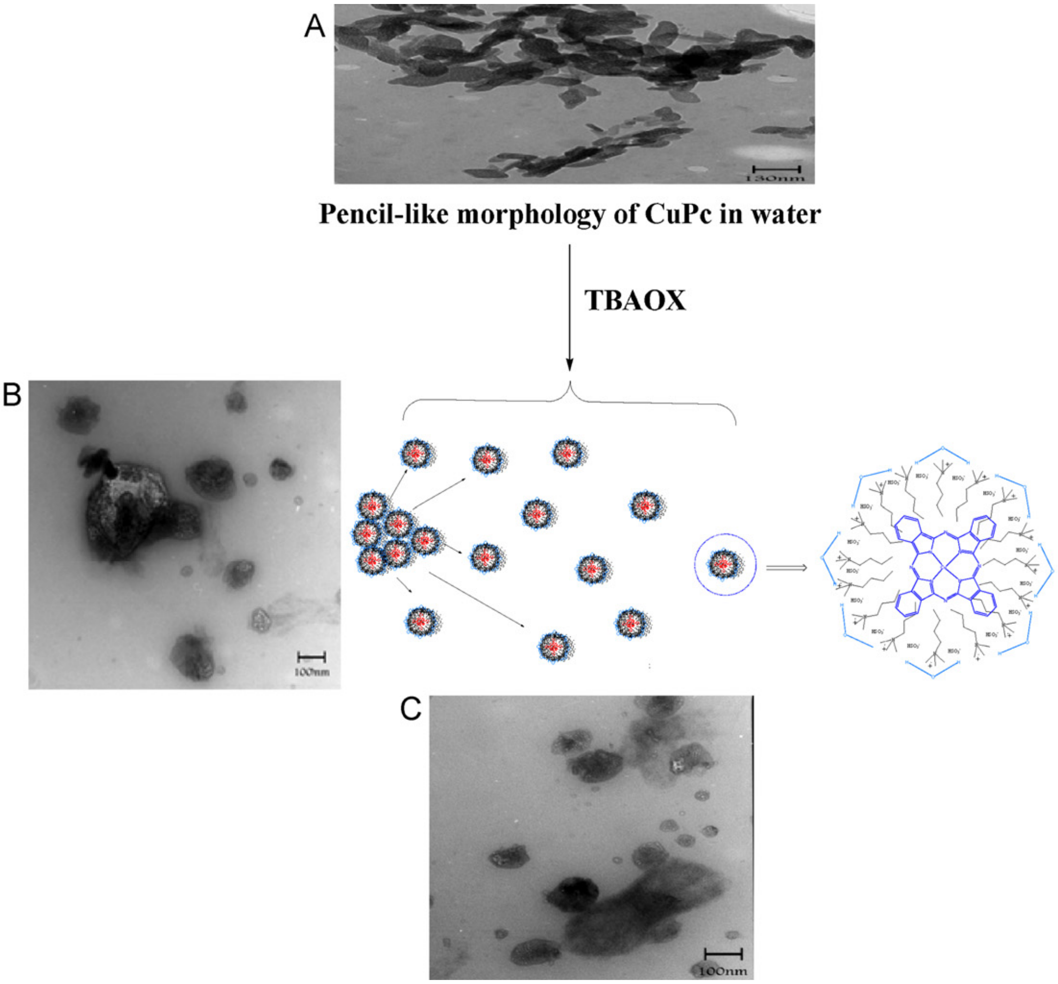


Fig. 4. Plausible mechanism for formation of CuPc nanoparticles in aqueous solution of TBAOX. TEM images represent: pencil-like morphology of CuPc in water (A), and spherical nanoparticles after addition of TBAOX (B) and (C).

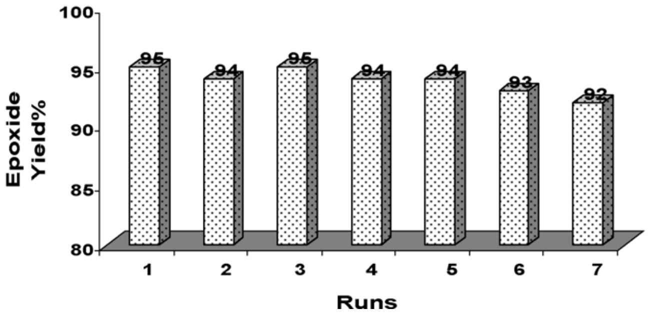


Fig. 5. Recycling of the catalytic system for the epoxidation of cyclooctene in water.

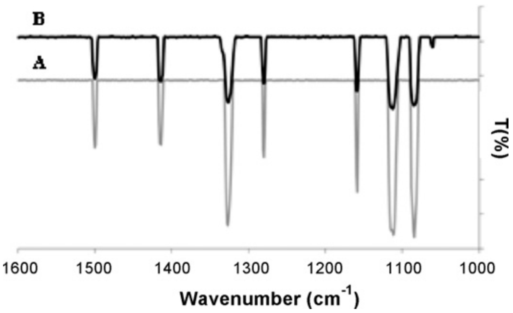


Fig. 7. The IR spectrum of the fresh CuPc complex (A) and after 7 times reuses in aqueous oxidation of cyclooctene (B).

(pencil-like morphology) with diameters of about 50–70 nm and lengths of 80–250 nm. By addition of TBAOX this morphology collapsed and spherical particles were obtained with size ranging between 20 and 50 nm (Fig. 4B and C). The good dipersibility of catalyst treated with TBAOX is due largely to the fact that TBAOX as a quaternary salt acts as a stabilizer [19,20] as well as oxidant, so that n-Bu$_4$N chains adhering to the pigment surface, prevent catalyst particles from agglomerating (Fig. 4) [21].

To examine the effect of D.E. on the catalytic activity of CuPc, oxidation of norbornene under different conditions was evaluated using aqueous solution of TBAOX at 60 °C. With magnetic stirring, a moderate yield of norbornene oxide (59%) was observed within 15 min. In second experiment aqueous mixture of CuPc was initially sonicated for 15 min. After that TBAOX was added and then the reaction mixture was stirred magnetically, which led to 68% yield of epoxide at the same time. When ultrasound was used as the stirring method, a significant increase in the epoxide yield was observed (92%). However, thorough mixing of the reactants and the production of hot spots should also be taken into account for enhancing reaction rate by ultrasonic irradiation [22].

These promising results encouraged us to evaluate the reusability of the catalyst. After isolation of water-insoluble products by using ethyl acetate as an environmentally benign solvent, the solid catalyst was separated from the aqueous solution by centrifuging and was reused for the subsequent reaction under the similar reaction conditions. The averaged isolated yield of cyclooctene oxide for seven runs was 93.8%, demonstrating well the high reusability of the catalyst in this oxidation system (Fig. 5). The stability of CuPc in this oxidation system was also established by spectrophotometry. It was found that the mediation of CuPc in the oxidation of cyclooctene with aqueous solution of TBAOX does not change noticeably the electronic absorption spectra of catalyst after seven runs (Fig. 6). In addition, the IR spectra were identical for the fresh and reused catalysts demonstrating the stability of the Pc structure under the real catalytic conditions (Fig. 7). Moreover, the reduced form of oxidant's (TBAHSO$_4$) was separated by lyophilizing of aqueous phase and reused in the preparation of TBAOX. Therefore, from the stand point of greener chemical processes, the use of CuPc as catalyst in combination with aqueous solution of TBAOX do not lead to three major sources of waste: organic solvents, catalysts and harmful by-products. These advantages for this high yielding oxidation method along with the low cost for preparation of CuPc offered ready scalability. For example, the use of a semi scale-up procedure (25 mmol) for epoxidation of cyclooctene and norbornene in the presence of CuPc led to isolation of the related epoxides in 92 and 95% yields, respectively.

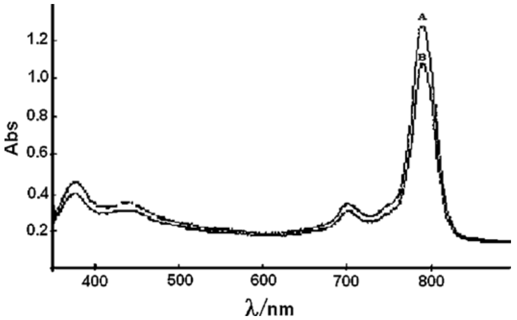


Fig. 6. UV–vis spectra (in H$_2$SO$_4$) of fresh CuPc complex (A) and after 7 times reuses in aqueous oxidation of cyclooctene (B).

4. Conclusion

In conclusion, hydrophobic CuPc complex dispersed in aqueous solution of TBAOX which yielded particles with average size of 30 nm, catalyzed efficiently epoxidation of olefins and oxygenation of saturated hydrocarbons to ketones in good/excellent yields and selectivities. No surfactants, additives, toxic reagents or solvents and by-product were involved and no laborious purifications were necessary. These conditions along with the use of water as a standard "green" solvent as well as easy and safe work-up procedure and reusability of catalyst and by-product are cost effective, environmentally benign and posses high generality which makes title methodology suitable for industrial goal.

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