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Efficient and highly selective aqueous oxidation of alcohols and sulfides catalyzed by reusable hydrophobic copper (II) phthalocyanine

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ABSTRACT

A practical innovative method for highly chemoselective oxidation of alcohols to the aldehyde and ketones and sulfides to the sulfones using tetra-n-butylammonium peroxomonosulfate (n-Bu_4NHSO_5) catalyzed by simple water-insoluble copper (II) phthalocyanine (CuPc) in neat water has been developed. Organic co-solvents, surfactants, co-catalyst and hydrophilic auxiliaries were completely missed in this heterogeneous catalytic strategy. The CuPc catalyst and by-product of oxidant ($TBAHSO_4$) could easily be recycled and reused without loss of activity providing readily scalability.

The selective oxidation of organic compounds by metal complexes has been extensively studied to develop new synthetic strategies for industrial applications [1,2]. Often-used catalysts for oxidation reactions are porphyrin and Schiff base complexes mimicking the heme-containing monooxygenase enzymes that show high catalytic activity and selectivity under different oxidation conditions [3]. However, a problem often encountered in the metalloporphyrin- and metallosalen-catalyzed oxidation reactions is the deactivation of the catalytic species by the oxidative degradation of ligands [4]. Moreover, the extensive use of toxic and volatile organic solvents in these oxidation systems has reduced considerably the practical importance of biologically inspired oxidation catalysis. Discarding of harmful organic solvents is the major problem in chemical industries which accounts around 80% of their wastes [5]. Thus, a new challenge is to make such processes by using non-toxic solvents in particularly aqueous media [6–10].

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 stabilities [11–14]. 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 [14]. Nevertheless, the separation of water-soluble catalysts from the aqueous phase is a time consuming process making them out of recycled materials.

Tetra-n-butylammonium peroxomonosulfate (n-Bu_4NHSO_5, TBAOX) was firstly introduced as a sluggish oxygen source for the oxidation of sulfides to sulfones [15]. For example, oxidation of thioanisole by 3 equivalents of TBAOX in CH_2Cl_2 took four days to produce 78% yield of the corresponding sulfone. A prolonged catalyst-free method for aqueous oxidation of alcohols using this oxidant has also been reported in which, low/moderate yields of the related carbonyl compounds were achieved [16]. Recently, efficient oxidation of alcohols in the presence of immobilized TEMPO in ionic liquid [bmim][PF6] has also been reported [17]. Our ongoing research on the development of new applications of TBAOX in the oxidation of organic compounds containing sulfides and alcohols [18–25] resulted in a novel and innovative strategy for clean and selective oxygenation of hydrocarbons in neat water catalyzed by water-insoluble Fe(III) and Mn (III) porphyrins [26]. Now, we wish to report the catalytic performance of water-insoluble copper (II) phthalocyanine (CuPc) as a cheap heterogeneous catalyst in the selective oxidation of alcohols to carbonyl compounds and sulfides to sulfones using TBAOX in neat water in the absence of any organic co-solvents and surfactants (Scheme 1). The catalyst and the reduction product n-Bu_4NHSO_4 ($TBAHSO_4$) from the oxidant TBAOX were easily recovered and reused in the procedure.

The oxidation of cyclohexanol using two equivalents of TBAOX (0.7 g) in water which did not proceed in the absence of catalyst was used as a model reaction. Preliminary catalytic experiments were addressed to the oxidation of cyclohexanol (1 mmol, 0.1 g) with TBAOX (2 mmol, 0.7 g) in the presence of a minute amount of cheap commercially available CuPc (0.5 mol%) in neat water at 25 °C under air which led to the formation of cyclohexanone in 40% yield after 10 h according to GC analysis. The addition of imidazole (35%)

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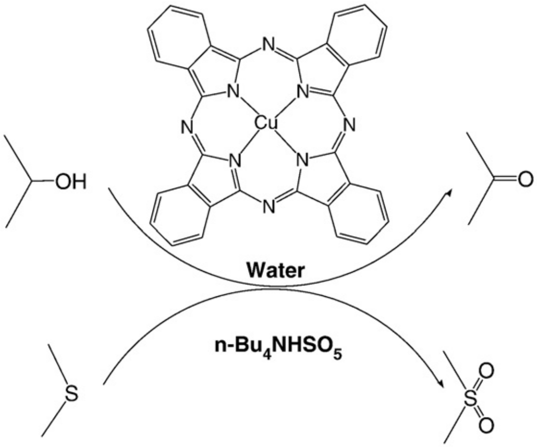


Scheme 1. Oxidation of alcohols and sulfides with aqueous solution of TBAOX catalyzed by CuPc.

and pyridine (42%) as common additives, the use of micellar solution of sodium dodecyl sulfate at CMC (0.008 mol/L) condition (39%) and also the use of copper (II) phthalocyanine-tetrasulfonic acid tetrasodium salt as a water-soluble catalyst (40%), did not affect the conversion rate in this oxidation method. Also, performing the reactions at controlled pH conditions using standard buffered solutions did not improve the yield of cyclohexanone (15, 30, 40, 17 and 37% yield at pH = 2, 4, 7, 9 and 13 respectively). It is worthy to mention that the addition of organic solvents such as ethanol, ethylacetate, dichloromethane, dichloroethane, n-hexane and acetone to the aqueous solution reduced the oxidation rate and yield of product (Table 1).

Then, the influence of temperature on the reaction rate was examined. It was observed that, an increase in the temperature in this oxidation system, promoted remarkably the effectiveness of the catalytic system and full conversion of cyclohexanol was achieved at 70 °C within 30 min (Fig. 1). Under these conditions the oxidation reaction proceeded smoothly (Fig. 2) and cyclohexanone was secured in 95% yield after a simple extraction from aqueous phase. It should be noted that blank experiments for oxidation of cyclohexanol using TBAOX at 70 °C gave only 15 percentage of cyclohexanone after 60 min.

The effect of catalyst loading has also been examined. Our experiments on the oxidation of cyclohexanol with TBAOX by using 0.1, 0.2, 0.5 and 1 mol% of CuPc led to 28, 60, 100 and 100% yields of cyclohexanone respectively. Thus, a low catalyst loading of 0.5 mol % was established for complete conversion of cyclohexanol in the desired time. Nevertheless, an increase in this ratio up to 5 mol% did not improve the conversion rate. The effect of simple copper salts for the activation of TBAOX and also other common oxidants including H_2O_2 (and also UHP), *t*-BuOOH, $NaIO_4$ and n-Bu_4NIO_4 in combination with CuPc was examined for the oxidation of cyclohexanol in water and found them virtually inactive at different temperatures.

Table 1
The effect of organic co-solvents on the aqueous oxidation of cyclohexanol using TBAOX catalyzed by CuPc.[a].

Solvent	Cyclohexanone%[b]
Dichloromethane/water	32
Dichloroethane/water	36
n-Hexane/water	4
Acetone/water	15
Ethylacetate/water	20
Water	40

[a] The reactions were run under air at room temperature in 1:1 V/V mixture of solvents for 10 h and the molar ratio of alcohol: TBAOX: catalyst was 200:400:1.

[b] GC yields.

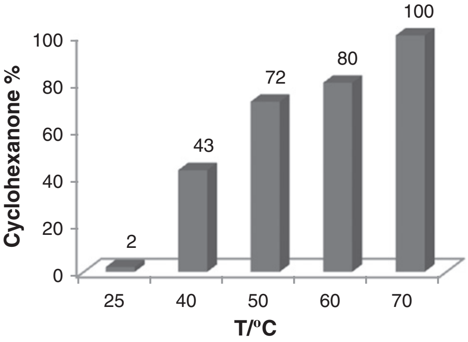


Fig. 1. The effect of temperature on the aqueous oxidation of cyclohexanol using TBAOX catalyzed by CuPc after 60 min.

In order to establish the general applicability of the present catalytic system, a wide range of primary and secondary aliphatic and benzylic alcohols was subjected to oxidation under the optimized conditions in water. Secondary alcohols are generally excellent substrates for this oxidation system (Table 2, entries1–7). Oxidation of primary alcohols including benzylic and aliphatic ones proceeded slowly and gave the low/moderate yields of the corresponding aldehydes (entries 8–10). However, the over oxidation of aldehydes to carboxylic acid was controlled completely. Moreover, the chemoselectivity of the procedure was prominent. Alcohol containing C–C double bond oxidized absolutely to the corresponding α, β-unsaturated ketone (entry 11). This was further supported by performing a competitive oxidation reaction between cyclooctene and cyclohexanol. Cyclohexanone was formed as sole product (>98%) in the oxidation of an equimolar mixture of alcohol and olefin at 70 °C after 15 min confirming the excellent chemoselectivity of CuPc towards oxidation of hydroxyl group.

Encouraged by promising results obtained in the oxidation of alcohols, we evaluated the oxidation activity of this clean catalytic system towards organic sulfides. Knowing that the oxidant has the ability to trigger sulfide oxidation, we performed the blank experiment using 1 mmol thioanisole (0.12 g) and 3 mmol of TBAOX (1 g) in neat water at 25 °C under air afforded a mixture of the related sulfoxide (31%) and sulfone (39%) after 1 h according to GC analysis. Nevertheless, addition of a catalytic amount of CuPc (0.005 mmol, 0.5 mol %) to the aqueous mixture led to complete conversion of thioanisole with the formation of the corresponding sulfone as the sole product at the same conditions. It should be noted that some attempts to control the reaction for selective production of sulfoxide in desired yield were unsuccessful (Table S1 in supporting information). Next, different sulfides were subjected to the reaction system in the presence of CuPc and the results are listed in Table 3. All substrates could be smoothly converted to sulfones with moderate/high yields and excellent selectivities were obtained under mild conditions (entries 1–6).

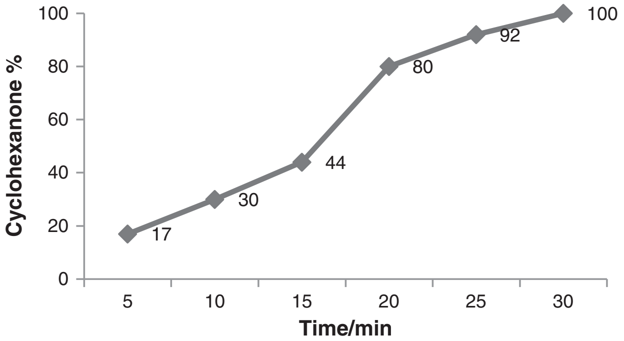
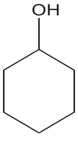
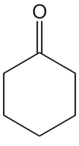
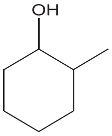
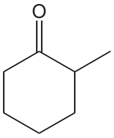
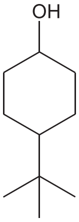
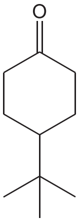
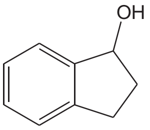
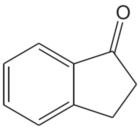
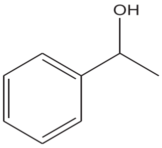
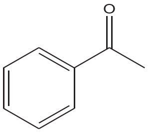
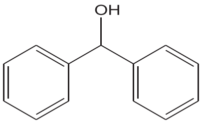
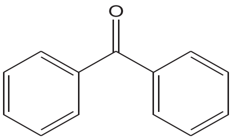
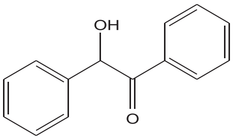
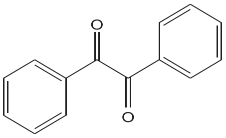
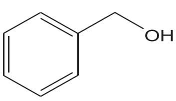
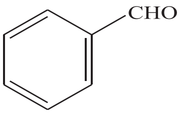
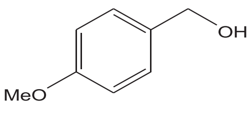
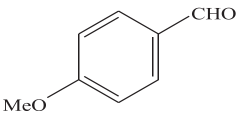
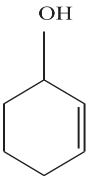
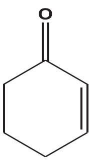


Fig. 2. The reaction profile for aqueous oxidation of cyclohexanol using TBAOX catalyzed by CuPc at 70 °C.

Table 2
Oxygenation of alcohols with aqueous solution of TBAOX catalyzed by CuPc.[a]

Entry	Alcohol	Product[b]	Yield%[c]
1			95
2			90
3			92
4			85
5			94
6			80
7			55
8			25
9			55
10	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	15
11			94

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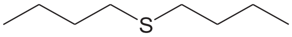
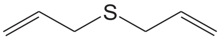
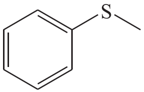
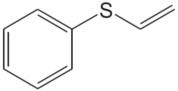
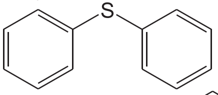
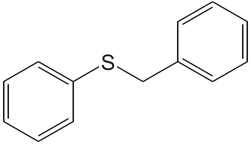
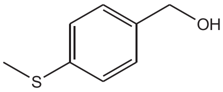
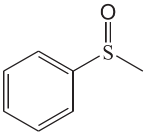
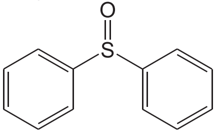
[a] The reactions were run under air at 70 °C for 30 min and the molar ratio of alcohol: TBAOX:catalyst was 200:400:1.
[b] All products were identified by comparison with commercial and authentic samples.
[c] Yields of isolated products. No over oxidation products were observed for all substrates.

Table 3
Oxidation of sulfides and sulfoxides with aqueous solution of TBAOX catalyzed by CuPc.[a]

Entry	Substrate	Sulfone yield%[b]
1		100[c]
2		100[c]
3		95
4		93
5		65
6		88
7		87
8		94
9		97

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[a] The reactions were run under air at room temperature for 1 h with a molar ratio of substrate/TBAOX/catalyst, 200:600:1.
[b] Yield of isolated sulfone products. All products were sulfones in 100% selectivity [29] except for entry 7 which gave 6% of the related sulfoxide “4-(methylsulfinyl) benzyl alcohol” [30].
[c] GC yield.

A salient feature of the present oxidation system is its excellent selectivity. Sulfones could be nearly stoichiometrically produced and no sulfoxide was detected, which makes this process a good alternative for sulfone production. Accordingly, sulfoxides oxidized easily to the related sulfones with excellent yields (entries 7,8). Also sulfides having a carbon–carbon double bond (entry 2, 4), or benzylic C–H bond (entry 6) were cleanly transformed into the corresponding sulfones in excellent yield without formation of any epoxide and benzylic oxidation by-products. Moreover, oxidation of 4-(methylthio)benzyl alcohol (entry 7) including sulfide and alcohol functionalities both of which are susceptible to oxidation in this catalytic system, gave 4-(methylsulfonyl) benzyl alcohol in 94% selectivity (<6% 4-(methylsulfinyl) benzyl alcohol), while the hydroxyl group remained intact. It was further supported by competition reaction between thioanisole and benzyl alcohol. Thioanisole converted selectively to the related sulfone (>97%) in the presence of benzyl alcohol which was oxidized slightly (0, 5% benzaldehyde at 25 °C and 70 °C respectively).

The comparison of non-catalytic oxidation of thioanisole and methyl phenyl sulfoxide with aqueous solution of TBAO (Table 4, entries 1 and 3) suggests a more facile oxidation of sulfide to sulfoxide relative to the over oxidation of sulfoxide to sulfone. Moreover, our outcome on catalytic oxidation of thioanisole and methyl phenyl sulfoxide giving the corresponding sulfone as sole product, clearly shows the ability of catalyst to promote both steps in the oxidation of sulfide

Table 4
Oxidation of PhSMe and PhSOMe with aqueous solution of TBAOX.[a].

Entry	Substrate	Oxidation system	Conversion%	Sulfoxide%[b]	Sulfone%[b]
1	PhSMe	TBAOX[c]	70	43	27
2	PhSMe	TBAOX/CuPc[d]	100	0	100
3	PhSOMe	TBAOX[c]	10	0	10
4	PhSOMe	TBAOX/CuPc[d]	100	0	100

[a] The reactions were run under air at room temperature for 1 h.
[b] GC yields.
[c] The molar ratio of substrate/TBAOX was 1/3.
[d] The molar ratio of substrate/TBAOX/catalyst was 200:600:1.

to the sulfone. The attachment of TBAO to the metal centre giving a six coordinate adduct [PcCu–O–OHSO$_3$] enhances the electrophilicity of Cu-coordinated oxygen atom of the oxidant. Despite the easy oxidation of sulfides and sulfoxides to sulfones using this species, oxidation of alcohols to aldehydes and ketones required higher temperature. Moreover, this less active oxidant does not have ability to oxidize aldehydes and ketones produced in the oxidation of alcohols. Presumably a high valent $[Cu{=}O]^+$ species should be provided for this over oxidation reaction [27] as well as oxidation of hydrocarbons [28]. However, the possible involvement of a high valent $[Cu{=}O]^+$ species as an intermediate cannot be excluded, due to its much higher activity towards oxidation of organosulfur compounds than the alcohols and hydrocarbons [26].

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 total turnover numbers obtained for CuPc in the oxidation of cyclohexanol (6500, with molar ratio of 10,000:20,000:1 for cyclohexanol/TBAOX/CuPc) and thioanisole (9100, with molar ratio of 10,000:60,000:1 for thioanisole/TBAOX/CuPc) indicating well the high efficiency and stability of the present catalytic system. These results encouraged us to evaluate the reusability of the catalyst. After easy isolation of hydrophobic 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 GC yields of cyclohexanone and methylphenyl sulfone for five runs were 94%, and 100% respectively, demonstrating well the high reusability of the catalyst in this oxidation system (Fig. 3). 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 cyclohexanol with aqueous solution of TBAOX does not change noticeably the electronic absorption spectra of catalyst after five run (Fig. 4). By comparing the absorbance ($\lambda_{max} = 792$ nm) at the end of the fifth run ($A = 1.1$) with that observed for fresh catalyst ($A = 1.3$) we found that 85% of the catalyst remained intact. In addition, it was established that the IR spectra were identical for the fresh and reused catalysts demonstrating the stability of the Pc structure under the real catalytic conditions (Fig. S1 in supporting information). Moreover, oxidant's by-product (TBAHSO$_4$) was separated by lyophilizing of aqueous phase and reused in the preparation of TBAOX [31]. Therefore, from the stand point of greener chemical processes, the use of CuPc as catalyst in combination with aqueous solution of TBAOX doesn't 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 the preparation of CuPc offered ready scalability. For example the use of a semi scale-up procedure (20 mmol) for the oxidation of thioanisole in the presence of CuPc led to the isolation of the related products in 93% yield.

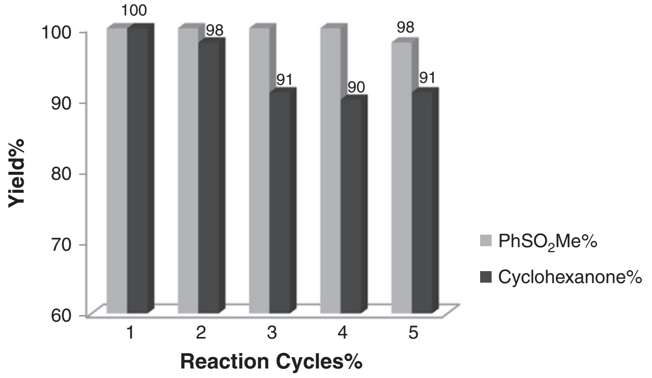

Fig. 3. Recycling of the catalytic system for the oxidation of cyclohexanol and thioanisole with aqueous solution of TBAOX catalyzed by CuPc according to GC analysis.

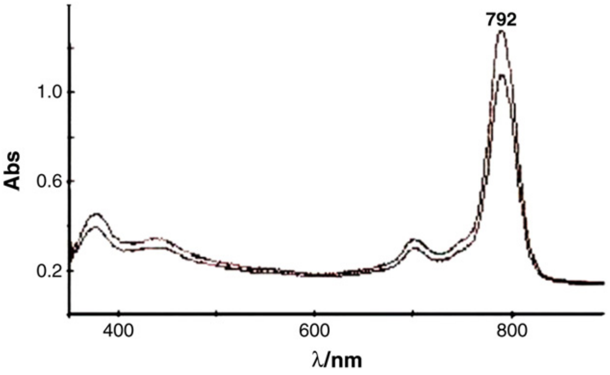

Fig. 4. UV–Vis spectral changes of CuPc complex in H$_2$SO$_4$ during the aqueous oxidation of cyclohexanol using TBAOX.

Conclusion

In conclusion, the catalytic performance of water-insoluble copper (II) Phthalocyanine in the oxidation of alcohols and sulfides using aqueous solution of TBAOX was established. The good/high yields and excellent selectivity were achieved for carbonyl and sulfone products in the absence of organic co-solvents, surfactants and nitrogenous bases. The employment of neat water as a standard ‘green’ solvent in this high yielding oxidation method as well as easy and safe work-up procedure and reusability of catalyst and by-product providing ready scalability, are strong points of this novel methodology making it more attractive for practical goal.

Supplementary materials related to this article can be found online at doi: 10.1016/j.inoche.2011.10.033.

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[31] General oxidation Procedure and recycling To a mixture of substrate (alcohol and sulfide) (1 mmol) and CuPc complex (0.005 mmol) in distilled water (10 ml) was added freshly prepared TBAOX (0.7 g for alcohol and 1 g for sulfide). The reaction mixture was stirred under reaction conditions mentioned in Tables 2 and 3. After completion of the reaction which was monitored by TLC and GC, the mixture was washed with ethylacetate (3 × 10 ml), and the organic phase was separated and evaporated. Then, the reaction mixture was centrifuged and the solid catalyst was separated, washed with ethylacetate, dried and reused for the subsequent reaction under the similar reaction conditions. The aqueous phase was lyophilized to obtain TBAHSO4 which can be reused in the preparation of TBAOX [17].