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ORIGINAL PAPER

Immobilized metalloporphyrins on 3-aminopropyl-functionalized silica support as heterogeneous catalysts for selective oxidation of primary and secondary alcohols

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Abstract Iron(III), manganese(III), and cobalt(II) complexes of *meso*-tetrakis(*p*-chlorophenyl)porphyrin (Fe(TClPP)X, Mn(TClPP)X, and Co(TClPP)X, X = Cl or OAc) were immobilized onto 3-aminopropyl-functionalized silica (SF-3-APTS). SF-3-APTS acts as both axial base and support for immobilization of these metalloporphyrins. The obtained heterogeneous catalysts were characterized by Fourier transform infrared (FT-IR), UV–Vis, and inductively coupled plasma (ICP) spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), and thermogravimetric analysis (TGA) techniques. Their catalytic activity as biomimetic catalysts was investigated for the selective oxidation of primary and secondary benzylic alcohols to the corresponding carbonyl compounds with *t*-butylhydroperoxide as oxidant. SF-3-APTS–Fe(TClPP)Cl demonstrated higher catalytic activity than SF-3-APTS–Mn(TClPP)Cl and SF-3-APTS–Co(TClPP)OAc. The presence of electron-withdrawing substituents on benzylic alcohols enhances the rate of catalytic oxidation. SF-3-APTS–Fe(TClPP)Cl could be reused at least four times without significant loss of its catalytic activity.

Keywords Metalloporphyrins · Biomimetic alcohol oxidation · 3-Aminopropyl-functionalized silica · Heterogeneous catalysis · *t*-Butylhydroproxide

Introduction

Oxidation of alcohols to the corresponding carbonyl compounds is a key reaction on both laboratory and industrial scales because of the importance of carbonyl compounds as chemical intermediates for the synthesis of various perfumes, drugs, and pharmaceuticals [1, 2]. Recent attempts have been directed to develop more efficient and inexpensive, cleaner, and reusable catalytic systems for the oxidation reactions [3–5]. Along this line, metalloporphyrins have been used as biomimetic models for the cytochrome P450 enzyme under homogeneous conditions [6]. These compounds play an important role in the oxidation of alcohols [7–9], sulfides [10, 11], epoxidation of alkenes [12, 13], and hydroxylation of alkanes [14–16]. Indeed, the synthesis of metalloporphyrins is challenging, often with low yield and tedious workup procedures. Furthermore, molecule aggregation caused by π–π stacking interactions or biomolecular self-oxidation reaction pathways lead to deactivation of metalloporphyrin species. However, immobilization of metalloporphyrins on solid supports not only enables the reusability of these catalysts but also reduces undesirable effects of the homogeneous conditions. Therefore, the supported metalloporphyrins will be more cost-effective [17]. In the past few decades, different kinds of supports such as silica [18–20], clay [21], zeolites [22, 23], MCM-41 [24, 25], and organic polymers [26] have been used for immobilization of metalloporphyrins. Amongst these different supports, silica gel is believed to be one of the most attractive inorganic supports due to its nontoxicity, high stability, good accessibility, low cost, and good surface attraction toward functional groups of organic compounds. In this work, we have studied the biomimetic enzymatic activity of the iron(III), manganese(III), and cobalt(II) complexes of *meso*-tetrakis-

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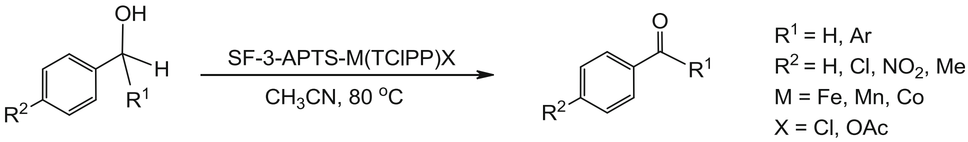
Scheme 1



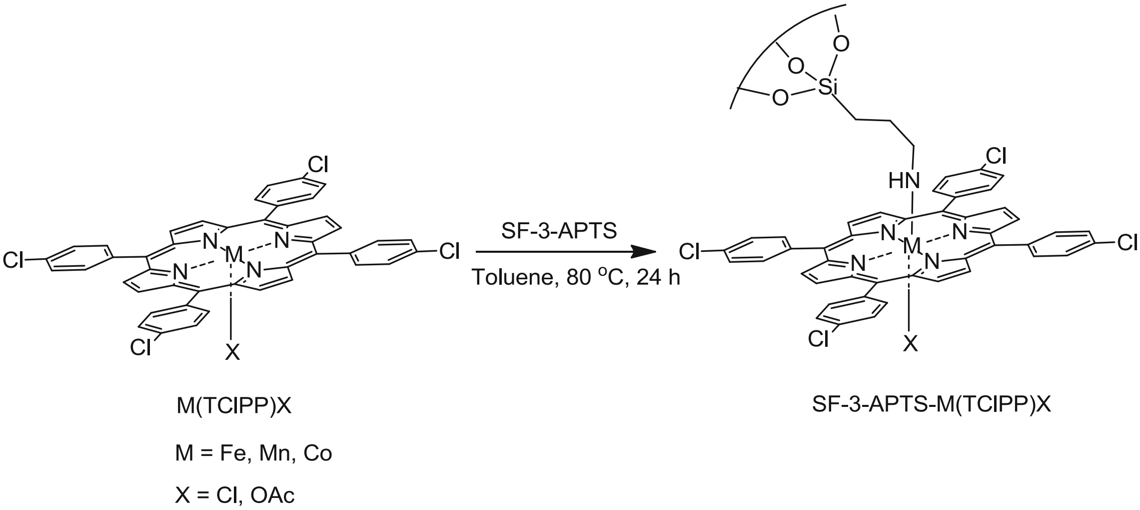
(*p*-chlorophenyl)porphyrin (Fe(TClPP)X, Mn(TClPP)X, and Co(TClPP)X, X = Cl or OAc) immobilized on silica gel modified with 3-aminopropyltriethoxysilane (3-APTS) groups for oxidation of alcohols. Herein, we report these hybrid materials, SF-3-APTS–Fe(TClPP)Cl (**1b**), SF-3-APTS–Mn(TClPP)Cl (**1c**), and SF-3-APTS–Co(TClPP)OAc (**1d**), as suitable catalysts for the selective oxidation of primary and secondary benzylic alcohols with *t*-butylhydroperoxide (TBHP) as oxidant (Scheme 1).

Results and discussion

The preparation of silica metalloporphyrin heterogeneous catalysts is shown in Scheme 2. In the first stage, the silica gel surface was modified with 3-APTS groups. Functionalization of silica gel with amine groups was confirmed by Fourier transform infrared (FT-IR) spectra (Fig. 1a). The amount of 3-APTS groups on the silica gel support was estimated by CHN elemental analysis (C: 5.75%, H: 1.47%, N: 1.58%). The results indicated that there is approximately 1 mmol of 3-APTS groups per gram of silica.

In the next stage, metalloporphyrins and modified silica gel (SF-3-APTS) (**1a**) were mixed in toluene at 80 °C for 48 h. Finally, after filtration and washing the hybrid materials, the heterogeneous catalysts were obtained and characterized by FT-IR and solid-state UV–Vis spectroscopy along with thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) techniques.

FT-IR spectra of silica gel and **1a–1d** are presented in Fig. 1. In the case of silica gel (Fig. 1a), a very broad band is observed at 3,700–3,200 cm^{-1} due to the O–H stretching vibration of the hydroxyl groups. Another band at 1,649 cm^{-1} is attributed to the H–O–H bending vibration of the adsorbed water. Furthermore, a strong band between 1,200 and 1,000 cm^{-1} and a band at 804 cm^{-1} are assigned to the Si–O–Si stretching vibrations [27]. After functionalization of the silica gel with 3-APTS groups, the intensity of the broad band of silica gel at 3,450 cm^{-1} decreased



Scheme 2

which confirmed the modification of silica gel with 3-aminopropyl groups. Additionally, new bands appear at 2,925 and 2,854 cm^{-1} due to CH_2 stretching vibrations of propyl groups. The NH_2 stretching vibrations are also overlapped with the O–H vibration band at 3,450 cm^{-1} (Fig. 1b). On the other hand, immobilization of metalloporphyrins on the silica support was confirmed by the appearance of new bands at 1,603 cm^{-1} (Fig. 1c–e). These bands are associated with the stretching vibrations of C=N and C=C in the pyridyl and phenyl rings in porphyrins [28].

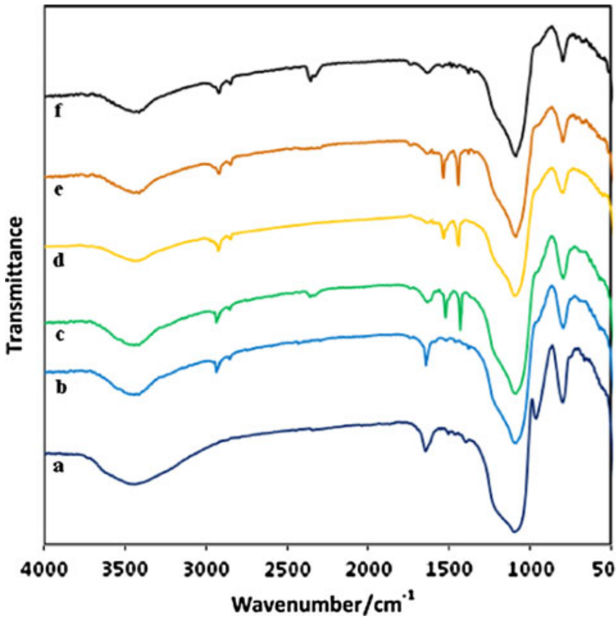


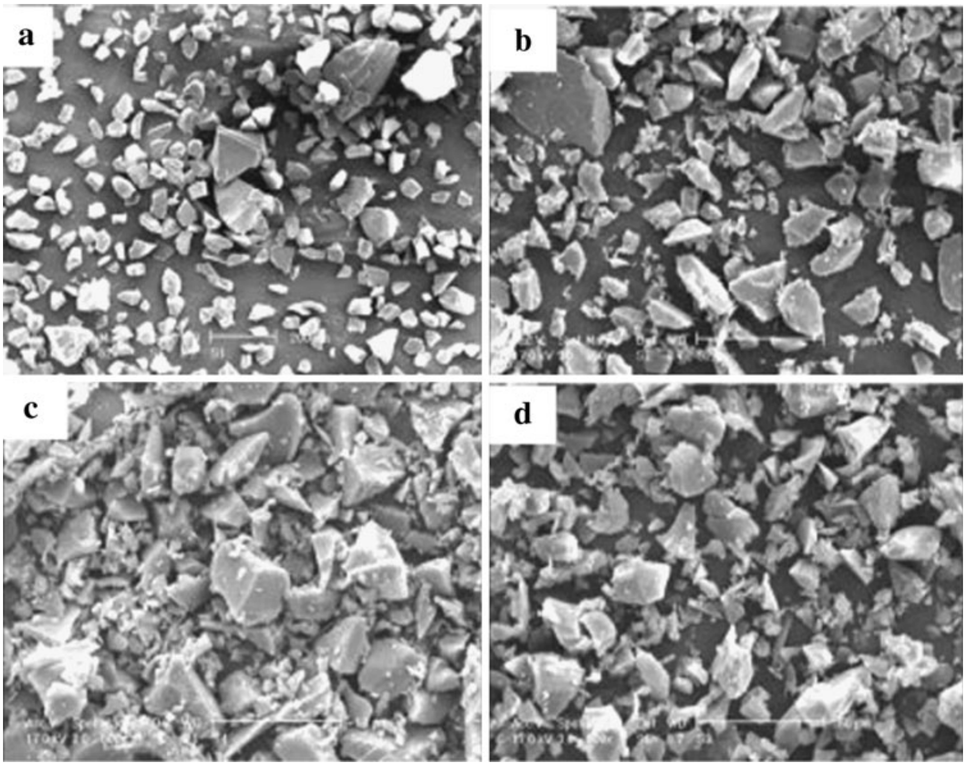
Fig. 1 FT-IR spectra of silica (*a*), **1a** (*b*), **1b** (*c*), **1c** (*d*), **1d** (*e*), and recovered catalyst **1b** (*f*)

The morphology of **1a**–**1d** determined by SEM is shown in Fig. 2. Immobilization of metalloporphyrins on the silica support was confirmed by these images. Furthermore, no considerable changes in the shape of the silica particles were observed after immobilization of the metalloporphyrins.

The presence of metalloporphyrins on the silica support was also confirmed by means of solid-state UV–Vis spectroscopy (Fig. 3). No absorption band is observed in the UV–Vis spectrum of silica gel (Fig. 3a). However, the Q and Soret bands appear after immobilization of metalloporphyrins on the silica support. Furthermore, a red shift in Q and Soret bands is observed after immobilization of the metalloporphyrins comparing with the pure metalloporphyrins. This shift is assigned to the symmetry changes of the metalloporphyrin after its metal ion coordinates to the NH_2 group of **1a**.

The quantitative analysis of metalloporphyrin loading in the heterogeneous catalysts **1b**–**1d** was estimated using inductively coupled plasma (ICP) spectroscopy. The obtained amounts were as follows: 4.9% Fe(TClPP)Cl in **1b**, 4.1% Mn(TClPP)Cl in **1c**, and 5.2% Co(TClPP)OAc in **1d**. Furthermore, the results of EDX analysis were consistent with the aforementioned loadings.

Fig. 2 Scanning electron micrographs of **1a** (**a**), **1b** (**b**), **1c** (**c**), and **1d** (**d**)



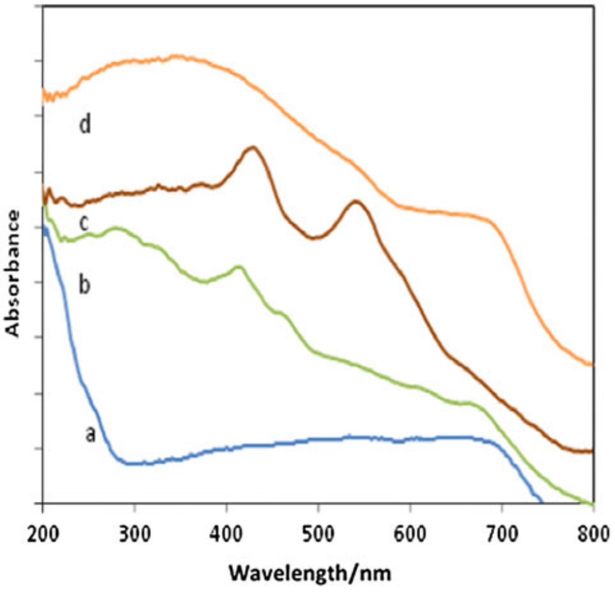


Fig. 3 UV–Vis spectra of **1a** (*a*), **1c** (*b*), **1d** (*c*), and **1b** (*d*)

The results of TGA of the heterogeneous catalysts **1b**–**1d** are shown in Fig. 4. The weight loss in samples of **1b**–**1d** occurs in three steps: below 100 °C, 200–420 °C, and above 420 °C. The first step ($T < 100$ °C) can be assigned to the evaporation of volatile solvents and water molecules which are physically adsorbed in the samples. The second step can be related to decomposition of metalloporphyrins and organic groups. The weight loss above 420 °C can be attributed to the further oxidation of the remaining organic compounds and the loss of silanol groups. These results indicate that the hybrids of silica metalloporphyrins **1b**–**1d** show relatively high thermal stability.

*Oxidation of benzhydrol by TBHP in the presence of heterogeneous catalysts **1b–1d***

Benzhydrol (**2a**) was used as the model substrate for oxidation by TBHP in the presence of heterogeneous catalysts **1b**–**1d**. In a systematic study, the effect of different factors such as catalyst loading, temperature, kind of active metal ion in the catalysts, and reaction time were investigated.

*Effect of catalyst loading of **1b**, reaction temperature, and oxidant*

Table 1 shows the influence of catalyst loading of **1b** on the yield of the model reaction. As the data in Table 1 show, only a trace amount (about 7%) of the oxidation product of benzophenone (**3a**) was detected at 60 °C after 10 h in the absence of catalyst **1b** (entry 1). However, the yield of reaction was improved with 4.4 mol% catalyst loading of **1b** (50 mg per 1 mmol of the substrate) to the reaction mixture under similar conditions. By decreasing the catalyst loading to 2.2 mol%, only 35% of the desired product was obtained. On the other hand, higher yields of 82 and 84% were obtained by the use of 8.8 and 17.6 mol% catalyst loadings, respectively (entries 4, 5). The best result in terms of calculated turnover number (TON) and yield was obtained with a catalyst loading of 8.8 mol% (entry 4). Furthermore, the progress of oxidation of **2a** was very slow at room temperature (entry 6). Therefore, the temperature is an important factor for this catalytic system. On the other hand, H_2O_2 afforded lower yields in the oxidation of benzhydrol under similar reaction conditions (cf. entries 4, 7). It is well known that H_2O_2 can produce hydroxyl radicals (OH·) which are more reactive than *t*-butoxyl (*t*-BuO·) radicals and may destroy the porphyrin moiety in the catalyst structure [29].

Fig. 4 TGA curves of **1c** (*a*), **1b** (*b*), and **1d** (*c*)

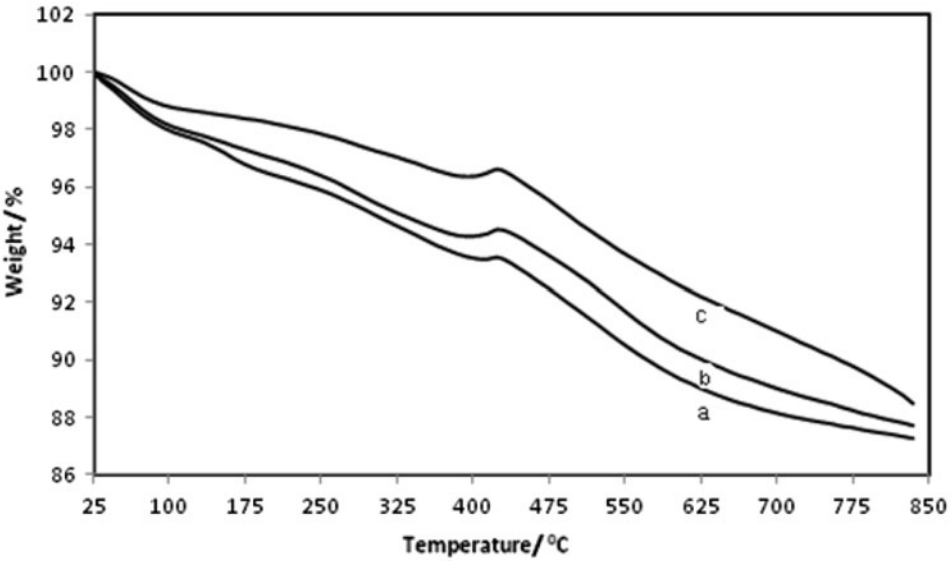
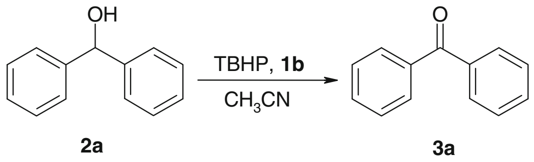


Table 1 Effect of catalyst loading on oxidation of benzhydrol (**2a**) in the presence of catalyst **1b**



Entry	Catalyst loading/mol%	*T*/°C	Yield[a]/%	TON[b]
1	No catalyst	60	7	–
2	2.2	60	35	15.9
3	4.4	60	66	15
4	8.8	60	82	9.3
5	17.6	60	84	4.8
6	8.8	25	32	3.6
7[c]	8.8	60	49	5.7

Conditions: benzhydrol (1 mmol), TBHP (1 mmol), 10 cm^3 CH_3CN, 10 h

[a] Yields obtained by GC

[b] Turnover number: mol of product per mol of catalyst

[c] H_2O_2 was used as oxidant

Effect of metal ion

Catalytic oxidation of benzhydrol by TBHP in the presence of silica supported metalloporphyrins **1b–1d** was also studied. Comparison of the catalytic activity of these heterogeneous catalysts shows that iron porphyrin **1b** demonstrates higher catalytic activity than manganese and cobalt porphyrins (**1c** and **1d**, respectively) in the oxidation of **2a** under similar conditions (Table 2). Therefore, **1b** was selected as the catalyst of choice for further catalytic studies in the benzhydrol oxidation by TBHP.

Effect of reaction time

The influence of reaction time on the yield of product **3a** was also investigated in the oxidation of benzhydrol by TBHP. As the results show in Table 3 and Fig. 5, the best yield was obtained after 10 h (82%) in terms of both calculated turnover frequency (TOF) and TON values. Only slight improvements in conversion of **2a** were experienced after 14 h (84%) or even 24 h (86%). On the other hand, lower yields were observed after reaction times less than 10 h.

Table 2 Oxidation of benzhydrol (**2a**) by TBHP in the presence of silica-supported metalloporphyrin catalysts **1b**–**1d**

Entry	Catalyst	Yield[a]/%	TON
1	SF-3-APTS–Fe(TClPP) (**1b**)	82	9.3
2	SF-3-APTS–Mn(TClPP) (**1c**)	78	8.9
3	SF-3-APTS–Co(TClPP) (**1d**)	51	5.8

Conditions: benzhydrol (1 mmol), TBHP (1 mmol), 8.8 mol% catalyst **1b**–**1d**, 10 cm^3 CH_3CN, 10 h, 60 °C

[a] Yields obtained by GC

Table 3 Effect of reaction time on oxidation of benzhydrol (**2a**) by TBHP in the presence of catalyst **1b**

Entry	Reaction time/h	Yield[a]/%	TON	TOF[b]/h^{-1}
1	1	22	2.5	2.50
2	4	45	5.1	1.28
3	8	62	7.1	0.88
4	10	82	9.3	0.93
5	14	85	9.7	0.69
6	24	87	9.9	0.41

Conditions: benzhydrol (1 mmol), TBHP (1 mmol), 8.8 mol% catalyst **1a**, 10 cm^3 CH_3CN, 60 °C

[a] Yields obtained by GC

[b] Turnover frequency: mol of product per mol of catalyst per hour

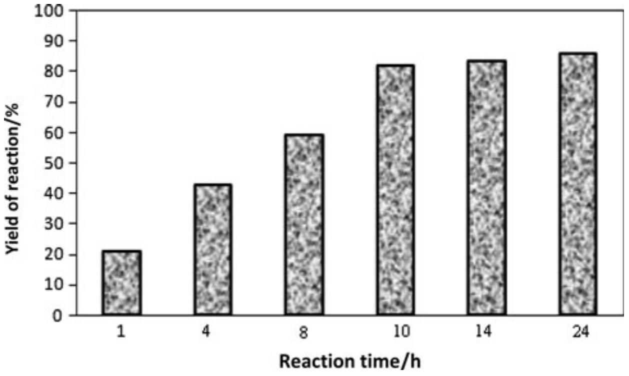


Fig. 5 Changes of product yield with reaction time. Reaction conditions: benzhydrol (1 mmol), TBHP (1 mmol), and 8.8%mol **1b**, 10 cm^3 CH_3CN, 60 °C

Oxidation of different benzylic alcohols by 1b

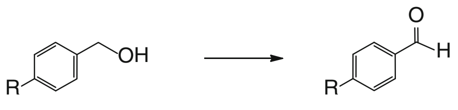
Primary benzylic alcohols were also subjected to oxidation under the optimized reaction conditions (8.8 mol% **1b**, CH_3CN). In general, primary alcohols are more reactive toward oxidation than secondary alcohols. Therefore, they require milder reaction conditions including lower temperature and shorter reaction time. Furthermore, the corresponding aldehydes or carboxylic acids can also be obtained. Therefore, controlled oxidation from an alcohol to an aldehyde, avoiding overoxidation to the carboxylic acid, is very important [30]. In our hands, primary benzylic alcohols **2b–2e** were selectively oxidized at room temperature and in shorter reaction time than with secondary benzhydrol (Table 3, entries 1–4) to afford high to quantitative yields of the corresponding aldehydes **3b–3e**.

Benzyl alcohol (**2b**) and 4-nitrobenzyl alcohol (**2c**) afforded quantitative yields of the corresponding aldehydes **3b** and **3c**, respectively. On the other hand, 4-chlorobenzyl alcohol (**2d**) and 4-methylbenzyl alcohol (**2e**) produced 88 and 82% of the desired products **3d** and **3e**, respectively. In the case of 4-methylbenzyl alcohol, complete conversion of the alcohol was observed. However, about 18% of 4-carboxybenzyl alcohol was detected as a by-product of the reaction. This observation can be attributed to the competitive oxidation of both benzylic positions in this substrate (Table 4).

*Proposed mechanism for oxidation of benzylic alcohols by TBHP in the presence of **1b***

The following mechanism for oxidation of benzylic alcohols **2a**–**2e** by TBHP in the presence of **1b** could be proposed according to literature and substituent effects (Scheme 3). When the "singlet oxygen donor" oxidants such as hydrogen peroxide and organic peroxides are used in oxidation catalyzed by metalloporphyrins, two general routes can be expected [31]: (i) the homolytic cleavage of the peroxidic O–O bond in the intermediate **I** which produces *t*-BuO· as active species (pathway A); (ii) the heterolytic cleavage of O–O bond in the intermediate **I** which produces high valent oxoiron(IV) species (intermediate **III**, pathway B). Subsequent hydrogen abstraction from the benzylic carbon of alcohol **2**, probably in a rate-determining step, gives the corresponding radical **IV** in both pathways. Hence, the difference in the reactivity of primary benzylic alcohols and benzhydrol can be interpreted by considering more steric effects in benzhydrol. Finally, hydride transfer from the intermediate **IV** to intermediate **II** affords product **3** and water as a by-product [32]. An alternative route for the last step may be considered by interaction of two intermediates **IV** to give rise to the product **3** and alcohol **2** (Scheme 3, bottom). Furthermore, the corresponding hydroperoxide of the used alcohols was not detected in the reaction product, most probably due to fast decomposition of any peroxide by the catalyst **1b**.

Table 4 Oxidation of benzylic alcohols with TBHP catalyzed by **1b** (Conditions: substrate (1 mmol), TBHP (1 mmol), 8.8 mol% catalyst **1a**, 10 cm^3 CH_3CN, 3 h, 25 °C)



2b-2e **3b-3e**

2, 3	R
b	H
c	NO_2
d	Cl
e	CH_3

Entry	Product	Time/h	Yield[a]/%	TON
1	**3b**	3	>99	11.4
2	**3c**	3	>99	11.4
3	**3d**	3	88	10
4	**3e**	3	82 (18[b])	9.3

[a] Yields obtained by GC

[b] 4-Carboxybenzyl alcohol was detected as by-product of the reaction

*Recyclability of the catalyst **1b***

The stability of the heterogeneous catalyst **1b** was determined by examining its reuse in consecutive oxidation reactions. After each reaction, the catalyst was completely washed in a Soxhlet extractor with the organic solvents acetonitrile, acetone, and methanol and then dried before using in subsequent runs. As the results in Table 5 show, the catalyst could be reused for four consecutive runs without significant loss of its catalytic activity. Furthermore, comparison of the FT-IR spectra before and after the reaction confirmed that no structure change of the catalyst occurred during the reaction (Fig. 1f).

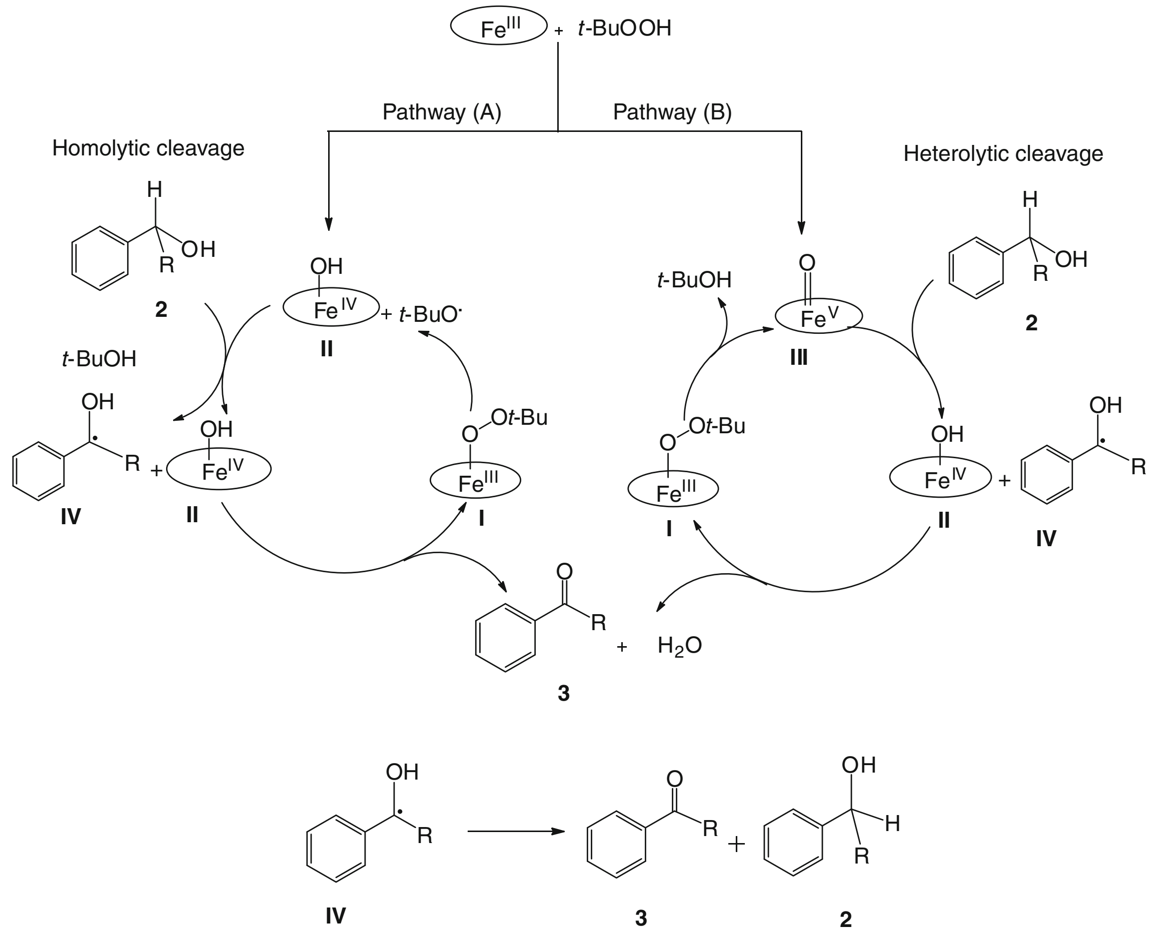
Experimental

Materials

All chemicals and solvents were purchased from Aldrich and Merck with maximum purity degree and used as received. *t*-Butylhydroperoxide (TBHP, 70% aqueous solution) was also obtained from Merck and used without further purification. Toluene and acetonitrile were dried with calcium hydride before using in reactions. Silica gel (Merck, 60/70–230) was activated at 250 °C under vacuum for 2 h. *meso*-Tetrakis(*p*-chlorophenyl)porphyrin was synthesized in our laboratory according to Adler's method [33]. Metallation of this complex of porphyrin was performed according to the literature [34].

Instrumentation

FT-IR spectra were obtained using KBr pellets on a Shimadzu 8400S spectrophotometer in the 4,000–500 cm^{-1} range. Electronic spectra (UV–Vis) were recorded on a double beam UV–Vis Shimadzu 2550 spectrophotometer. TGA was performed by using a Netzsch TG-209 F1 thermogravimetric analyzer in the 25–850 °C temperature range with a heating rate of 10 °C min^{-1} under N_2 atmosphere. Scanning electron micrographs of samples were imaged by a Philips XL30 SEM system. A Philips XL30 EDX system was used for determination of metalloporphyrin contents on the silica support. Elemental analysis (CHN) measurements were carried out in a Perkin–Elmer 2400 instrument. The yield of oxidation



Scheme 3

Table 5 Results of recovery of catalyst **1b** in oxidation of benzhydrol

Run	Yield[a]/%	TON
1	82	9.3
2	80	9.0
3	75	8.5
4	74	8.4

Conditions: benzhydrol (1 mmol), TBHP (1 mmol), 8.8 mol% catalyst **1a**, 10 cm^3 CH_3CN, 10 h, 60 °C

[a] Yields obtained by GC

reactions was calculated using a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector (FID) detector and capillary column (30 m).

Modification of silica gel surface with 3-APTS groups

The following procedure was used for preparing of 3-aminopropyl-functionalized silica **1a**: A mixture of 5 g silica gel, 5 cm^3 3-APTS, and 75 cm^3 toluene was degassed and sealed under nitrogen. The suspension was refluxed at 80 °C for 24 h. The product was filtered and exhaustively washed in a Soxhlet extractor with absolute ethanol for 24 h, then dried at 80 °C under vaccum for 24 h. The obtained solid **1a** was characterized by FT-IR and CHN elemental analysis [20].

*Immobilization of metalloporphyrins on modified silica **1a***

In a 250-cm^3 flask, a mixture of 0.3 g metalloporphyrin and 3 g SF-3-APTS was suspended in 80 cm^3 toluene. Then, the mixture was vigorously stirred by magnetic stirring at 80 °C for 48 h. After cooling to room temperature, the solid was filtered and exhaustively washed in a Soxhlet extractor with dichloromethane (14 h), methanol (12 h), and ether (10 h) to remove any non-supported metalloporphyrin. The obtained solid was dried in vaccum at 25 °C for 12 h. The presence of metalloporphyrin on the silica support was confirmed by solid state UV–Vis and FT-IR spectroscopy and SEM [35]. Furthermore, the amount of immobilized metalloporphyrins on silica was determined by ICP and EDX analysis.

*General procedure for oxidation of benzhydrol catalyzed by silica-supported metalloporphyrins **1b–1d***

A mixture of benzhydrol (**2a**, 1 mmol), TBHP (1 mmol), and 100 mg heterogeneous catalyst **1b–1d** in 10 cm^3 CH_3CN was stirred in a 50-cm^3 two-necked flask equipped with a septum at 60 °C. The progress of the reaction was monitored by TLC. The heterogeneous catalysts were separated from the reaction mixture by filtration. The filtrate was analyzed by GC after 10 h. The yield of the reaction was calculated from the calibration curves using benzophenone (**3a**) and *n*-octane as authentic sample and external standard, respectively.

Catalyst reusability

The reusability of the heterogeneous catalysts **1b–1d** was investigated by using them in sequential oxidation reactions of benzhydrol as model substrate. The used catalyst was completely washed in a Soxhlet extractor with acetone, methanol, and acetonitrile and dried before reusing in another oxidation reaction.

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