

Oxidation of alcohols with hydrogen peroxide catalyzed by supported Fe(III) porphyrins

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Mild and efficient oxidation of alcohols with hydrogen peroxide catalyzed by iron(III) tetrakis(*p*-sulfonatophenylporphyrinato)acetate, supported on polyvinylpyridine and Amberlite IRA-400 at room temperature is reported. The catalysts used in this study show high activity, not only in the oxidation of benzyl and linear alcohols but also in the oxidation of secondary alcohols at room temperature. The catalysts can be reused several times without significant loss of their activity.

Keywords: Catalysts, Supported catalysts, Oxidation, Alcohols, Metalloporphyrins, Hydrogen Peroxide, Iron

Metalloporphyrins have been successfully used as models for the cytochrome P-450 enzyme with respect to the oxidation of organic compounds such as hydrocarbons¹⁻³. Development in this area is based on different strategies with the aim of designing selective and stable catalytic systems with high turnover⁴. It was found that when metalloporphyrins were used as catalysts, organic compounds could be oxidized by oxygen donors⁵⁻¹¹ such as PhIO, ClO⁻, H₂O₂, ROOH or IO₄⁻. Oxidation over metal catalysts using eco-friendly oxidants such as hydrogen peroxide and molecular oxygen are preferred now for environmental and economical benefits. Development in this area is based on different strategies with the aim of designing selective, stable, and high turnover catalytic systems.

However, these expensive catalysts are difficult to recover and unstable, which limited their application in synthetic chemistry. Heterogenization of these homogeneous catalysts stabilizes the metalloporphyrin or enhances the catalytic performance by preventing the formation of inactive dimers. On the other hand, such immobilization can influence the chemoselectivity, regioselectivity and stereoselectivity of the catalyzed reaction¹²⁻¹⁶.

Immobilized oxidation catalysts have been developed that are supported on organic and inorganic polymers, silica gel and metal oxides. These heterogeneous catalysts can be recovered from the reaction media by simple filtration and reused. They also increase the selectivity without contaminating the product solution. As the transition metal complexes are expensive or difficult to purchase, immobilizing them on a support allows them to be simply extracted and recycled, which makes for commercial advantage as well as ease of manipulation.

The present study aims to investigate the catalytic reactivity of copper porphyrin as a heterogeneous catalyst. We wish to report an efficient protocol in which H₂O₂ has been used as the oxidizing agent in the presence of iron porphyrins for the chemoselective oxidation of alcohols to their carbonyl compounds in high chemical yield and short reaction times.

Experimental

All materials were of commercial reagent grade. Alcohols were obtained from Merck or Fluka. Fe(TPPS) was prepared, metalated, and supported according to the literature procedure^{17,18}, only instead of manganese salt, Fe₂(NO₃)₃·3H₂O was used. IR spectra were recorded in KBr disks with a Matson 1000 FT-IR spectrophotometer. ¹H NMR spectra of oxidation products in DMSO-*d*₆ solution were recorded on a Bruker 250 MHz spectrometer. The reaction products of oxidation were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μm × 0.25 μm).

In a typical procedure for the oxidation of alcohols with H₂O₂, catalyzed by supported Fe(III) porphyrins, a solution of H₂O₂ (6 mmol) was added to a mixture of alcohol (1 mmol), supported Fe(III) porphyrins (20 μmol) and imidazole (0.4 mmol) in CH₃CN (10 mL). The progress of the reaction was monitored by GC. The reaction mixture was filtered and diluted with water (20 mL). The products were extracted with CH₂Cl₂ (2 × 10 mL) and were purified on silica-gel plates or a silica-gel column (CCl₄-Et₂O, 4:1). ¹H NMR spectral data was used to confirm the identities of the products.

All the reactions were carried out at room temperature in a 25 mL flask equipped with a magnetic stirrer bar.

Stability of the supported Fe(III) porphyrins was studied in four consecutively repeated oxidation reactions. Oxidation of benzyl alcohol was chosen as a model substrate for studying the reuse and stability of the catalysts. The reactions were carried out as described above. On completion of each reaction, the catalysts were recovered by filtration, washed exhaustively with water, methanol, acetonitrile and diethyl ether, successively, and dried before being reused with fresh benzyl alcohol and hydrogen peroxide. The amount of iron that leached into the filtrates was determined by atomic absorption spectrometry.

Results and discussion

We first investigated the ability of these supported iron(III) porphyrins as catalysts in the oxidation of benzyl alcohol in the presence of hydrogen peroxide. Of the four solvents tested, including 1:1 mixtures of methanol, ethanol, acetone, and acetonitrile with water, the 1:1 acetonitrile/water mixture was chosen as the solvent because it gave a higher carbonyl yield. The iron porphyrin is not an efficient catalyst for oxidation of alcohols in the absence imidazole as axial ligand because imidazole coordinates to Fe and activates the catalyst. The effect of different axial

ligands on the oxidation rate of benzyl alcohol was also investigated. The results show that imidazole is most suitable for this reaction (Table 1). The optimum condition for the oxidation of benzyl alcohol with this heterogenized system is catalyst, oxidant, imidazole and substrate in a molar ratio of 1:100:10:50. During the course of oxidation, the reaction solution remained colourless and there was no evidence for leaching of the catalyst from the polymeric support into the solution. This was also investigated by examining the UV-vis spectrum of the filtered reaction mixture (Table 2). This heterogeneous catalyst can be applied to reactions using a wide variety of primary and secondary alcohols. As shown in Table 3, benzyl alcohol and substituted benzyl alcohols are converted to their corresponding aldehydes efficiently. The results show that the substituents have no significant effect on the oxidation of benzyl alcohols. Linear alcohols were oxidized efficiently with H_2O_2 by these supported catalysts. These heterogenized catalysts were also used for the oxidation of secondary alcohols; their corresponding ketones were obtained in good yields.

Table 1—Effect of different axial ligands on the oxidation of benzyl alcohol with Fe(III)porphyrin/ H_2O_2 system. [Time: 4 h]

Ligand	Yield ^a (%)
Imidazol	93
1-Methylimidazole	84
4- <i>t</i> -Butyl pyridine	32
Pyridine	12
No ligand	6

^a GC yields

Table 2—Catalyst reuse and stability after consecutive runs of oxidation of benzyl alcohol

Run	Fe(TPPS)-Ad IRA-400		Fe(TPPS)-PVP	
	Yield (%) ^a	Fe leached (%) ^b	Yield (%) ^a	Fe leached (%) ^b
1	94	2.0	93	1.9
2	92	1.7	92	1.5
3	91	0	91	0
4	91	0	90	0

^aGC yield based on starting alcohol.

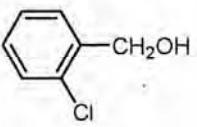
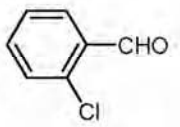
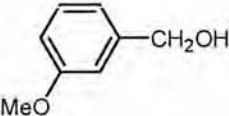
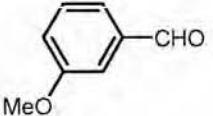
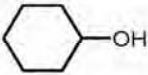
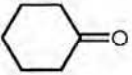
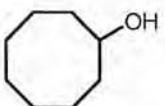
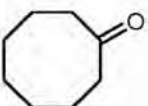
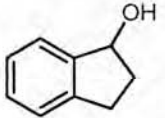
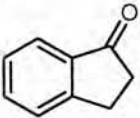
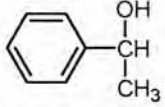
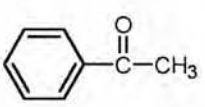
^bDetermined by atomic absorption spectroscopy.

Table 3—Performance of catalysts in the oxidation of alcohols with H_2O_2

Entry	Alcohol	Product	Fe(TPPS)-Ad IRA-400		Fe(TPPS)-PVP	
			Time (h)	Yield (%) ^a	Time (h)	Yield (%) ^a
1			4	91	4	90
2			4	90	3	90
3			3	89	3	90

(Contd.)

Table 3—Performance of catalysts in the oxidation of alcohols with H_2O_2 (Contd.)

Entry	Alcohol	Product	Fe(TPPS)-Ad IRA-400		Fe(TPPS)-PVP	
			Time (h)	Yield (%) ^a	Time (h)	Yield (%) ^a
4			4	92	4	92
5			4	90	4	93
6			5	91	5	90
7			5	45	5	48
8			5	44	5	48
9			5	81	5	82
10			5	87	5	86
11			8	76	7	74
12			5	90	4	86

^aGC yield based on starting alcohol.

The stability of the supported catalysts was monitored using multiple sequential oxidations of benzyl alcohol with hydrogen peroxide. After the catalysts were reused four consecutive times, the benzaldehyde yield was still 90 % (Table 2). These supported iron porphyrins can be used as robust,

reusable and active heterogeneous catalysts in the oxidation of primary and secondary alcohols with hydrogen peroxide. An efficient catalytic oxidation procedure that allows the transformation of simple alcohols into carbonyl compounds has been described in this study.

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