

Mild and Efficient Oxidation of Alcohols with NaIO_4 Catalyzed by a Manganese Porphyrin-polyoxometalate Hybrid Material

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Efficient and selective oxidation of alcohols with NaIO_4 catalyzed by an organic-inorganic hybrid material in which manganese(III)5,10,15,20-tetrakis(4-aminophenyl)porphyrin chloride, $\text{Mn}^{\text{III}}(\text{TAPP})\text{Cl}$, is covalently linked to a Lindqvist structure of polyoxometalate, $\text{Mo}_6\text{O}_{19}^{2-}$, at room temperature is reported. The effect of various parameters such as catalyst amount, solvent and oxidant were studied. The catalyst, MnP-POM, showed high activity not only in the oxidation of benzylic and linear alcohols but also in the oxidation of secondary alcohols and their corresponding ketones were obtained in good yields. A good selectivity observed in the case of cinnamyl alcohol and the only alcoholic group is oxidized and no epoxide was obtained. The MnP-POM catalyst is stable under the reaction conditions and While, the homogeneous $\text{Mn}^{\text{III}}(\text{TAPP})\text{Cl}$ cannot recover even one time, the hybrid catalyst can be filtered and reused several times without significant loss of its initial activity. Covalent linkage of the $\text{Mn}^{\text{III}}(\text{TAPP})\text{Cl}$ to the POM provide way of stabilizing the metalloporphyrin against deactivation during the catalytic cycles.

Keywords: Polyoxometalate, Porphyrin, Hybrid material, Oxidation, Heterogeneous catalyst, Alcohols

INTRODUCTION

The oxidation of alcohols to carbonyl compounds is an important reaction in both organic chemistry and industry [1,2]. Recently, more and more efforts have been paid in the highly efficient catalytic process for the oxidation of alcohols [3-9]. Although there are several methods to synthesize carbonyl compounds, the most common process of alcohols oxidation may use toxic, corrosive, expensive oxidants such as chromium(VI). These reagents are needed in stoichiometric amounts and hard to be separated from products, which are not environmentally friendly and economically.

Over the past decade, organic-inorganic hybrid materials have attracted significant research attention owing to their potential of combining the distinct properties of both organic and inorganic functional entities together [10].

Among the organic-inorganic hybrid materials, porphyrins, which are composed of four pyrrole units linked together through their α -positions by methine bridges, are promising candidates because of the large π -conjugated system, tunability by chemical derivatization, intense visible absorption bands, high stability and flexibility of excited state properties [11-13]. Thus, with appropriate metal ions, they are well suited as electron donors, and they are used for the construction of supramolecular complexes [14].

On the other hand, Polyoxometalates (POMs) are inorganic metal-oxygen clusters formed by the early transition metals with many applications in catalysis, biology, pharmacy and materials science [15-17]. In particular, POM anions are a kind of good electron acceptor and able to exchange many electrons without significant structural changes. This remarkable property makes them fascinating building blocks which can play an important role in supramolecular [18,19]. The stability of the Lindqvist anion, $\text{Mo}_6\text{O}_{19}^{2-}$ (Fig. 1), under strongly oxidizing

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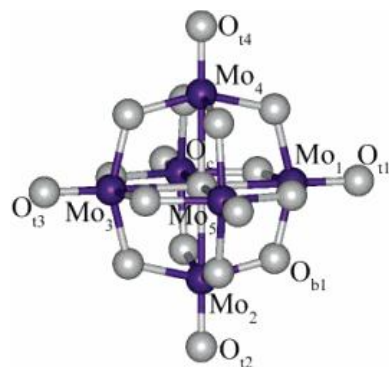
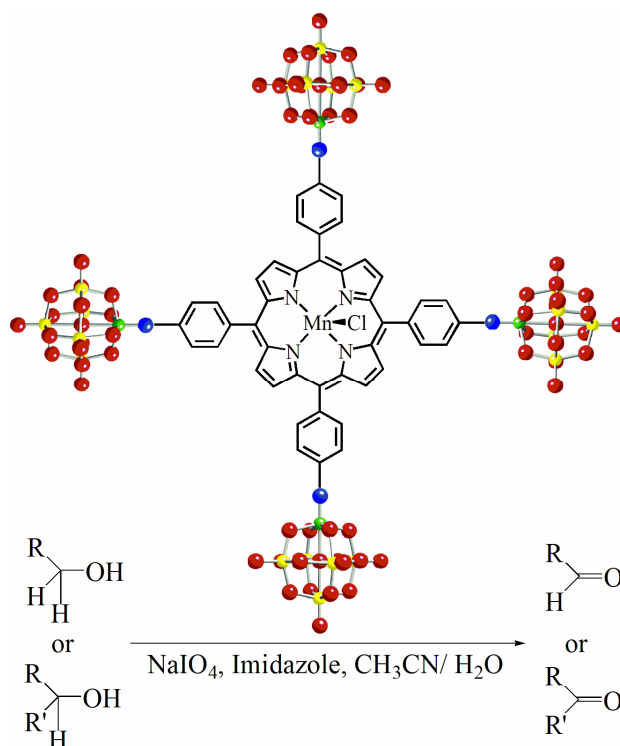


Fig. 1. The structure of the hexamolybdate ion $[\text{Mo}_6\text{O}_{19}]^{2-}$.



Scheme 1. Oxidation of primary and secondary alcohols with NaIO_4 in the presence of MnP-POM

conditions, has made POMs extremely attractive as oxidation catalysts [20,21].

Because the diverse photochemical, and coordination chemistry of porphyrins and POMs are in many ways complementary rather than overlapping, there are a few reports on the activity of materials containing both types of molecules which mainly focus on their catalytic properties

[22-38]. In catalytic applications, these associations may provide ways of stabilizing the metalloporphyrins against deactivation during the catalytic cycles [36].

Different types of interactions, *via* coordination, *via* electrostatic or *via* covalent attachment, have been used to form polyoxometalate-porphyrin hybrid complexes. However, systems with stronger links and better control of

the stoichiometry of the components would be of interest for some applications such as catalysis. Covalent linkage of porphyrin ligands to the POMs appears as the way of choice [37,38].

Previously, we reported the oxidation of alkenes catalyzed by a porphyrin-polyoxometalate hybrid compound in which manganese(III) tetrakis(*p*-aminophenylporphyrin) chloride is covalently linked to a Lindqvist structure of polyoxometalate [37]. Here, we report the use of this catalyst in the oxidation of alcohols with NaIO₄ at room temperature (Scheme 1).

EXPERIMENTAL

All materials were of commercial reagent grade. Alcohols were obtained from Merck or Fluka. Manganese (III)porphyrin-polyoxometalate hybrid compound, MnP-POM, was prepared according to our recently reported method [37]. Atomic absorption analysis was carried out on a Shimadzu 120 spectrophotometer. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 M and *n*-decane was used as internal standard. The ICP analyses were performed on an ICP-Spectrociros CCD instrument. Conversions and yields were obtained by GC experiments and the products were identified after isolation and purification.

General Procedure for Oxidation of Alcohols with NaIO₄ Catalyzed by MnP-POM

All of the reactions were carried out at room temperature under air in a 25 ml flask equipped with a magnetic stirrer bar. To a mixture of alcohols (1 mmol), imidazole (0.2 mmol), catalyst (110 mg, 0.018 mmol) and CH₃CN (10 ml), a solution of NaIO₄ (1 mmol) in H₂O (10 ml) was added. The progress of the reaction was monitored by GLC. The reaction mixture was diluted with Et₂O (20 ml) and filtered. 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). FT-IR and ¹H NMR spectral data were used to confirm the identities of the products.

Reusability of the Catalyst

The reusability of the catalyst was studied in the repeated oxidation reaction of 4-chlorobenzyl alcohol as a

model substrate. The reactions were carried out as described above. When each of the repeated reactions was completed, the catalyst was filtered, washed with diethyl ether and dried before using with fresh 4-chlorobenzyl alcohol and NaIO₄. The amount of manganese leached into the filtrates was determined by ICP.

RESULTS AND DISCUSSIONS

Oxidation of Alcohols with NaIO₄ Catalyzed by MnP-POM

Figure 2 shows the structure of the hybrid catalyst [37]. The catalytic activity of the MnP-POM was initially investigated in the oxidation of the 4-chlorobenzyl alcohol with NaIO₄. First, the reaction parameters such as catalyst amount, solvent and oxidant were optimized. Among the 1:1 mixture of methanol, ethanol, acetone and acetonitrile with water (single-phase systems), dichloromethane, chloroform and carbon tetrachloride (two-phase systems with *n*-Bu₄NBr as phase transfer catalyst), the 1:1 acetonitrile/water mixture was chosen as the solvent in which higher carbonyl yield was observed (Table 1). Different ratios of acetonitrile/water mixture were also examined to find the ratio between solvents. The results showed that the 1:1 mixture of acetonitrile/water is the best. The higher catalytic activity in the acetonitrile/water mixture is attributed to the polarity of solvent and the solubility of NaIO₄ in it.

Different amounts of catalyst were used to optimize the catalyst amount. The best results were obtained using 110 mg (0.018 mmol) of MnP-POM.

As reported previously, in the oxidation of hydrocarbons with NaIO₄ catalyzed by supported metalloporphyrins, imidazole plays a co-catalytic role [13]. In these experiments, imidazole was used as the co-catalyst.

The catalytic activity of [(*n*-C₄H₉)₄N]₂[Mo₆O₁₉] was also investigated in the oxidation of the 4-chlorobenzyl alcohol with NaIO₄ or H₂O₂. The result showed that the amount of 4-chlorobenzaldehyde was less than 10%. This result showed that the catalytically active species is manganese porphyrin.

A blank experiment, in the presence of the oxidant and in the absence of the catalyst, was also investigated in the oxidation of 4-chlorobenzyl alcohol. The results showed

Table 1. The Effect of Solvent on the Oxidation of 4-Chlorobenzyl Alcohol with NaIO₄ Catalyzed by MnP-POM at Room Temperature^a

Solvent	Time (min)	Yield (%) ^b
CH ₃ CN/H ₂ O (1:1)	45	100
CH ₃ CN/H ₂ O (1:2)	45	87
CH ₃ CN/H ₂ O (2:1)	45	65
CH ₃ COCH ₃ /H ₂ O	45	59
CH ₃ OH/H ₂ O	45	50
CH ₃ CH ₂ OH/H ₂ O	45	52
CHCl ₃ /H ₂ O	45	29
CCl ₄ /H ₂ O	45	18

^aReaction conditions: 4-chlorobenzyl alcohol (1 mmol), NaIO₄ (2 mmol), imidazole (0.2 mmol), catalyst (0.018 mmol). ^bGC yield based on the starting 4-chlorobenzyl alcohol.

Table 2. Optimization of Catalyst Amount in the Oxidation of 4-Chlorobenzyl Alcohol with NaIO₄ Catalyzed by MnP-POM at Room Temperature after 45 min^a

Entry	Catalyst amount (mg, mmol)	Yield (%) ^b
1	0 (0)	10
2	50 (0.008)	49
3	70 (0.011)	75
4	90 (0.015)	89
5	100 (0.016)	94
6	110 (0.018)	100
7	120 (0.020)	100

^aReaction conditions: 4-chlorobenzyl alcohol (1 mmol), NaIO₄ (2 mmol), imidazole (0.2 mmol), H₂O/CH₃CN (10 ml/10 ml). ^bGC yield based on the starting 4-chlorobenzyl alcohol.

Table 3. Oxidation of Alcohols with NaIO₄ Catalyzed by MnP-POM at Room Temperature^a

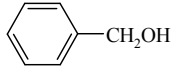
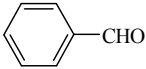
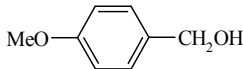
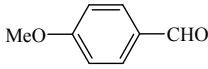
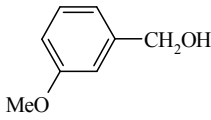
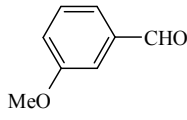
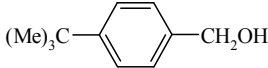
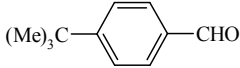
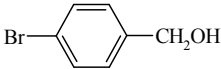
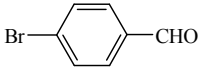
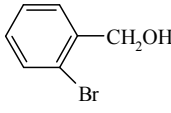
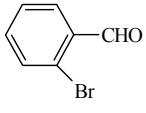
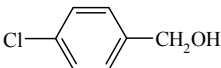
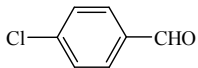
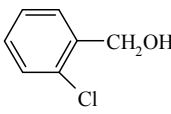
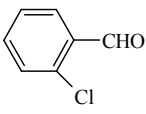
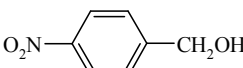

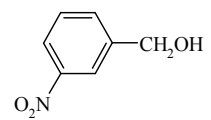
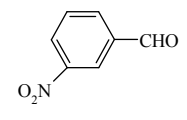
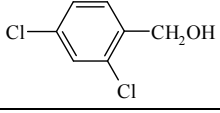
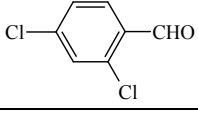
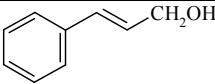
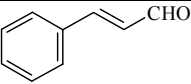
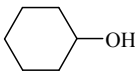
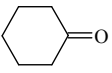
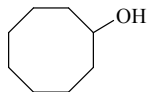
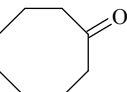
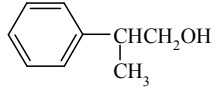
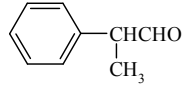
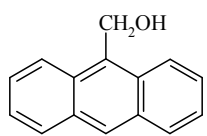
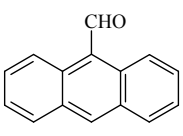
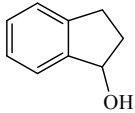
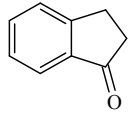
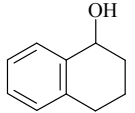
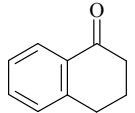
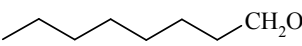
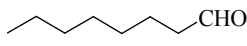
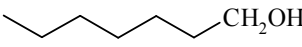
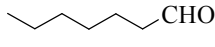
Entry	Alcohol	Product	Yield (%) ^b	Time (min)	TOF (h ⁻¹) ^c
1			100	45	70.07
2			100	40	83.42
3			100	50	66.70
4			100	80	41.68
5			100	45	70.07
6			100	50	66.70
7			100	45	70.07
8			100	55	60.65
9			100	60	55.56
10			95	60	52.78
11			97	70	46.22

Table 3. Continued

12			93	80	38.76
13			90	95	31.59
14			89	100	29.68
15			93	80	38.76
16			89	95	31.23
17			82	95	28.78
18			91	85	35.70
19			76	125	20.27
20			80	120	22.22

^aReaction conditions: alcohol (1 mmol), NaIO₄ (2 mmol), imidazole (0.2 mmol), catalyst (0.018 mmol), CH₃CN/H₂O (10 ml/10 ml). ^bGLC yield based on starting alcohol. ^cTOF (Turnover frequency) = mmol of product per mmol of catalyst per hour.

that NaIO₄ has a poor ability to oxidize the 4-chlorobenzyl alcohol.

Under the optimized conditions, the MnP-POM/NaIO₄ catalytic system was applied for oxidation of a wide range of primary and secondary alcohols. As shown in Table 3,

benzyl alcohol and substituted benzyl alcohols are converted to their corresponding aldehydes efficiently. In the case of benzyl alcohol, after 45 min, only benzaldehyde was obtained in 100% yield. In longer reaction times (1 h), the obtained products are 70% benzaldehyde and 30%

Table 4. The Results of the Catalyst Recovery Investigation and the amounts of Manganese Leached in the Oxidation of 4-Chlorobenzyl Alcohol with NaIO₄^a

Run	4-Chlorobenzaldehyde (%) ^b	Time (min)	Mn leached (%) ^c
1	100	45	0.6
2	98	45	0
3	98	45	0
4	98	45	0
5	97	45	0
6	97	45	0
7	97	45	0
8	96	45	0
9	96	45	0
10	95	45	0

^aReaction conditions: 4-chlorobenzyl alcohol (1 mmol), NaIO₄ (2 mmol), imidazole (0.2 mmol), catalyst (0.018 mmol). ^bGC yield based on the starting 4-chlorobenzyl alcohol.

^cDetermined by atomic absorption spectroscopy.

Table 5. Benzyl Alcohol Oxidation Using Various Heterogeneous Catalysts

Catalyst	Oxidant	Time (h)	Benzyl alcohol conversion (%)	Selectivity of aldehyde (%)	Ref.
MnP-POM	NaIO ₄	0.75	100	100	Our catalyst
Mn(TPPS)-Ad-IRA 400	NaIO ₄	5.00	95	100	[39]
Mn(TPPS)-PVP	NaIO ₄	5.00	95	100	[39]
MnTPyP-CMP	NaIO ₄	0.75	90	100	[40]
VPO/HMS (20 wt%)	TBHP ^a	8.00	63.6	76.5	[41]
DPPH/WO ₃ /Al ₂ O ₃	O ₂	4.00	65	95	[42]
Au/CuO-ZnO	O ₂	1.00	94	100	[43]

^a*Tert*-butyl hydroperoxide.

benzoic acid. The results show that the substituents have no significant effect on the oxidation of benzylic alcohols. In the case of linear alcohols such as *n*-octanol, the result showed that octanal was obtained in 76% yield. A good selectivity observed in the case of cinnamyl alcohol and the only alcoholic group is oxidized and no epoxide was obtained.

This hybrid catalyst was also used for oxidation of secondary alcohols and their corresponding ketones were obtained in good yields.

The oxidation of benzyl alcohol by the various catalytic systems is given in Table 5. In comparison with the previous catalytic systems, the MnP-POM/NaIO₄ catalytic system has higher catalytic activity [39-43]. For our catalytic system, also, the selectivity is 100%. Therefore, this catalytic system is suitable for the oxidation of alcohols.

Catalyst Reuse and Stability

Heterogeneous catalysis is of great practical importance in the modern industry due to the numerous advantages it involves. On the other hand, the reusability of a supported catalyst is of great importance from economical and environmental points of view, because transition metal complexes are often expensive and very toxic. Therefore, heterogenization of homogeneous catalysts makes them useful for commercial applications. Since the catalyst MnP-POM is insoluble in the reaction mixture, the reusability of the catalyst was also investigated. The reusability of MnP-POM was monitored by using multiple sequential oxidation 4-chlorobenzyl alcohol with NaIO₄ (Table 4). The catalyst was consecutively reused several times (10 times were checked) without loss of its initial activity. The amount of catalyst leaching was also determined. The results showed that the amount of Mn leached is very low which confirms the strong attachment of Mn porphyrin to hexamolybdate. The catalytic behavior of the separated liquid was also tested by addition of fresh 4-chlorobenzyl alcohol and NaIO₄ to the filtrates after each run. Continuation of the oxidation reaction under the same reaction conditions as with catalyst showed that the obtained results were as same as for the blank experiments.

CONCLUSIONS

In this paper we have demonstrated the utility of MnP-POM catalyst in the oxidation of primary and secondary alcohols to carbonyl compounds with NaIO₄. This hybrid catalyst is highly reactive in the oxidation of a wide range of primary and secondary alcohols. It showed the expected advantages of heterogenous catalysts, namely, easy handling and recyclability. The catalyst was highly reusable and recycled 10 times without appreciable decrease in its initial activity.

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