Alkylimidazolium / Alkylpyridinium octamolybdates catalyzed oxidation of sulfides to sulfoxides / sulfones with hydrogen peroxide

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Abstract

β -Mo₈O₂₆ based alkyl imidazolium and pyridinium salts of general formula [Bmim]₄Mo₈O₂₆ (Bmim = 1-butyl-3-methylimidazolium), [Hmim]₄Mo₈O₂₆ (Hmim = 1-hexyl-3-methylimidazolium), [Dhmim]₄Mo₈O₂₆ (Dhmim = 1,2-dimethyl-3-hexylimidazolium) and [Hpy]₄Mo₈O₂₆ (Hpy = 1-hexylpyridinium) have been used as catalysts for the oxidation of sulfides using 30 % hydrogen peroxide as oxidant. The examined β -Mo₈O₂₆ salts prove to be highly active and are self-separating. A high selectivity towards either sulfoxides or sulfones can be nicely controlled by variation of the reaction conditions. In both cases, the catalysts can be recycled and reused for several times without significant loss of activity, representing a good stability of the catalysts.

Keywords: Sulfide oxidation, Polyoxomolybdate, Homogeneous catalysis, Hydrogen peroxide

1. Introduction

There is a growing need for environmentally friendly chemical producing processes in industry. A major goal is to develop green catalysts or catalytic methods with “atom economic” use of raw materials, low energy consumption, and without or minimize the production of wastes. Sulfide oxidation is one of important industrial processes, which is the most straightforward method for producing sulfoxides or sulfones [1,2].

Many transition metal based catalysts are highly efficient to catalyze the oxidation of sulfides to sulfoxides / sulfones using H₂O₂ as environmentally friendly oxidant [4-8].

Among various examined catalysts, polyoxometalates (POMs) have been received much attention both in academia and in industry in the past decades [9,10]. Some

Keggin type POM catalysts such as PW₁₂O₄₀³⁻ or PMo₁₂O₄₀³⁻ based organic salts are found to be able to activate H₂O₂ molecule and are very efficient phase transfer catalysts for the oxidation of olefins, alcohols, aromatic compounds, as well as

1 sulfides [11,12]. The simple organic β -octamolybdate salts bearing quaternary
2 ammonium cation have also been reported as highly active catalysts for oxidation
3 reactions [13-17]. While comparing to the well-established Keggin type POM catalyst,
4 β -octamolybdate is advantageous since it is cheaper, more stable and easy to prepare.
5 Nevertheless, to the best of our knowledge, their catalytic application has not yet been
6 well developed so far.

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11 Our laboratory has developed several imidazolium or pyridinium based β -
12 octamolybdates catalysts [13], and they have been applied as excellent self-separating
13 catalyst for olefin epoxidations. Recently, these catalysts were also successfully
14 applied in sulfide oxidations. Sulfide can be oxidized to either sulfoxide or sulfone,
15 and the selectivity control in these transformations is very important. However, when
16 reviewing the literature work, we find that most established catalytic methods only
17 described the oxidation of sulfide to one of the oxidation product (either sulfoxide or
18 sulfone). The highly selective oxidation of sulfide to both sulfoxide and sulfone using
19 β -octamolybdate based catalytic system has never been described. We have recently
20 found that, by controlling the reaction condition, the imidazolium or pyridinium based
21 β -octamolybdates can catalyze the selective oxidation of sulfide to both sulfoxide and
22 sulfone in high selectivity. Moreover, the catalysts are also self-separating, and can be
23 reused for several times without significant loss of activity. Therefore, we wish to
24 report one primarily results of this work herein.

2. Results and Discussion

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40 Four alkylimidazolium or alkylpyridinium octamolybdates including [Bmim]₄Mo₈O₂₆
41 (Bmim = 1-butyl-3-methylimidazolium) **1**, [Hmim]₄Mo₈O₂₆ (Hmim = 1-hexyl-3-
42 methylimidazolium) **2**, [Dhmim]₄Mo₈O₂₆ (Dhmim = 1,2-dimethyl-3-
43 hexylimidazolium) **3** and [Hpy]₄Mo₈O₂₆ (Hpy = 1-hexylpyridinium) **4** have been
44 synthesized and characterized as described previously [13] (See preparation details
45 and characterization data in the Supplementary Material). They have been examined
46 as catalysts for sulfide oxidations using 30% hydrogen peroxide as oxidant. In general,
47 the sulfides could be selectively oxidized to sulfoxide at room temperature in high
48 yield. On the other hand, if sulfone is the targeted product, it is favorable to perform
49 the reaction at higher temperatures (> 60 °C) with excess amount of oxidant. The
50 selective sulfide oxidations towards both sulfoxides and sulfones have been examined

by using compounds **1-4** as catalysts and 30% hydrogen peroxide as oxidant. In both cases, the reaction optimizations were carried out by using compound **1** as a catalyst, thioanisole as a standard sulfide substrate, and 30% hydrogen peroxide as the oxidant (Scheme 1).

Scheme 1 Oxidation of thioanisole

2.1 Selective oxidation of sulfides to sulfoxides

Sulfoxides can be used as synthetic intermediates for the preparation of a variety of chemically or biologically value-added compounds such as drugs, flavors andgermicides [13-15]. To our delight, the oxidation of thioanisole under the optimal condition - [Bmim]₄Mo₈O₂₆ (0.5 mol%), H₂O₂ (1.5 equiv.), CH₃CN (1 mL), rt (see details in Table S1) - affords the desire products in good yield and selectivity. A time-dependent yield of sulfoxide and sulfone was examined by applying 0.1 mol % of catalysts **1-4** in order to give a more detailed determination of the catalyst performance (Figure 1). In general, all the catalysts show similar time-dependent curves and oxidation yields towards both products. The turn over frequencies (TOF) of **1-4** are 132, 110, 135 and 97 min⁻¹ (after 5 min), respectively. In general, the alkyl pyridinium cation based β-Mo₈O₂₆ compound **4** show comparatively lower activity than the alkyl imidazolium based compounds. Catalysts **1-4** result in 86, 82, 82, 81 % of **2a** respectively after 1 hour of the reaction, whereas **1** proved to be the most efficient catalyst. It can be observed that, ca. 10-15 % of sulfone are formed even at 5 min of the reaction, and the yields are kept almost unchanged with the increase of reaction time.

After adding H₂O₂, the catalyst solids were completely dissolved and finally resulted in a yellow solution, indicating the formation of active species. It has been reported that the dissociated oxodiperoxo compounds might be the real catalytic active species for the oxidation reactions [27]. While after the consumption of H₂O₂, the white catalyst solids can be precipitated in CH₃CN. Therefore, the catalysts can be recycled simply by filtration. The recycled catalysts were purified by washing with water, dried under vacuum and then used directly for the next catalytic run. The catalytic results for the recycled catalyst **1** are shown in Figure 2. The overall recycling yields are

above 95 % after each run. The recycled catalyst $[\text{Bmim}]_4\text{Mo}_8\text{O}_{26}$ can be used at least 8 times without significant loss of activity, indicating a good stability of the catalyst.

Figure 1 Time-dependent yield using catalysts **1-4** for the oxidation of thioanisole to **2a** (●**1**, ***2**, ■**3**, ▲**4**) or **2b** (○**1**, ×**2**, □**3**, △**4**).

Figure 2 Reuse of catalyst **1** in the oxidation of thioanisole.

The scope of reaction was then extended to other substrates. It is found that the electronic effects of different functional groups on the phenyl ring of aromatic sulfides significantly affect the activity and selectivity (Table 1, entries 1-5). The aromatic sulfides bearing electron-donating groups display higher activity than the ones bearing electron-withdrawing groups. The reaction conversions are in the order *p*-methoxy thioanisole > *p*-methyl thioanisole > thioanisole > *p*-chlorine thioanisole > *p*-nitro thioanisole, which is in accordance with the order of the electron donating

abilities of different functional groups. However, the order of selectivity towards sulfoxide is opposite. Such a result is also reasonable since high activity might accelerate the oxidation of sulfides to sulfones. 100 % selectivity towards sulfoxide can be achieved for strong electron-withdrawing nitro derived 4-nitro thioanisole. While in the case of [(n-C₄H₉)₄N]₄(α-Mo₈O₂₆)/H₂O₂ catalytic system, the catalyst displays higher activity as compared to our system and all the functional groups derived thioanisoles result in almost 100 % conversions [13]. Accordingly, the subtle functional group effects on the activities are not easily observed. Furthermore, most aliphatic sulfides exhibit higher activity than aromatic sulfides, in which almost 100% of sulfoxide conversion and selectivity could be obtained for aliphatic sulfides even with 1 equiv. of H₂O₂ applied (Table 1, entries 6-9). However, due to the strong steric effect of tert-butyl groups, the reaction displays comparatively low activity for tert-butyl sulfide, resulting in 90 % of oxidation yield after 3 h of the reaction (Table 1, entry 10).

Table 1 Oxidation of different sulfides to sulfoxides with H₂O₂ using [Bmim]₄Mo₈O₂₆ as catalyst^a

$$R^1-S-R^2 \xrightarrow[CH_3CN]{[Bmim]_4Mo_8O_{26}/H_2O_2} R^1-\overset{\overset{O}{\parallel}}{S}-R^2 + R^1-\overset{\overset{O}{\parallel}}{\underset{\parallel}{S}}-R^2$$

SO SO₂

Entry	R ¹	R ²	Conv. (%)	Yield(%)		Sel. (%) SO
				SO	SO ₂	
1	4-OCH ₃ C ₆ H ₄	CH ₃	98	74	24	76
2	4-CH ₃ C ₆ H ₄	CH ₃	95	76	19	80
3	C ₆ H ₅	CH ₃	95	84	11	88
4	4-Cl-C ₆ H ₄	CH ₃	90	79	11	88
5	4-NO ₂ -C ₆ H ₄	CH ₃	82	82	0	100
6 ^b	C ₂ H ₅	C ₂ H ₅	100	>99	trace	>99
7 ^b	CH ₃	CH ₂ =CHCH ₂	100	>99	trace	>99
8 ^b	CH ₂ =CHCH ₂	CH ₂ =CHCH ₂	100	97	2	97
9 ^b	(CH ₂) ₃ CH ₃	(CH ₂) ₃ CH ₃	100	95	5	95

10^c C(CH₃)₃ C(CH₃)₃ 90 86 4 96

^aThe reaction was carried out using substrate (0.5 mmol), [Bmim]₄Mo₈O₂₆ (0.5mol%), H₂O₂ (1.5 equiv.) in CH₃CN (1 mL) at rt for 40 min; ^b1 equiv. of H₂O₂ was applied; ^cthe reaction was performed for 3 h.

2.2 Selective oxidation of sulfides to sulfones

Based on the above studies, the capability of the catalytic system towards oxidation of sulfides to sulfones was further investigated. The optimal condition obtained was [Bmim]₄Mo₈O₂₆ (0.2 mol%), H₂O₂ (3.0 equiv.), CH₃CN (1 mL) at 60 °C for 1h (see details in Table S2). Under optimal condition, the oxidation of sulfides to sulfones reaction was examined for different substrates, and the results are shown in Table 2. It is satisfactory to see that most reactions result in almost 100% conversion of substrates with 100 % of selectivity towards sulfones. While in the case of *p*-chlorine thioanisole and *p*-nitro thioanisole bearing electron-withdrawing groups on the phenyl ring, only a poor to moderate selectivity towards sulfones can be obtained. The catalysts also show similar time-dependent curves of yields for catalysts 1-4. In this system, the white catalyst powder was also easily precipitated from the solution after the reaction. Thus, the catalyst was recycled by filtration, washed with water, dried under vacuum and used directly for the next run (Fig. S1-S2).

Table 2 Oxidation of different sulfides to sulfones with H₂O₂ using [Bmim]₄Mo₈O₂₆ as catalyst^a

Entry	R ¹	R ²	Conv. (%)	Yield (%)
1	4-OCH ₃ C ₆ H ₄	CH ₃	100	100
2	4-CH ₃ C ₆ H ₄	CH ₃	100	>99
3	C ₆ H ₅	CH ₃	100	>99
4	4-Cl-C ₆ H ₄	CH ₃	100	54 (46 ^c)
5	4-NO ₂ -C ₆ H ₄	CH ₃	100	19 (80 ^c)
6	C ₂ H ₅	C ₂ H ₅	100	100
7	CH ₃	CH ₂ =CHCH ₂	100	>99

8	$\text{CH}_2=\text{CHCH}_2$	$\text{CH}_2=\text{CHCH}_2$	100	>99
9	$(\text{CH}_2)_3\text{CH}_3$	$(\text{CH}_2)_3\text{CH}_3$	100	>99
10	$\text{C}(\text{CH}_3)_3$	$\text{C}(\text{CH}_3)_3$	100	>99

^aThe reaction was carried out using substrate (0.5 mmol), [Bmim]₄Mo₈O₂₆ (0.2 mol%), H₂O₂ (3 equiv.) in CH₃CN (1 mL) at 60 °C for 1 h. ^bSelectivity towards sulfone. ^cYield of sulfoxide.

Conclusions

The selective oxidation of sulfides to either sulfoxides or sulfones is studied using imidazolium or pyridinium based octamolybdate salts as efficient catalysts in the presence of hydrogen peroxide as green oxidants. A high selectivity towards either sulfoxides or sulfones can be nicely controlled by variation of reaction temperature, amounts of catalysts and the amounts of oxidant applied. All the catalysts display good self-separating property and stability. Recycling experiments indicate that the catalysts can be recycled and reused for several times without significant loss of activity. The catalytic system provides a green and easy handling strategy for the synthesis of sulfoxides or sulfones under mild conditions.

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Graphical Abstract

β-Mo₈O₂₆ based alkylimidazolium and alkylpyridinium salts are used as green and efficient self-separating catalysts for highly selective oxidation of sulfides to sulfoxides or sulfone with hydrogen peroxide.