



Short communication

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



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ABSTRACT

β - Mo_8O_{26} based alkyl imidazolium and pyridinium salts of general formula $[\text{Bmim}]_4\text{Mo}_8\text{O}_{26}$ (Bmim = 1-butyl-3-methylimidazolium), $[\text{Hmim}]_4\text{Mo}_8\text{O}_{26}$ (Hmim = 1-hexyl-3-methylimidazolium), $[\text{Dhmim}]_4\text{Mo}_8\text{O}_{26}$ (Dhmim = 1.2-dimethyl-3-hexylimidazolium) and $[\text{Hpy}]_4\text{Mo}_8\text{O}_{26}$ (Hpy = 1-hexylpyridinium) have been used as catalysts for the oxidation of sulfides using 30% hydrogen peroxide as oxidant. The examined β - Mo_8O_{26} 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.

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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 [1–3]. Many transition metal based catalysts are highly efficient to catalyze the oxidation of sulfides to sulfoxides/sulfones using H_2O_2 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 $\text{PW}_{12}\text{O}_{40}^{3-}$ or $\text{PMo}_{12}\text{O}_{40}^{3-}$ based organic salts are found to be able to activate H_2O_2 molecule and are very efficient phase transfer catalysts for the oxidation of olefins, alcohols, aromatic compounds, as well as sulfides [11,12]. The simple organic β -octamolybdate salts bearing quaternary ammonium cation have also been reported as highly active catalysts for oxidation reactions [13–17]. While comparing to the well-established Keggin type POM catalyst, β -octamolybdate is advantageous since it is cheaper, more stable and easy to prepare. Nevertheless, to the best of our knowledge, their catalytic application has not yet been well developed so far.

Our laboratory has developed several imidazolium or pyridinium based β -octamolybdates catalysts [13], and they have been applied as excellent self-separating catalyst for olefin epoxidations. Recently, these catalysts were also successfully applied in sulfide oxidations.

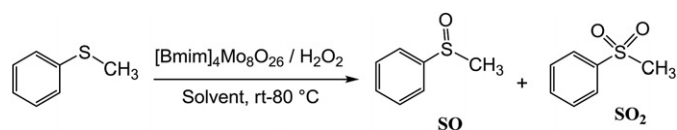
Sulfide can be oxidized to either sulfoxide or sulfone, and the selectivity control in these transformations is very important. However, when reviewing the literature work, we find that most established catalytic methods only described the oxidation of sulfide to one of the oxidation product (either sulfoxide or sulfone). The highly selective oxidation of sulfide to both sulfoxide and sulfone using β -octamolybdate based catalytic system has never been described. We have recently found that, by controlling the reaction condition, the imidazolium or pyridinium based β -octamolybdates can catalyze the selective oxidation of sulfide to both sulfoxide and sulfone in high selectivity. Moreover, the catalysts are also self-separating, and can be reused for several times without significant loss of activity. Therefore, we wish to report one primarily results of this work herein.

2. Results and discussion

Four alkylimidazolium or alkylpyridinium octamolybdates including $[\text{Bmim}]_4\text{Mo}_8\text{O}_{26}$ (Bmim = 1-butyl-3-methylimidazolium) **1**, $[\text{Hmim}]_4\text{Mo}_8\text{O}_{26}$ (Hmim = 1-hexyl-3-methylimidazolium) **2**, $[\text{Dhmim}]_4\text{Mo}_8\text{O}_{26}$ (Dhmim = 1.2-dimethyl-3-hexylimidazolium) **3** and $[\text{Hpy}]_4\text{Mo}_8\text{O}_{26}$ (Hpy = 1-hexylpyridinium) **4** have been synthesized and characterized as described previously [13] (See preparation details and characterization data in the Supplementary Material). They have been examined as catalysts for sulfide oxidations using 30% hydrogen peroxide as oxidant. In general, the sulfides could be selectively oxidized to sulfoxide at room temperature in high yield. On the other hand, if sulfone is the targeted product, it is favorable to perform the reaction at higher temperatures ($>60^\circ\text{C}$) with excess amount of oxidant. The selective sulfide oxidations towards both sulfoxides and sulfones have been examined by using compounds **1–4** as catalysts and

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Scheme 1. Oxidation of thioanisole.

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).

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 and germicides [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 desired 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 (Fig. 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 h 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 oxidoperoxo compounds might be the real catalytic active species for the oxidation reactions [13]. 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 Fig. 2. The overall recycling yields are above 95% after each run. The recycled catalyst [Bmim]₄Mo₈O₂₆ can be used at least 8 times without significant loss of activity, indicating a good stability of the catalyst.

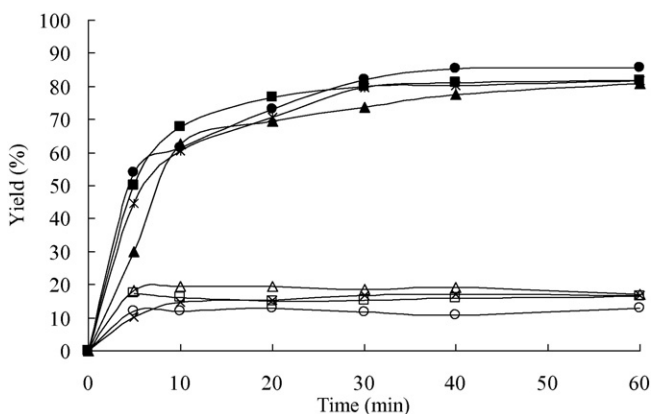


Fig. 1. Time-dependent yield using catalysts **1–4** for the oxidation of thioanisole to **2a** (●, *2, ■, ▲) or **2b** (○, ×2, □, △).

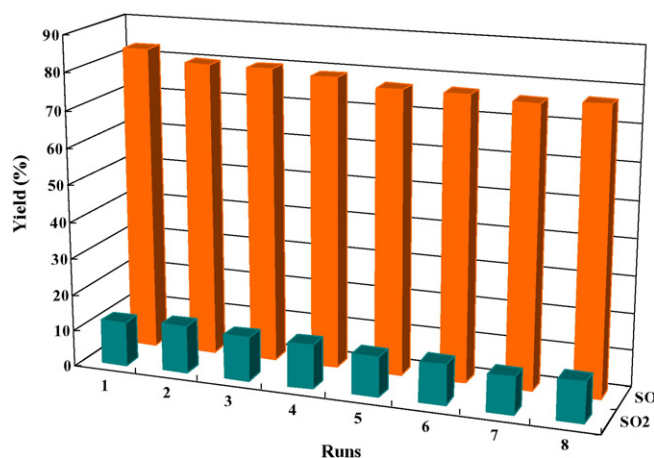


Fig. 2. Reuse of catalyst **1** in the oxidation of thioanisole.

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.

Entry	R ¹	R ²	Conv. (%)	Yield (%)		Sel. (%)
				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(CH ₃) ₃	C(CH ₃) ₃	90	86	4	96

^a The reaction was carried out using substrate (0.5 mmol), [Bmim]₄Mo₈O₂₆ (0.5 mol%), H₂O₂ (1.5 equiv.) in CH₃CN (1 mL) at rt for 40 min.

^b 1 equiv. of H₂O₂ was applied.

^c The reaction was performed for 3 h.

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