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Immobilized molybdenum acetylacetonate complex on expanded starch for chemoselective

oxidation of sulfides to sulfoxides with t-BuOOH at room temperature

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Abstract

We explored a highly efficient protocol for the oxidation of alkyl aryl sulfides to sulfoxides with high selectivities catalyzed by a molybdenum acetylacetonate complex immobilized on expanded corn starch (ECS-MoO₂(acac)₂) in the presence of 70% *t*-BuOOH solution (water). We obtained predominantly the monooxygenated product. The resulting products were obtained in good to excellent yields within a reasonable time. The catalyst could readily be separated from the reaction mixture and reused for several runs without significant loss in catalytic efficiency.

Keywords: Molybdenum (VI) acetylacetonate complex; expanded corn starch; selective oxidation; sulfide; sulfoxide

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Introduction

Chemoselective oxidation of organic sulfides represents one of the most fundamentally important reactions in the domain of organic chemistry, which is fascinating from both chemical and biological perspectives.¹ Sulfoxides are indispensable as they appear in numerous natural products and drug molecules, act as chiral auxiliaries and C-C bond forming reagents.² They also have widespread utilization as convenient intermediates or reagents in organic syntheses. Indeed, a number of drugs in therapeutic areas such as antiulcerative, cardiotonic, antihypertensive as well as psychotonics and vasodilators contain a sulfoxide functionality.³ Because of this, numerous reagents and methods have been developed in an effort to produce sulfoxides as selectively and inexpensively as possible. Furthermore, with the growing emphasis on environmentally benign processes, more and more chemists have sought out ways to bring about this transformation with minimal waste as possible. As a result, a vast number of useful transition metal based catalysts have emerged over the years for the oxidation of sulfides by H₂O₂. ⁴⁻⁸ Although H₂O₂, being easily available and environmentally benign most of the oxidation processes require a large excess of H_2O_2 (4–8.0 equiv. with respect to sulfide) to attain high yields of the sulfoxides.^{9, 10} In that context, *t*-BuOOH appears to be a perfect alternative as it is inexpensive, has high thermal stability and is safe to handle even in large quantities for the efficient and selective production of sulfoxides.¹¹ In addition, the probability of decomposition by trace metallic impurities is less than that of H_2O_2 .¹² The by-product of oxidation, *t*-BuOH can be easily removed by distillation or rotary evaporation, thus avoiding the need for aqueous work

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up. So far, some interesting transition metal catalysts have been reported for sulfide oxidation, including La,¹¹ Bi,¹³ Fe,¹⁴ V¹⁵ and Mn¹⁶ in the presence of *t*-BuOOH. However, most of them present disadvantages, such as difficulty in recovery of the catalyst,¹³ high cost,¹⁶ the requirement of a promoter or a co-catalyst,¹³ high temperature,¹⁴ long reaction time.¹⁴ Therefore, simple, convenient and environmentally benign methods for the oxidation of sulfides to sulfoxides using *t*-BuOOH as a green oxidant are still highly desired. The use of heterogeneous catalysts in the liquid phase has the inherent advantages of easier handling, separation, recovery and recycling, and enhanced stability.

High-valence oxomolybdenum complexes have proven to be excellent catalysts for the reduction and oxidation of organic compounds.^{17, 18} As the homogeneous Mo-complexes have some well known disadvantages (difficulties with separation and recyclability), many attempts to immobilize the Mo-complexes have been performed.^{19, 20} Recently, we disclosed the excellent performance of molybdenum acetylacetonate complex immobilized on expanded corn starch (ECS-MoO₂(acac)₂) in stillingia oil epoxidation using *t*-BuOOH as the oxidant.²¹ Encouraged by these exciting results, we decided to explore further their catalytic activity in oxidation processes. Interested in developing a system according to the green chemistry principles, in the present study, we report an efficient method for the selective oxidation of sulfides to sulfoxides using *t*-BuOOH as the oxidant under mild reaction conditions in ethanol as green solvent with ECS-MoO₂(acac)₂ (Scheme 1). More importantly, the catalysts could be separated and efficiently reused for four cycles without a significant loss in catalytic activity. To the best of our knowledge, this is the first report on the oxidation of sulfides by molybdenum complex using *t*-BuOOH as the oxidant.

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Results and Discussion

To improve the yield of the reaction and find the optimized conditions, several reactions were carried out in the same conditions with changing parameters. We investigated the oxidation of methyl phenyl sulfide (thioanisole) as a model substrate and the trials were performed with different amounts of molybdenum acetylacetonate supported on expanded corn starch, reaction times, solvents and various oxidants at room temperature. It can be seen that the conversion increased from 86% to 97% when the amount of ECS-MoO₂(acac)₂ increased from 0.5 mol% to 1 mol% after 6 h. The selectivity of sulfoxide increases with the addition of catalyst from 0.5 mol% to 1.5 mol% (Table 1, entry 1 and entry 2). When the amount of catalyst is increased from 97 to 90%. The conversion of sulfide almost did not change. It indicated that the excess catalyst promote the over-oxidation of sulfoxide. According to these results, 1.5 mol% of ECS-MoO₂(acac)₂ was selected as the optimum amount of catalyst.

To analyze the solvent effect, the reaction was carried out in different solvents like 9:1 (v/v) mixture of n-hexane/methanol, methanol, ethanol, toluene and acetonitrile following the same protocol. The results listed in Table 2 show that the solvent has a remarkable influence on the reaction outcome. The oxidation carried out in ethanol gives the highest yield of sulfoxide. A

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conversion of 94% was obtained with a sulfoxide selectivity of 97% (Table 2, entry 3). In the case of other solvents a lower selectivity of sulfoxide was obtained.

Table 3 shows the results for the thioanisole oxidation as a function of reaction time using ECS- $MoO_2(acac)_2$ as catalyst. It can be observed that the sulfoxide selectivity increased with the reaction time up to 6 h (Table 3, entry 3), and then it decreased by prolonging the reaction time to 20 h. In all cases the conversion of thioanisole remained almost constant.

To examine the effect of oxidant on the oxidation of thioanisole, the reaction was performed with different oxidants by using the same reaction conditions (Table 4). When 2 equiv. of 30% H₂O₂ (water) was used as oxidant, the reaction gave the corresponding sulfoxide in 36% yield and 36% selectivity (Table 4, entry 1). In the presence of 2 equiv of 70% *t*-BuOOH (water) the yield was 72% with 73% selectivity (Table 4, entry 2). The effect of the concentration of *t*-BuOOH used on the conversion and product selectivity was studied at various *t*-BuOOH/substrate molar ratios in the presence of 1.5 mol% catalyst. The selectivity pattern changed with varying amounts of *t*-BuOOH in the oxidation of thioanisole. With 1.5 equiv. of *t*-BuOOH, desired yields and selectivity of sulfoxide were achieved (Table 4, entry 4). Nevertheless, a further increase in this ratio significantly reduced the selectivity of the reaction products.

On the ground of the optimization studies, ECS-MoO₂(acac)₂ (1.5 mol%) and 1.5 equiv 70% *t*-BuOOH (water) in EtOH at room temperature were the best reaction conditions for the oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide. In an effort to establish the scope of the protocol, we have assessed the catalytic activity of ECS-MoO₂(acac)₂ under the optimized conditions, using a series of various types of aliphatic and aromatic sulfides. As shown in Table 5, aromatic substrates with various substituents including $-CH_3$, $-OCH_3$, -Cl, -CN and $-NO_2$

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could be tolerated and the sulfoxides were obtained in good to excellent yields (Table 5, entries 1-5). Whereas, a strong electron-withdrawing group at the para-position showed a negative effect on the reaction. In particular, a much longer reaction time (15 h) was needed for 4-nitrothioanisole to complete the reaction (Table 5, entry 4), presumably due to the strong electron withdrawing effects of the nitro group. Not only aryl sulfides but also linear alkyl ones (Table 5, entries 7 and 8) could be oxidized to the corresponding sulfoxides in high yields. On the other hand, bulky sulfides such as diphenyl sulfide (Table 5, entry 6) react smoothly under the present conditions. The chemoselectivity of the method was also notable. Sulfides having a carbon-carbon double bond (Table 5, entry 9) and hydroxyl group (Table 5, entry 10) were cleanly transformed into the corresponding sulfoxides in excellent yield without formation of any epoxide and carbonyl by-products.

Lastly, recyclability of the catalyst being an attractive feature, we studied the recyclability for the oxidation of thioanisole to the corresponding sulfoxide. The reaction mixture was centrifuged after the first run and the obtained solid residue was washed with ethanol, dried under vacuum and reused for four runs. The sulfoxide yields of the reused catalysts were 90%, 90%, 88% and 87%, respectively, when the catalyst was used for 1, 2, 3, 4 cycles under the optimized reaction conditions (Figure S 1 Supplemental Materials). These results suggested that the catalyst developed in this study can be recycled without significant loss in catalytic activity for at least 4 times. To further assess the recyclability of catalysts, the hot filtration test (separation of catalyst at the reaction temperature) was performed for ECS-MoO₂(acac)₂ by filtering off the reaction solution after 30% on conversion of the catalytic oxidation at room temperature, and leaving them to react for 10 h. No sulfide conversion was observed after the filtration step for ECS-

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 $MoO_2(acac)_2$. ICP analysis of the used catalyst (after four runs) showed 0.4% leaching of molybdenum.

Experimental

Materials and Methods

All chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. The resulting reaction mixtures were analyzed by gas chromatography-mass spectroscopy (GC-MS) and GC. The GC-MS (Agilent 7890A, Agilent 5975C MSD) and GC (Agilent 7890A) instruments were equipped with a DB-5 capillary. The ICP analyses were carried out by a Perkin-Elmer optima 2000 DV spectrometer. Melting points were obtained with a Shimadzu DSC-50 thermal analyzer. ¹H and ¹³C NMR spectra were obtained on a Bruker RX-500 Advance spectrometer in CDCl₃ using tetramethylsilane as internal standard. The Supplemental Materials contains sample characterization data for the products obtained.

Typical sulfide oxidation procedure

A mixture of methyl phenyl sulfide (1 mmol), 70% *t*-BuOOH (1.5 equiv.), ECS-MoO₂(acac)₂ catalyst (1.5 mol%) in ethanol (3 mL) was stirred at 25 °C. Completion of the reaction was indicated by TLC (n-hexane/ethylacetate 10 : 1) and gas chromatography (GC). After completion, ethyl acetate was added to it. The reaction mixture was then centrifuged and decanted to separate the molybdenum compound. The aqueous phase was extracted with ethyl acetate 3-4 times. After drying with anhydrous sodium sulfate, the organic residue was analyzed

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by GC and then purified by column chromatography on silica gel with ethyl acetate/hexane to give methyl phenyl sulfoxide. The separated catalyst was washed with EtOH and dried under vacuum. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.65-7.63 (m, 2H), 7.55-7.47 (m, 3H), 2.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 145.8, 131.2, 129.5, 123.6, 44.1; EI-MS, *m/z*: [M]⁺ 139.99.

Conclusions

In conclusion, we have explored a new method for the selective oxidation of various aromatic and aliphatic sulfides to the corresponding sulfoxides with 70% *t*-BuOOH (water) as the oxidant catalyzed by ECS-MoO₂(acac)₂. The described method in this paper clearly indicate that the methodology involves mild, environmentally friendly and selective synthesis of sulfoxides from both aromatic and aliphatic sulfides. The resulting products were obtained in good yields. This catalyst can be considered as heterogeneous version of $MoO_2(acac)_2$ and easily prepared from commercially available starting materials. The properties of high activity, high stability, easy recoverability, and reusability of the catalyst render it potentially valuable catalyst in industrial applications.

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Table 1 Optimization of the catalyst amount on the oxidation of thioanisole as a model reactioncatalyzed by ECS-MoO2($acac)_2^a$

Entry	Catalyst amount(mol%)	Conversion ^b (%)	Yield ^b (%)	Selectivity ^c (%)
1	0.5	86	43	50
2	1	97	89	92
3	1.5	94	91	97
4	2	93	86	92
5	2.5	93	84	90

^{*a*} Reaction conditions: 3 mL of solvent; 1 mmol of thioanisole; 1.5 mmol of 70% *t*-BuOOH (water); RT (25 °C); 6 h; with stirring. ^{*b*} Determined by GC on the crude reaction mixture. ^{*c*} Selectivity = sulfoxide/(sulfoxide + sulfone).

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Entry	Solvent	Conversion ^b (%)	Yield ^b (%)	Selectivity ^c (%)		
1	n-	96	80	83		
	Hexane/Methanol					
	(9:1, v:v)					
2	Methanol	91	76	84		
3	Ethanol	94	91	97		
4	Toluene	97	83	86		
5	Acetonitrile	93	65	70		

Table 2 Effect of various solvents on oxidation of thioanisole catalyzed by ECS-MoO₂(acac)₂^a

^{*a*} Reaction conditions: 1 mmol of thioanisole; 1.5 mmol of 70% *t*-BuOOH (water); 1.5 mol% of ECS-MoO₂(acac)₂; RT (25 °C); 6 h; with stirring. ^{*b*} Determined by GC on the crude reaction mixture. ^{*c*} Selectivity = sulfoxide/(sulfoxide + sulfone).

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Entry	Time (h)	Conversion ^b (%)	Yield ^b (%)	Selectivity ^c (%)
1	2	93	78	84
2	4	93	82	88
3	6	94	91	97
4	8	95	78	82
5	20	96	61	64

Table 3 Effect of reaction time on oxidation of thioanisole catalyzed by ECS-MoO₂(acac)₂ ^{*a*}

^{*a*} Reaction conditions: 3 mL of ethanol; 1 mmol of thioanisole; 1.5 mmol of 70% *t*-BuOOH (water); 1.5 mol% of ECS-MoO₂(acac)₂; RT (25 °C); with stirring. ^{*b*} Determined by GC on the crude reaction mixture. ^{*c*} Selectivity = sulfoxide/(sulfoxide + sulfone).

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Table 4 Effect of different oxidants and the concentration of *t*-BuOOH on the oxidation of thioanisole catalyzed by ECS-MoO₂(acac)₂ at room room temperature^{*a*}

Entry	Oxidant	Conversion ^b (%)	$\text{Yield}^{b}(\%)$	Selectivity ^c
				(%)
1	H ₂ O ₂ (2 equiv.)	99	36	36
2	t-BuOOH (2	98	72	73
	equiv.)			
3	t-BuOOH (1	54	38	70
	equiv.)			
4	<i>t</i> -BuOOH (1.5	94	91	97
	equiv.)			

^{*a*} Reaction conditions: 3 mL of ethanol; 1 mmol of thioanisole; 1.5 mol% of ECS-MoO₂(acac)₂; RT (25 °C); 6 h; with stirring. ^{*b*} Determined by GC on the crude reaction mixture. ^{*c*} Selectivity = sulfoxide/(sulfoxide + sulfone).

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Table 5 Oxidation of sulfides to the corresponding sulfoxides by using 70% t-BuOOH and ECS-MoO₂(acac)₂ catalyst^a

				Conversion ^b		Selectivity ^c
Entry	Substrate	Product	Time (h)	(%)	Yield [®] (%)	(%)
1	S_	1	5	96	93	97
2	MeO	2	5	97	95	98
3	CI	3	7	94	91	97
4	O ₂ N S	4	15	93	89	96
5	NC	5	7	96	94	98
6	C S C S C S S S S S S S S S S S S S S S	6	24	88	85	97
7	∕_s∕∕	7	6	96	92	96
8	∽s∽	8	6	97	94	97
9	∕∕_S	9	7	93	90	97

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^{*a*} Reaction conditions: 3 mL of ethanol; 1 mmol of sulfide; 1.5 mol% of ECS-MoO₂(acac)₂; 1.5 mmol of 70% *t*-BuOOH (water); RT (25 °C); with stirring. ^{*b*} Determined by GC on the crude reaction mixture. ^{*c*} Selectivity = sulfoxide/(sulfoxide + sulfone).

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Scheme 1 Selective oxidation of sulfides to sulfoxides.

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