

Article

The Selective Oxidation of Sulfides to Sulfoxides or Sulfones with Hydrogen Peroxide Catalyzed by a Dendritic Phosphomolybdate Hybrid

Qiao-Lin Tong[†], Zhan-Fang Fan[†], Jian-Wen Yang, Qi Li, Yi-Xuan Chen, Mao-Sheng Cheng and Yang Liu *[®]

Key Laboratory of Structure-Based Drug Design & Discovery of Ministry of Education, School of Pharmaceutical Engineering, Shenyang Pharmaceutical University, Shenyang 110016, China; qltongchina@163.com (Q.-L.T.); FZF11201604@163.com (Z.-F.F.); fyysy123@163.com (J.-W.Y.); liqicherry@163.com (Q.L.); cyx2047259245@163.com (Y.-X.C.); mscheng@syphu.edu.cn (M.-S.C.)

* Correspondence: y.liu@syphu.edu.cn

+ Qiao-Lin Tong and Zhan-Fang Fan contributed equally to this work.

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Abstract: The oxidation of sulfides to their corresponding sulfoxides or sulfones has been achieved using a low-cost poly(amidoamine) with a first-generation coupled phosphomolybdate hybrid as the catalyst and aqueous hydrogen peroxide as the oxidant. The reusability of the catalyst was revealed in extensive experiments. The practice of this method in the preparation of a smart drug Modafinil has proved its good applicability.

Keywords: dendritic phosphomolybdate hybrid; sulfides; selective oxidation; hydrogen peroxide; reusability

1. Introduction

Many biologically and chemically active molecules are constructed from sulfoxides and sulfones [1–5]. The oxidation of sulfides is a fundamental reaction as one of the most straightforward methods to afford sulfoxides and sulfones [6]. Many reagents, including peracids and halogen derivatives, are used in the common approaches of sulfoxidation reactions [7,8]. However, these common reactions often suffer from the formation of many environmentally unfriendly byproducts and low oxygen atom efficiency [6,9]. The development of environmentally benign catalysts and oxidants has become a research hotspot in recent green chemistry pursuits.

Among various oxidants, aqueous hydrogen peroxide, which is inexpensive, is readily available, has a high effective oxygen content, is safe in operation and storage, and yields stoichiometric amounts of environmentally friendly water as a byproduct, is generally considered one of the most environmentally benign "green oxidants". These characteristics of aqueous hydrogen peroxide have led to the development of many valuable methods for the oxidation of sulfides to sulfoxides and sulfones with various transition metal catalysts, including Ti(SO₄)₂/GOF [10], PDDA-SiV₂W₁₀ [11], the cobalt(III)–salen ion [12], TiO₂/AA/MoO₂ [13], a copper–Schiff base complex [14], $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)]\cdot H_2O$ [6], vanadium Schiff base complexes [15], and so on [16–19].

Polyoxometalates (POMs), which are composed of anionic transition metal–oxygen clusters [20–23], have been widely studied in the field of catalysis due to their excellent catalytic characteristics, including efficient catalytic activity and selectivity, controllable redox potential and acidity through the choice of the countercations and constituent elements [24,25]. Among these POMs, Keggin-type phosphomolybdic acid ($H_3Mo_{12}O_{40}$, HPMo) has shown excellent catalytic performance in oxidation reactions with aqueous hydrogen peroxide [26–29].



Dendritic poly(amidoamine) (PAMAM), which contains many amino groups, is an excellent organic modifier for POMs [30–32]. PAMAMs can be functionalized to couple to various POMs, and the dendritic structure, which is different from the common organic modifier, can provide a local microenvironment for the POMs, which may result in a helpful "dendritic effect" on the reaction [33,34]. PAMAM-G1 (poly(amidoamine) with the first generation) dendrimers have been used in industrial production and are relatively inexpensive. Moreover, the amino groups of the PAMAM-G1 dendrimer can be protonated by HPMo, and the PMo anions and PAMAM-G1 can strongly bond together through electrostatic interactions [35].

Herein, we report a heterogeneous, simple, recyclable, efficient, and green protocol for the oxidation of sulfides to sulfoxides and sulfones with 30 wt% H_2O_2 under mild conditions in excellent yield, catalyzed by a composite based on PAMAM-G1 and HPMo (denoted as PAMAM-G1-PMo). To the best of our knowledge, this is the first report of PAMAM-G1-PMo as the catalyst used in the oxidation of sulfides to sulfoxides and sulfones.

2. Results and Discussion

In this oxidation system, PAMAM-G1-PMo is utilized as the catalyst, and $30 \text{ wt}\% \text{ H}_2\text{O}_2$ is used as the oxidant. We selected thioanisole (1a) as a model substrate and found that less than 5% of 1a could be directly oxidized by $30 \text{ wt}\% \text{ H}_2\text{O}_2$ alone, even when the reaction time lasted to 6 h (Table 1, entry 1). However, when 50 mg of PAMAM-G1PMo was added to the above mixture, sulfoxide (1b) was generated soon as the oxidation product. In addition, control experiments were performed to assess the individually catalytic activity of HPMo and PAMAM-G1 dendrimer. Regrettably, only 8% of starting material could be oxidized by $30 \text{ wt}\% \text{ H}_2\text{O}_2$ catalyzing by HPMo alone (Table 1, entry 2), and much less yield was obtained when catalyzing by PAMAM-G1 dendrimer alone (Table 1, entry 3). When the reaction was carried out in the presence of PAMAM-G1-PMo, up to 85% of 1a could be oxidized within 4 h (Table 1, entry 4), indicating that PAMAM-G1-PMo played a very significant role in prompting the process of this oxidation effectively.

Ia S		30%H ₂ O ₂ 95% EtOH	\rightarrow \downarrow \downarrow $\overset{\vee}{\overset{\vee}{\overset{\vee}{\overset{\vee}{\overset{\vee}{\overset{\vee}{\overset{\vee}{\overset{\vee}$	
Entry	Catalyst	Time (h)	Temperature (°C)	Yield ^b (%)
Entry 1	Catalyst —	Time (h) 6.0	Temperature (°C) 25	Yield ^b (%) 4
Entry 1 2	Catalyst — HPMo	Time (h) 6.0 8.0	Temperature (°C) 25 25	Yield ^b (%) 4 8
Entry 1 2 3	Catalyst — HPMo PAMAM-G1	Time (h) 6.0 8.0 8.0	Temperature (°C) 25 25 25 25 25	Yield ^b (%) 4 0.5

Table 1. Control experiments with different components as catalyst ^a.

^a Reaction conditions: 1a (62 mg, 0.5 mmol), solvent (8 mL), catalyst (50 mg), 30 wt% H₂O₂ (63 mg, 0.55 mmol); ^b Isolated yield. HPMo: Keggin-type phosphomolybdic acid. PAMAM-G1: poly(amidoamine) with the first generation. PAMAM-G1-PMo: composite based on PAMAM-G1 and HPMo.

To optimize the conditions for the oxidation of sulfides to sulfoxides, we first investigated the effects of the solvent in the PAMAM-G1-PMo-catalyzed reaction system. The results are listed in Table 1. After screening different solvents, we observed that when MeOH or 95% EtOH was used as the solvent in the presence of PAMAM-G1-PMo, we obtained the desired sulfoxide products (1b) in relatively high yields of 85–90% and a minor amount of starting material (1a) remained, without any sulfones (Table 2, entries 1–2). However, the conversion was relatively poor when the reaction was carried out in other solvents, including EtOH, CH₃COCH₃, CH₃COOC₂H₅, and *i*-PrOH (Table 2, entries 3–6). After comprehensive considerations of various factors, we selected environmentally friendly and low-cost 95% EtOH as the solvent. Next, the temperature of the reaction was optimized.

As shown in Table 2, when the temperature increased from 25 °C to 30 °C, the yield of the desired product increased to more than 90% and reaction time reduced to 2 h, but when the temperature increased to 35 °C, the yield of the sulfoxide appeared to decrease due to the increase in byproduct sulfone formation (Table 2, entries 2, 7–9). Hence, 30 °C was the optimal temperature for the oxidation of sulfides to sulfoxides in the system of 30 wt% H_2O_2 /PAMAM-G1-PMo.

S 30%H ₂ O ₂ , PAMAM-G1-PMo				
		solvent		
	1a		11	b
Entry	Solvent	Time (h)	Temperature (°C)	Yield ^b (%)
1	MeOH	4.0	25	90
2	95%EtOH	4.0	25	85
3	EtOH	4.0	25	60
4	CH ₃ COCH ₃	4.0	25	45
5	CH ₃ COOC ₂ H ₅	4.0	25	40
6	<i>i</i> -PrOH	4.0	25	52
7	95%EtOH	2.0	25	72
8	95%EtOH	2.0	30	91
9	95%EtOH	2.0	35	88

Table 2. Oxidation of sulfide to sulfoxide in different conditions ^a.

 a Reaction conditions: 1a (62 mg, 0.5 mmol), solvent (8 mL), catalyst (50 mg), 30 wt% $\rm H_2O_2$ (63 mg, 0.55 mmol); b Isolated yield.

Furthermore, 1a was still chosen to be the model substrate to optimize the conditions for the oxidation of sulfides to sulfones. In our experience, the formation of sulfones needs higher concentration of the oxidant. The contrast experiments demonstrated that 30 wt% H_2O_2 itself, even if the amount was increased to 300 mol%, could not complete the oxidation. However, once more, this process was greatly promoted by the catalyst PAMAM-G1-PMo. The temperature of the reaction was firstly optimized. As shown in Table 3, when the temperature increased from 30 °C to 40 °C in the system of 30 wt% H_2O_2 /PAMAM-G1-PMo, the yield of the desired sulfone product (1c) increased, but when the temperature increased to 50 °C, the yield of sulfone did not notably change (Table 3, entries 1–3). Hence, 40 °C was the optimal temperature for the oxidation of sulfides to sulfones in the system of 30 wt% H_2O_2 /PAMAM-G1-PMo. In addition, the effects of 30 wt% H_2O_2 in the reaction were investigated. When the amount of 30 wt% H_2O_2 increased from 300 mol% to 400 mol%, there was no major difference in the yield of the desired product (Table 3, entries 2,4). However, if the amount of 30 wt% H_2O_2 decreased to 200 mol%, the yield of the desired product decreased accordingly (Table 3, entry 5). Hence, 300 mol% was an optimal quantity of 30 wt% H_2O_2 for this catalytic oxidation reaction.

Next, we studied the scope of application of this system by testing a diverse range of sulfides, and the results are presented in Table 4. Notably, we observed that most of the substrates tested in the oxidation system were converted to their corresponding products in excellent yields under the optimized reaction conditions. However, we found that (2-chloro-4-nitrophenyl)(phenyl)sulfane (5a), with a strong electron-deficient phenyl group, did not successfully convert to 2-chloro-4-nitro-1-(phenylsulfinyl)benzene (5b) (Table 4, entry 5) and 2-chloro-4-nitro-1-(phenylsulfonyl)benzene (5c) (Table 4, entry 12). Additionally, (2-chlorophenyl)(methyl)sulfane (6a) did not successfully convert to 1-chloro-2-(methylsulfonyl)benzene (6c) (Table 4, entry 13), partially because the *ortho*-substituted chlorine on the benzene ring is also an electron-withdrawing group and has a certain steric hindrance.

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$\begin{array}{c} & & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ $				
	1a	95% EtOH	1c	
Entry	30 wt% H ₂ O ₂ (mol%)	Time (h)	Temperature (°C)	Yield ^b (%)
1	300	3.0	30	60
2	300	3.0	40	93
3	300	3.0	50	92
4	400	3.0	40	93
5	200	3.0	40	81

Table 3. Oxidation of sulfide to sulfone in different conditions ^a.

^a Reaction conditions: 1a (62 mg, 0.5 mmol), 95% EtOH (10 mL), catalyst (150 mg); ^b Isolated yield.

Table 4. The oxidation of sulfides to sulfoxides and sulfones with 30 wt% H_2O_2 catalyzed by PAMAM-G1-PMo ^{a,b}.

Entry	Substrates	Products	Time (h)	Yield ^c (%)
1	الم اa	° s 1b	2.0	91
2	2a	∼o⊂⊂s∼2b	1.5	90
3	O ₂ N 3a	O ₂ N 3b	3.0	85
4	C ^s C _{4a}	o š 4b	3.5	85
5	O ₂ N CI 5a		5.0	trace
6	CI 6a	ci 6b	6.0	93
7	CI S Ta	ci și 7b	4.5	93
8	الم	o, solution of the second seco	3.5	93
9	s2a	~2c	2.0	94
10	O ₂ N 3a		4.0	92
11	C ^s C _{4a}		4.0	93

Entry	Substrates	Products	Time (h)	Yield ^c (%)
12			5.0	NA ^d
13	CI 6a	o.s cl 6c	5.0	trace
14	ci s 7a	cı 7c	4.0	91

Table 4. Cont.

^a Reaction conditions of sulfides to sulfoxides: sulfide (0.5 mmol), 95% EtOH (8 mL), catalyst (50 mg), 30 wt% H_2O_2 (63 mg, 0.55 mmol), 30 °C; ^b Reaction conditions of sulfides to sulfones: sulfide (0.5 mmol), 95% EtOH (10 mL), catalyst (150 mg), 30 wt% H_2O_2 (170 mg, 1.5 mmol), 40 °C; ^c Isolated yield; ^d Not available.

To study the recyclability of the PAMAM-G1-PMo catalyst, we again chose the oxidation of thioanisole (1a) to (methylsulfinyl)benzene (1b) or (methylsulfonyl)benzene (1c) as model reactions. The catalyst PAMAM-G1-PMo was easily recovered by filtration after the reaction, washed with 95% EtOH, and dried in a vacuum at room temperature. After the above treatment, the catalyst was reused for subsequent experiments (up to five runs), and no major differences in the yield or required reaction times were observed, as summarized in Figure 1.



Figure 1. Study of the PAMAM-G1-PMo recyclability for the oxidation of thioanisole to sulfoxide (**left**) and sulfone (**right**).

After being used for five times and separated from the reaction system, the catalysts were characterized by Fourier-transform infrared spectroscopy (FT-IR, Figure 2), X-ray diffraction (XRD, Figure 3), and scanning electron microscopy (SEM, Figure 4). As shown in Figure 2, the IR frequencies of reused PAMAM-G1-PMo (958, 3373, 3100 cm⁻¹) are consistent with those of fresh-prepared PAMAM-G1-PMo, indicating the PMo anions are still successfully immobilized on protonated PAMAM-G1. As shown in Figure 3, the XRD patterns for both fresh-prepared PAMAM-G1-PMo and reused one show a broad band in the range of $2\theta = 14-40^\circ$, which confirms the high dispersion of the PMo anions on PAMAM-G1 support. At last, it can be observed via the SEM spectra (Figure 4) that fresh-prepared PAMAM-G1-PMo and reused one have similar micromorphology, such as the tiny projections on the amorphous surface. The results of all the above detections prove that the PAMAM-G1-PMo, no matter fresh-prepared or reused, has a higher surface-to-volume ratio and more reactive cavities. Besides, there are no noticeable differences between the fresh-prepared catalysts and the reused ones, demonstrating that the catalysts have good stability in the process of oxidation reaction.



Figure 2. The IR spectra of fresh-prepared PAMAM-G1-PMo (left) and reused PAMAM-G1-PMo (right).



Figure 3. The XRD patterns of fresh-prepared PAMAM-G1-PMo (**left**) and reused PAMAM-G1-PMo (**right**).



Figure 4. The SEM spectra of fresh-prepared PAMAM-G1-PMo (top) and reused PAMAM-G1-PMo (bottom).

The present catalytic system was also applied to the preparation of a well-known smart drug Modafinil (2-[(diphenylmethyl)sulfinyl]acetamide, 9), which is a clinically wakefulness-promoting agent to treat disorders such as narcolepsy and excessive daytime sleepiness. Traditionally, Modafinil was produced by the oxidation of 2-[(diphenylmethyl)thio]acetamide (8) with 30 wt% H₂O₂ in acetic acid. However, a considerable amount of sulfone as the main by-product was often generated and difficult to be removed by recrystallization due to its similar physical property with Modafinil [36]. Inspired by the selective oxidation property of the 30 wt% H₂O₂/PAMAM-G1-PMo system, we practiced its application for the oxidation process in preparation of Modafinilf. The final product was obtained in a good yield of 89% and excellent purity of 99.79% after the crude product was collected and recrystallized with acetone (Scheme 1).



Scheme 1. The oxidation process in preparation of Modafinil.

3. Materials and Methods

All reactants and solvents were directly obtained from commercial sources and used without further purification. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance-III 600 spectrometer (Bruker, Zürich, Switzerland). The purity of the products was determined by HPLC with areas of peak normalization method (pump: waters 1525, detector: waters 2489. Chromatographic column: WondaSil C-18, monitoring wavelength used 210 nm).

Infrared spectra were obtained from Fourier-transform infrared spectroscopy (FT-IR, Thermo Scientific IS5) at universal attenuated total reflection (ATR) mode in the range 400–4000 cm⁻¹, using catalyst samples supported on KBr wafers. X-ray diffractometer (XRD, PERSEE XD-3, Beijing Persee instrument co. LTD, Beijing, China.) with monochromated Cu–K α radiation source at 30 kV and 30 mA was used to investigate the crystal structure change between fresh-prepared and reused catalysts, and X-ray diffraction patterns were obtained in a scan range $2\theta = 10-80^{\circ}$ with a scan rate of 4° /min. SEM spectra was obtained from Scanning electron microscope (SEM, FEIQ45, Hitachi, Tokyo, Japan.).

3.1. Preparation and Characterization of PAMAM-G1-PMo

In a typical experiment, PAMAM-G1 (1.0 g, 2.0 mmol) was dissolved in deionized water (35 mL) under room temperature, and Keggin-type $H_3PMo_{12}O_{40}$ (7.3 g, 4.0 mmol) was added while stirring. The resulting mixture was stirred for 48 h and filtered. The solids were washed with deionized water and ethanol, and dried under vacuum at 40 °C for 12 h to afford an aqua powder of PAMAM-G1-PMo.

3.2. Catalytic Reactions

3.2.1. General Experimental Procedure for the Oxidation of Sulfides to Sulfoxides

A 50 mL, three-necked flask was charged with sulfide (0.5 mmol), the catalyst (50 mg), and 95% EtOH (8 mL). The resulting solution was stirred at 30 °C, and 30 wt% H_2O_2 (63 mg, 0.55 mmol) was added slowly into the above mixture. The reaction was monitored by TLC (petroleum ether:ethyl acetate = 7:3). After the reaction was finished, the catalyst was separated from the mixture by filtration, washed with 95% EtOH, and dried in a vacuum at room temperature overnight for recycle use. The filtrate and the washing solution were combined, concentrated under reduced pressure, followed by a freeze-drying. The crude products were purified by column chromatography on a silica gel column

with *n*-hexane/ethyl acetate (2:1) as eluent to afford the desired products. The ¹H NMR and ¹³C NMR data and spectra for corresponding products are available online at Supplementary Materials.

3.2.2. General Experimental Procedure for the Oxidation of Sulfides to Sulfones

A 50 mL, three-necked flask was charged with sulfide (0.5 mmol), the catalyst (150 mg), and 95% EtOH (10 mL). The resulting solution was stirred at 40 °C, and 30 wt% H_2O_2 (170 mg, 1.5 mmol) was added slowly into the above mixture. The reaction was monitored by TLC (petroleum ether:ethyl acetate = 7:3). After the reaction was finished, the catalyst was separated from the mixture by filtration, washed with 95% EtOH, and dried in a vacuum at room temperature overnight for recycle use. The filtrate and the washing solution were combined, concentrated under reduced pressure, followed by a freeze-drying. The crude products were purified by column chromatography on a silica gel column with *n*-hexane/ethyl acetate (2:1) as eluent to afford the desired products. The ¹H NMR and ¹³C NMR data and spectra for corresponding products are available online at Supplementary Materials.

3.2.3. Synthesis of Modafinil

A 250 mL, three-necked flask was charged with 2-[(diphenylmethyl)thio]acetamide (13 g, 50 mmol), the catalyst (5 g), and 95% EtOH (80 mL). The resulting solution was stirred at 30 °C, and 30 wt% H₂O₂ (6.3 g, 55 mmol) was added slowly into the reaction mixture. The mixture was allowed stirring for 2 h at 30 °C. After the reaction was finished, the catalyst was separated from the mixture by filtration, washed with 95% EtOH, and treated for recycle use. The filtrate and washings were combined and transferred to a 1 L beaker containing 500 mL deionized water to form white solid, which was collected by filtration and purified by a recrystallization with 30 mL of acetone to provide 12.3 g of desired product with a HPLC purity of 99.79%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.66–7.49 (m, 5H), 7.44–7.28 (m, 7H), 5.34 (s, 1H), 3.36 (d, *J* = 13.7 Hz, 1H), 3.22 (d, *J* = 13.6 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 165.22, 133.37, 133.06, 128.46, 128.37, 127.93, 127.85, 127.79, 127.66, 70.50, 50.56. The ¹H NMR, ¹³C NMR and HPLC spectra for Modafinil are available online at Supplementary Materials.

4. Conclusions

In summary, we developed a PAMAM-G1-PMo-catalyzed method for the oxidation of sulfides to sulfoxides or sulfones via an efficient and mild procedure. This system is environmentally benign since $30 \text{ wt}\% \text{ H}_2\text{O}_2$ and 95% EtOH are used as the oxidant and solvent, respectively, and the catalysts are recyclable. Moreover, the catalysts are inexpensive, stable during the reaction, and easily recovered by filtration after the reaction and for reuse in additional runs without a noticeable loss of catalytic activity. This is the first report of PAMAM-G1-PMo as the heterogeneous catalyst used in the oxidation of sulfides to sulfoxides or sulfones, which will help the enrichment and development of future research on the dendrimers' hybrid.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/10/791/s1, Figure S1: XRD patterns of HMo.

Author Contributions: Y.L. and M.-S.C. supervised the whole experiment and provided technical guidance. Q.-L.T. and Z.-F.F. performed the preparation and identification of the catalysts, and the investigation of the oxidation conditions. J.-W.Y., Q.L. and Y.-X.C. assisted in the synthesis work.

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Conflicts of Interest: The authors declare no conflict of interest.

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