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Short Communication

Highly efficient selective oxidation of sulfides to sulfoxides by montmorillonite-immobilized metalloporphyrins in the presence of molecular oxygen

Xian-Tai Zhou, Hong-Bing Ji *

School of Chemistry and Chemical Engineering, Sun Yat-sen University, 510275 Guangzhou, China

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ABSTRACT

Highly efficient and selective oxidation of sulfides to sulfoxides with dioxygen catalyzed by cationic *meso*-tetrakis (1-methyl-4-pyridyl) (TM4PyP) metalloporphyrins immobilized into montmorillonite (MT) interlayer was achieved. Manganese (II) porphyrin (MnTM4PyP-MT) presented excellent activity for the oxidation of sulfides under ambient conditions. In the model oxidation, thioanisole was converted completely and the selectivity towards sulfoxide was up to 95%. This catalyst also showed high activity and selectivity for the most sulfides. The catalyst could be reused consecutively five times without significant loss of activity.

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1. Introduction

The selective oxidation of organic sulfides to sulfoxides without any over-oxidation to sulfones is a challenging research interest in synthetic organic chemistry, partly because of the importance of sulfoxides as intermediates in biologically active compounds [1–3]. Among all methods described so far, the oxidation of sulfides by various metal catalysts is one of the most attractive routes [4–6]. Metalloporphyrins have been used as cytochrome P-450 models and have been found to be highly efficient homogeneous catalyst for sulfide oxidation in the presence of various oxidants e.g. NaOCl, oxone and hydrogen peroxide [5–12]. However, decomposing easily and difficulty of recovery is the main weakness, which limit their practical applications in both synthetic chemistry and industrial processes.

Great efforts have been made to immobilize metalloporphyrins onto supports to promote stability in the catalytic oxidations [13–15]. Polystyrene-bound manganese (III) porphyrins were applied in the selective oxidation of sulfides by using sodium periodate as oxidant [16]. Recently, silica supported manganese (III) porphyrins were prepared and used as efficient heterogeneous catalysts for biomimetic oxidation of sulfides with sodium periodate [17]. From economic and environmental viewpoints, immobilizing metalloporphyrins onto one kind of expensive, stable support is gathering more interest.

Due to the large specific surface area, chemical and mechanical stability, layered structure and high cation exchange capacity, montmorillonite is preferable to be used as the support for preparing heterogeneous metalloporphyrins [18]. Although the montmorillonite immobilized metalloporphyrins have been applied in the oxidation of cyclohexene and 2-mercaptoethanol [19–21], the selective oxidation of sulfide catalyzed by montmorillonite-immobilized metalloporphyrins with dioxygen is still unknown. In continuation of our ongoing research on the metalloporphyrin-based oxidation of sulfides [22,23], we report herein an efficient and highly selective oxidation of sulfides to sulfoxides catalyzed by montmorillonite-supported metalloporphyrins catalysts under ambient conditions. The heterogeneous catalyst showed excellent activity and could be reused consecutively five times without significant loss of activity.

2. Experimental

2.1. Materials and instruments

Sulfides were of analytical grade and purchased from Alfa Aesar without further purification unless indicated. Pyrrole and isobutyraldehyde were redistilled before use. Other solvents were all of analytical grade. Montmorillonite-supported metalloporphyrin catalysts were prepared as previously reported, and then characterized by diffuse reflectance UV spectra, infrared, X-ray diffraction, nitrogen adsorption isotherm and scanning electron microscopy [19].

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* Corresponding author. Tel.: +86 20 84113658; fax: +86 20 84113654.
E-mail address: jihb@mail.sysu.edu.cn (H.-B. Ji).

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2.2. Aerobic oxidation of sulfide

A 20 mL Schlenk flask was charged with sulfide (1 mmol), catalyst (0.015 g), toluene (4 mL), isobutyraldehyde (3 mmol), 0.2 mmol naphthalene (inert internal standard) and then the mixture was stirred at 80 °C with a O_2 balloon (1 atm). The product was analyzed by GC (Shimadzu GC-2010 plus) equipped with a flame ionization detector (FID) (conditions of GC: Rtx-5 capillary column, 30 m × 0.25 mm × 0.25 μm, over temperature of 110 °C) and GC–MS (Shimadzu GCMS-QP2010 plus) equipped with Rxi-5 ms capillary column (30 m × 0.25 mm × 0.25 μm).

For the recycling experiments, the catalyst was recovered by centrifugation and first washed with water (5 mL) for 5 times, and then with acetonitrile (10 mL) to remove the occluded reactants and products. After washing, the acetonitrile solution was checked for the existence of reactants/products using gas chromatography. The recycled catalysts were then dried in vacuum at 80 °C for 6 h and re-used using the same experimental conditions as described above. In recycling experiments, the loss of catalyst was compensated in the next catalytic oxidation.

3. Results and discussion

3.1. Catalysis of the various supported metalloporphyrins

With thioanisole as model compound, the effects of various montmorillonite-supported metalloporphyrin catalysts on the oxidation in the presence of dioxygen and isobutyraldehyde have been investigated. The loaded amounts of the MnTM4PyP, CoTM4PyP and FeTM4PyP [*meso*-tetrakis (1-methyl-4-pyridyl) (TM4PyP) manganese, cobalt and iron porphyrins] was 4.7×10^{-5} mol/g, 3.8×10^{-5} mol/g and 3.5×10^{-5} mol/g, respectively. Hence, the weight of MnTM4PyP, CoTM4PyP and FeTM4PyP was 15 mg, 18 mg and 20 mg based on the same mole of each catalyst, 0.7×10^{-3} mmol. The profiles for the yields of sulfoxide and sulfone in the oxidation of thioanisole catalyzed by different metalloporphyrins with molecular oxygen were presented in Fig. 1.

As shown in Fig. 1, the catalytic activity of the metalloporphyrins is dependent on the nature of their central ions. The results show that montmorillonite-supported manganese porphyrins are considerably more selective than cobalt and iron porphyrin catalysts for the aerobic oxidation. The catalytic activity of different metalloporphyrins is probably influenced by their electric potential and the stability of different valences of metal atoms. During the catalytic oxidation reaction, the central metal ion of metalloporphyrin undergoes a transition from high-spin states to low-spin states and finishes electron-transfer by the change of its own valences. For catalyst with higher redox potential, high valent metal-oxo intermediate is more easily reduced to initial valence. In addition, the BET surface area of MnTM4PyP, CoTM4PyP and FeTM4PyP was 83 m^2/g, 67 m^2/g and 62 m^2/g, respectively. Therefore, the catalytic performance for this heterogeneous catalyst is positive related with surface area.

3.2. Effect of catalyst amount on the aerobic oxidation of thioanisole

The influence of MnTM4PyP-MT catalyst amount on the aerobic oxidation of thioanisole in the presence of molecular oxygen and isobutyraldehyde was summarized in Fig. 2.

As shown in Fig. 2, only 4% thioanisole was converted in blank experiment as the reaction was conducted for 45 min with 87% selectivity towards sulfone. The conversion of thioanisole was considerably enhanced when the heterogeneous manganese porphyrin catalyst was used. The MnTM4PyP-MT catalyst crucial in the reaction could be demonstrated from the fact that the conversion of thioanisole was up to 40% even if the amount of catalyst was only 0.005 g (0.23×10^{-3} mmol). As depicted clearly in Fig. 2, the reaction rate increased with the increasing catalyst contents. Thioanisole could be converted completely when the amount of catalyst was 0.015 g (MnTM4PyP: 0.7×10^{-3} mmol), in which the selectivity of sulfoxide was up to 95%. However, as the amount of catalyst was increased continually, the selectivity towards sulfoxide declined apparently. It indicated that the excess catalyst promote the over-oxidation of sulfoxide.

To illustrate whether the selectivity of sulfoxides is influenced by the increasing amount of catalyst, as a comparison, we carried out the homogeneous oxidation of sulfides with the same mole of metal center. It was also observed that the larger amount of catalyst was unfavorable the selectivity towards sulfoxides (selectivity of sulfoxide was 79% with MnTM4PyP 0.94×10^{-3} mmol, while 99% selectivity of sulfoxide was obtained with 0.7×10^{-3} mmol MnTM4PyP catalyst). The increasing amount of catalyst has little influence on the conversion of sulfides (Fig. 2). Therefore, the effect of mass transport limitation on the selectivity towards sulfoxides could be excluded.

3.3. Effect of temperature on the aerobic oxidation of thioanisole

The effect of reaction temperature on the conversion of thioanisole were studied, the results were presented in Fig. 3. The conversion of thioanisole increased greatly with the rising temperature from 50 °C to 80 °C, then kept unchanged at temperature over 80 °C. When the oxidation was conducted under 80 °C, an excellent selectivity towards sulfoxide was obtained. The selectivity towards sulfoxide decreased

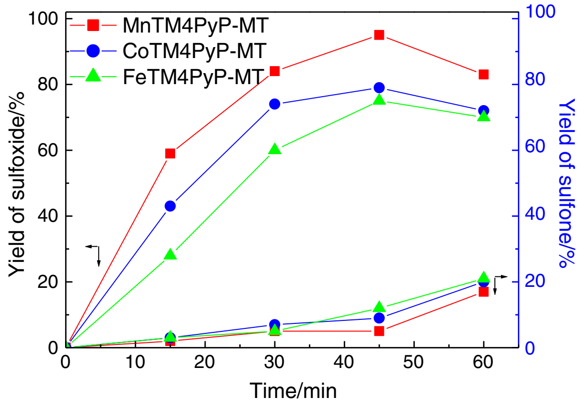


Fig. 1. Profiles of the conversion and yield of sulfoxide for the thioanisole catalyzed by various montmorillonite-supported metalloporphyrins, thioanisole (1 mmol), isobutylaldehyde (3 mmol), toluene (4 mL), catalyst (0.7×10^{-3} mmol), O_2 balloon (1 atm), 80 °C.

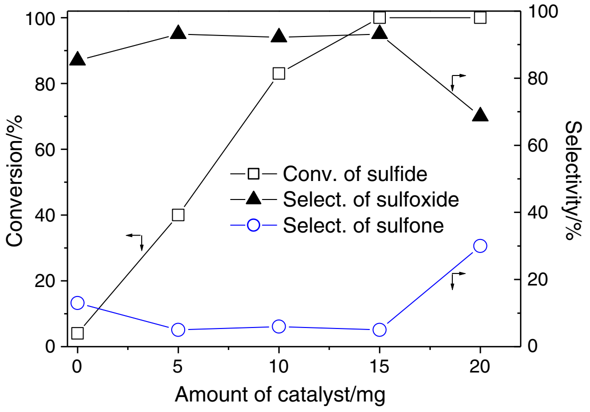


Fig. 2. Effect of the amount of catalyst on the selective aerobic oxidation of thioanisole catalyzed by MnTM4PyP-MT, thioanisole (1 mmol), isobutylaldehyde (3 mmol), toluene (4 mL), O_2 balloon (1 atm), 80 °C, 45 min.

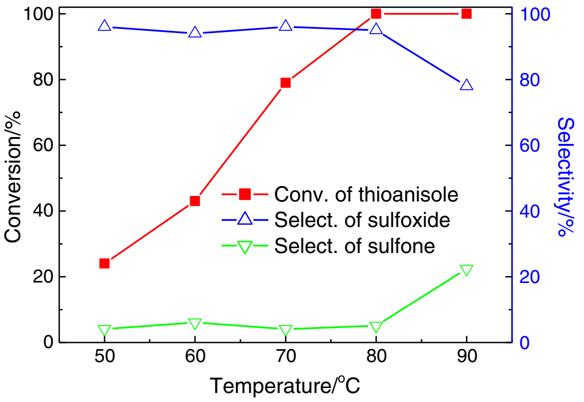


Fig. 3. Effect of the temperature on the selective aerobic oxidation of thioanisole catalyzed by MnTM4PyP-MT, thioanisole (1 mmol), MnTM4PyP-MT (0.7 × 10^{-3} mmol), isobutylaldehyde (3 mmol), toluene (4 mL), O_2 balloon (1 atm), 45 min.

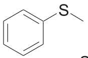
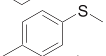
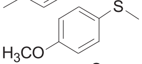
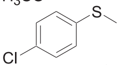
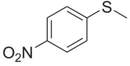
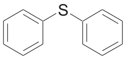
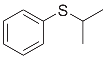
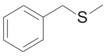
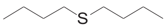
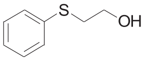
while the temperature was over 80 °C. Evidently, sulfoxide could be further oxidized to sulfone at higher temperature.

3.4. Aerobic oxidation of various sulfides catalyzed by MnTM4PyP-MT catalyst

To evaluate the scope of the catalytic system, various sulfides were subjected to the reaction system using only 0.015 g of montmorillonite-supported manganese porphyrins (Table 1). As shown in Table 1, most substrates could be smoothly selective converted to corresponding sulfoxides with high conversion rate and excellent selectivity.

It can be observed that the efficiency of the oxidation in this catalytic system is related with the electronic property of substrates. Compared with the electron-withdrawing groups at *p*-position of phenyl ring, the electron-donating groups were more favorable to the conversion of sulfides. It indicated that the electron-withdrawing effect retarded the oxidation (entries 1–5). The influence of steric effects could be observed. In the oxidation of diphenyl sulfide and isopropyl phenyl sulfide, the conversion was 82% and 89% after much longer reaction time (entries 6–7), respectively. Comparing with thioanisole, methyl benzyl sulfides could be converted under the same conditions with slightly longer reaction time (entry 8). Sulfoxidation of the linear chain di-n-butyl sulfide smoothly proceeded with high conversion and selectivity (entry 9). In addition, the catalytic system exhibited specific selective oxidation performance towards the sulfide contains hydroxyl group, and no products from hydroxyl group oxidation were detected (entry 10).

Table 1
Selective aerobic oxidation of various sulfides catalyzed by MnTM4PyP-MT[a].

Entry	Substrate	Time (min)	Conv. (%)	Select. (%)	
				Sulfoxide	Sulfone
1		45	>99	95	5
2		45	>99	96	4
3		90	97	98	2
4		90	89	98	2
5		120	90	96	4
6		120	82	98	2
7		60	89	94	6
8		60	99	96	4
9		45	>99	94	6
10		60	90	89	11

[a] Sulfide (1 mmol), MnTM4PyP-MT (0.7 × 10^{-3} mmol), isobutylaldehyde (3 mmol), toluene (4 mL), O_2 balloon (1 atm), 80 °C.

Large scale thioanisole oxidation experiment was carried out. To a stirring solution of toluene (40 mL), thioanisole (10 mmol), isobutyraldehyde (30 mmol) and MnTM4PyP-MT catalyst (0.15 g) were added in the presence of molecular oxygen. After reaction, the crude products were purified via column chromatographic (silica gel, eluting agent: $V_{acetic\ ester}/V_{petroleum\ ether} = 1/3$) to obtain pure sulfoxide (1.27 g, isolated yield 91%).

3.5. Catalyst reuse and stability

The stability of the MnTM4PyP-MT catalyst was monitored using multiple sequential aerobic oxidation of thioanisole in the presence of isobutyraldehyde. The catalyst was recovered by centrifugation, filtration, washed with acetonitrile and dried before using it in the subsequent run. The results are presented in Fig. 4.

From Fig. 4, the catalyst was consecutively reused five times without a significant loss of its activity. The leaching of the metalloporphyrins from the support to the reaction medium was checked by taking UV–vis spectra of the solution at the end of the reaction. No presence of manganese porphyrins, characterized by the Soret band was observed, indicating that the metalloporphyrins remain tightly bound to the support during the oxidation reaction. The results indicated that the supported catalyst was active in the oxidation and could be reused without significant decrease in the catalytic activity and with almost similar selectivity.

3.6. Plausible mechanism of MnTM4PyP-MT catalyzed oxidation of sulfide

As reported previously, the homogeneous oxidation catalyzed by metalloporphyrin complexes plus aldehyde is considered to involve a radical and high-valent metal intermediate mechanism. The feature of radical-involved reaction could be informed from the facts that the oxidation was subsequently quenched in the presence of a free radical inhibitor. High-valent intermediate is generally accepted as the active species for the oxidations catalyzed by metalloporphyrins [24–26]. The oxidation of sulfides was assumed to occur via reactive high-valent metal oxo intermediates, which was generated from a series of radical species in the presence of dioxygen and aldehyde.

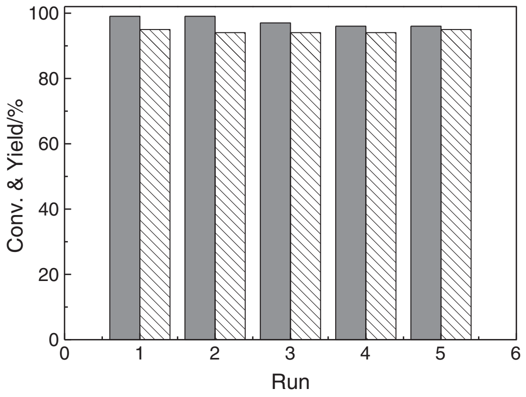


Fig. 4. The stability and reuse of MnTM4PyP-MT catalyst in the aerobic oxidation of thioanisole, (■): conversion of thioanisole, (▨): selectivity towards epoxide.

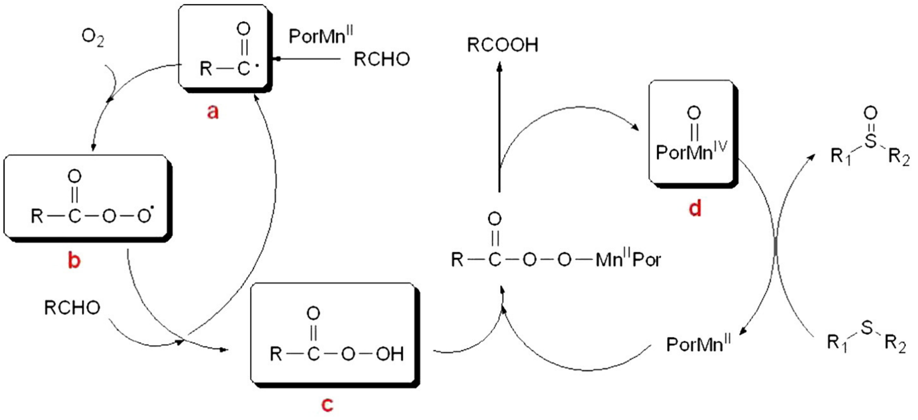


Fig. 5. The plausible mechanism of sulfide oxidation catalyzed by MnTM4PyP-MT catalyst.

Therefore, in the oxidation of sulfides with dioxygen catalyzed by montmorillonite-supported manganese porphyrin system, the high-valent Mn porphyrin intermediate was generated firstly. The proposed mechanism was shown in Fig. 5. The manganese (II) porphyrin reacts with the aldehyde to generate an acyl radical (a) at first. The acyl radical then reacts with dioxygen to give an acylperoxy radical (b). The acylperoxy radical acts as a carrier by reacting with another aldehyde molecule to give peroxyacid (c). Then manganese (IV)-oxo porphyrin intermediate (d) was formed by the reaction of the peroxyacid with the manganese (II) porphyrin. Finally, the sulfoxide was produced by direct oxygen transfer from manganese (IV)-oxo porphyrin to the sulfide [27].

4. Conclusion

In conclusion, highly efficient oxidation of sulfides by molecular oxygen in the presence of montmorillonite-immobilized metalloporphyrins has been reported. The cationic *meso*-tetrakis (1-methyl-4-pyridyl) (TM4PyP) porphyrins (Co, Mn and Fe) immobilized into montmorillonite catalysts were prepared. MnTM4PyP-MT is considerably more selective than cobalt and iron porphyrins catalysts for the oxidation of sulfides. In the model oxidation, thioanisole could be converted completely at 80 °C with 45 min when the amount of catalyst was 0.015 g (Mn: 0.7×10^{-3} mmol), in which the selectivity of sulfoxide was up to 95%. The catalyst could be reused consecutively five times without significant loss of activity.

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References

[1] P.K. Khatri, S.L. Jain, B. Sain, Ind. Eng. Chem. Res. 50 (2011) 701.
[2] E. Muthuswamy, S.L. Brock, J. Am. Chem. Soc. 132 (2010) 15849.
[3] C. Mealli, A. Ienco, A. Poduska, R. Hoffmann, Angew. Chem. Int. Ed. 47 (2008) 2864.
[4] G.E. O'Mahony, A. Ford, A.R. Maguire, J. Org. Chem. 77 (2012) 3288.
[5] P.P. Zhao, M.J. Zhang, Y.J. Wu, J. Wang, Ind. Eng. Chem. Res. 51 (2012) 6641.
[6] F. Gregori, I. Nobili, F. Bigi, R. Maggi, G. Predieri, G. Sartori, J. Mol. Catal. A 286 (2008) 124.
[7] A. Kumar, I. Goldberg, M. Botoshansky, Y. Buchman, Z. Gross, J. Am. Chem. Soc. 132 (2010) 15233.
[8] Q.L. Zhou, K.C. Chen, Z.H. Zhu, J. Mol. Catal. 72 (1992) 59.
[9] J.Y. Huang, S.J. Li, Y.G. Wang, Tetrahedron Lett. 47 (2006) 5637.
[10] S. Rayati, S. Zakavi, H. Kalantari, J. Porphyrins Phthalocyanines 15 (2011) 131.
[11] E. Baciocchi, M.F. Gerini, A. Lapi, J. Org. Chem. 69 (2004) 3586.
[12] P. Le Maux, G. Simonneaux, Chem. Commun. 47 (2011) 6957.
[13] A.L. Faria, T.C.O. Mac Leod, M.D. Assis, Catal. Today 133 (2008) 863.
[14] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, M. Moosavifar, J. Mol. Catal. A 302 (2009) 68.
[15] G. Huang, J. Luo, C.C. Cai, Y.A. Guo, G.W. Luo, Catal. Commun. 9 (2008) 1882.
[16] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, A.A. Abbasi-Larki, Appl. Catal. A. 349 (2008) 177.
[17] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, H. Kargar, M. Araghi, Appl. Catal. A. 353 (2009) 61.
[18] K.G. Bhattacharyya, S. Sen Gupta, Adv. Colloid Interf. 140 (2008) 114.
[19] X.T. Zhou, H.B. Ji, J. Porphyrins Phthalocyanines 16 (2012) 1032.
[20] M. Hassanein, S. Gerges, M. Abdo, S. El-Khalafy, J. Mol. Catal. A 240 (2005) 22.
[21] A.M. Machado, F. Wypych, S.M. Drechsel, S. Nakagaki, J. Colloid Interf. Sci. 254 (2002) 158.
[22] X.T. Zhou, H.B. Ji, Z. Cheng, J.C. Xu, L.X. Pei, L.F. Wang, Bioorg. Med. Chem. Lett. 17 (2007) 4650.
[23] X.T. Zhou, H.B. Ji, Q.L. Yuan, J.C. Xu, L.X. Pei, L.F. Wang, Chin. J. Chem. 26 (2008) 1114.
[24] N.A. Stephenson, A.T. Bell, J. Am. Chem. Soc. 127 (2005) 8635.
[25] X.T. Zhou, H.B. Ji, Chem. Eng. J. 156 (2010) 411.
[26] C.C. Lu, S.D. George, T. Weyhermuller, E. Bill, E. Bothe, K. Wieghardt, Angew. Chem. Int. Ed. 47 (2008) 6384.
[27] E. Baciocchi, M.F. Gerini, O. Lanzalunga, A. Lapi, M.G. Lo Piparo, Org. Biomol. Chem. 1 (2003) 422.