

[Mn(salophen)Cl] Supported on Modified Polystyrene as a Selective Heterogeneous Catalyst for Oxidation of Sulfides under Ultrasonic Irradiation

V. Mirkhani*, S. Tangestaninejad, M. Moghadam, I. Mohammadpoor-Baltork and Z. Saedi
Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan, 81746-73441, Iran

(Received 12 June 2008, Accepted 30 September 2009)

The use of ultrasonic irradiation for the selective synthesis of sulfone in the oxidation of sulfides with NaIO₄ catalyzed by Mn(Salophen) supported on chloromethylated polystyrene-bound imidazole, [Mn(Salophene)-PSI], is reported. This heterogeneous catalyst efficiently catalyzed selective oxidation of sulfides to sulfones under ultrasonic irradiation and no sulfoxide was detected in the reaction mixture.

Keywords: Oxidation, Ultrasonic irradiation, Heterogeneous catalyst, Sulfone, Sodium periodate

INTRODUCTION

Transition metal complexes of porphyrins, phthalocyanines and Schiff bases have been used for mimicking the function of P-450 enzymes [1]. The catalytic activity of these homogeneous catalysts decreases in the reaction media due to the ligand oxidation or formation of dimeric oxo- and peroxo-bridged complexes [2,3]. On the other hand, these catalysts can not be recovered and reused. One practical way to overcome these problems is the immobilization of transition metal complexes on solid supports. Such immobilization makes catalysts recoverable, reusable and desirable for commercial applications. Schiff base complexes (salen or salophen) can be immobilized on supports by non-covalent immobilization in diatomites, clay, zeolite, activated carbon and siloxane membranes, covalent grafting onto inorganic supports such as silica or MCM-41, co-polymerization of a functionalized salen monomer into an organic polymer and attachment or build-up of a salen structure to a preformed polymer [4-23].

Ultrasonic waves are known to play a vital role in the synthesis of organic compounds. The spectacular effects of the ultrasonic waves are due to the cavitation phenomena which lead to the production of free radicals and generation of local hot spots (local conditions of high temperature and pressure) [24]. Ultrasound can be successfully utilized to enhance the selectivity as well as conversion of the desired product by enhancing the rate of the reaction [25].

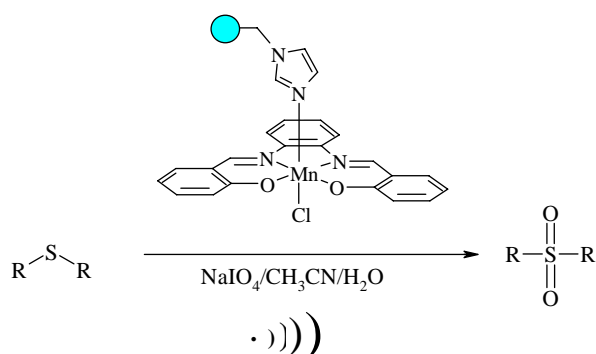
Oxidation of sulfides under ambient conditions is the most straightforward method for the synthesis of sulfoxides and sulfones [26,27]. The synthesis of sulfones has attracted much attention in fine organic synthesis due to their increasing use as agrochemicals, pharmaceutical products and lubricants [26,28].

In the present work, oxidation of sulfides to sulfones with sodium periodate in the presence of [Mn(salophen)Cl]-PSI, as a heterogeneous catalyst and under ultrasonic irradiation is reported (Scheme 1).

EXPERIMENTAL

All materials were commercial reagent grade.

*Corresponding author. E-mail: mirkhani@sci.ui.ac.ir



Scheme 1

Chloromethylated polystyrene (4-5% Cl content and 2% cross-linked with divinylbenzene) was a product of Merck. The Schiff base ligand was prepared by the standard procedure of refluxing ethanolic solutions of the corresponding diamine and salicylaldehyde derivative in a 1:2 molar ratio [29,30]. [Mn(salophen)Cl-PSI] was synthesized according to our previously reported method [22]. A UP 400S ultrasonic processor equipped with a 3 mm wide and 140-mm long probe, which was immersed directly in the reaction mixture, was used for sonication.

General Procedure for the Catalytic Oxidation of Sulfides with Sodium Periodate Catalyzed by [Mn(salophen)Cl]-PSI under Ultrasonic Irradiation

All of the reactions took place under ultrasonic irradiation in a 25 ml flask. A solution of NaIO₄ (2 mmol) in H₂O (10 ml) was added to a mixture of sulfide (1 mmol), [Mn(salophen)Cl]-PSI (0.096 mmol) in CH₃CN (5 ml). The mixture was exposed to ultrasonic irradiation. The progress of the reaction was monitored by TLC. At the end of the reaction, the catalyst was filtered and the reaction products were extracted with Et₂O (2 × 10 ml) and purified on a silica-gel plate or a silica-gel column. ¹H NMR and IR spectral data confirmed the identity of the product (Table 1).

RESULTS AND DISCUSSION

The catalytic activity of [Mn(salophen)Cl]-PSI was studied in the oxidation of diphenyl sulfide in order to optimize

reaction conditions.

Since the best solvent in the alkene epoxidation was CH₃CN/H₂O mixture, the oxidation of diphenyl sulfide was studied in different ratios of acetonitrile/ water as solvent at room temperature (Table 1) where upon the 1:2 ratio of acetonitrile/water mixture was chosen as the desired reaction medium.

Sulfide Oxidation with NaIO₄ Ccatalyzed by [Mn(salophen)Cl]-PSI under Ultrasonic Irradiation

It is well-known that the catalytic ability of manganese Schiff-bases is improved by the use of a nitrogen base as a cocatalyst [31,32]. In this study, the polystyrene-bound imidazole functions not only as a support, but also plays the axial ligand role in the catalytic system. Reactions took place under ultrasonic irradiation in CH₃CN/H₂O containing the sulfide, the oxidant and the catalyst. The results which are summarized in Table 2 showed that this catalytic system was able to catalyze the oxidation of various sulfides such as aromatic, linear cyclic and heterocyclic sulfides with NaIO₄ under ultrasonic irradiation and the corresponding sulfones were obtained in excellent yields (80-100%). Previously, we had reported the sulfide oxidation with homogeneous Mn(salophen)Cl/NaIO₄ catalytic system [33]. The obtained results showed that the products were sulfoxide and sulfone, while in the present system, sulfones were obtained selectively under ultrasonic irradiation. The use of different amounts of oxidant could not change the reaction product and no sulfoxide was detected in the reaction mixture.

Catalyst Reuse and Stability

The stability of [Mn(salophen)Cl]-PSI catalyst was studied in repeated oxidation reactions under ultrasonic irradiation. The oxidation of diphenyl sulfide was chosen as a model substrate to study the catalyst reuse and stability. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with methanol and dried carefully before using it in the subsequent run. After the use of the catalyst for four consecutive times, the sulfone yield was 95%.

The filtrates were used for the determination of manganese leached by atomic absorption spectroscopy. The results showed that only a small amount of the catalyst had been leached in the two first runs (Table 3). Such a finding

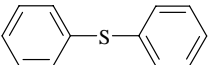
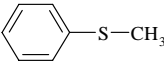
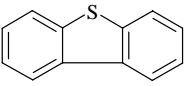
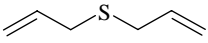
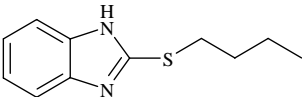
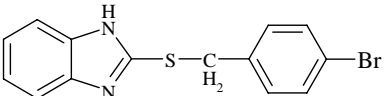
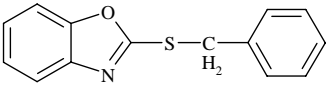
[Mn(salophen)Cl] Supported on Modified Polystyrene

Table 1. Effect of Solvent on the Oxidation of Diphenyl Sulfide with NaIO₄ Catalyzed by [Mn(salophen)Cl]-PSI under Ultrasonic Irradiation^a

Solvent	Conversion (%)	Sulfone (%)	Time (min)
CH ₃ CN/H ₂ O (1:2)	100	100	7
CH ₃ CN/H ₂ O (1:1)	100	100	15
CH ₃ CN/H ₂ O (2:1)	100	100	25

^aDiphenyl sulfide (1 mmol), NaIO₄ (2 mmol), catalyst (0.096 mmol), CH₃CN (5 ml), H₂O (10 ml).

Table 2. Oxidation of Sulfides with NaIO₄ Catalyzed by [Mn(salophen)Cl]-PSI under Ultrasonic Irradiation^a

Entry	Sulfide	Conversion (%)	Sulfone (%)	Time (min)
1		100	100	7
2		100	100	25
3		100	100	15
4		80	80	25
5		100	100	10
6		100	100	85
7		100	100	75

^aSulfide (1 mmol), NaIO₄ (2 mmol), catalyst (0.096 mmol), CH₃CN (5 ml), H₂O (10 ml).

confirmed the strong covalent bonding of the polymer and the metallosalophen, in which the [Mn(salophen)Cl] catalyst was not leached from the polymer during the oxidation reaction.

CONCLUSIONS

The selective oxygenation of organic compounds catalyzed by transition metal compounds is one of the most productive

and elegant techniques for the oxo functionalization of organic substrates. Mn(salophen)Cl supported on polystyrene bound imidazole, ([Mn(salophen)Cl]-PSI) is an efficient catalyst for oxidation of sulfides with NaIO₄ under ultrasonic irradiation. The results showed that the ultrasonic irradiation enhanced the product yield and selectivity. Moreover, the catalyst could be reused several times without significant loss of its catalytic activity.

Table 3. Catalyst Reuse and Stability in the Oxidation of Diphenyl Sulfide under Ultrasonic Irradiation

Entry	Conversion (%)	Time (min)	Mn leached (%) ^a
1	100	7	0.5
2	98	7	0.2
3	95	7	0
4	95	7	0

^aDetermined by atomic absorption spectroscopy.

ACKNOWLEDGEMENTS

The financial support of this work by the Research Council of the University of Isfahan is gratefully acknowledged (Project No. 860308).

REFERENCES

- [1] a) T. Katsuki, *J. Mol. Catal. A: Chem.* 113 (1996) 87; b) T. Katsuki, *Coord. Chem. Rev.* 140 (1995) 189; c) W. Nam, S.E. Park, I.K. Lim, M.H. Lim, J. Hong, J. Kim, *J. Am. Chem. Soc.* 125 (2003) 14674.
- [2] K. Srinivasan, P. Michaud, J.K. Kochi, *J. Am. Chem. Soc.* 108 (1986) 2309.
- [3] J.P. Collman, V.J. Lee, C.J. Kellen-Yuen, X. Zhang, J.A. Brauman, *J. Am. Chem. Soc.* 117 (1995) 692.
- [4] A.R. Silva, C. Freire, B. de Castro, M.M.A. Freitas, J.L. Figueiredo, *Micropor. Mesopor. Mater.* 46 (2001) 211.
- [5] A.R. Silva, C. Freire, B. de Castro, M.M.A. Freitas, J.L. Figueiredo, *Langmuir* 18 (2002) 8017.
- [6] A.R. Silva, J. Vital, J.L. Figueiredo, C. Freire, B. de Castro, *New J. Chem.* 27 (2003) 1511.
- [7] I. Kuzniarska-Biernacka, A.R. Silva, A.P. Carvalho, J. Pires, C. Freire, *J. Mol. Catal. A: Chem.* 278 (2007) 82.
- [8] S.P. Varkey, C. Ratnasamy, P. Ratnasamy, *J. Mol. Catal. A: Chem.* 135 (1998) 295.
- [9] M. Silva, C. Freire, B. de Castro, J.L. Figueiredo, *J. Mol. Catal. A: Chem.* 258 (2006) 327.
- [10] J.M. Fraile, J.I. Garcia, J. Massam, J.A. Mayoral, *J. Mol. Catal. A: Chem.* 136 (1998) 47.
- [11] M.R. Maurya, S.J. Titinchi, S. Chand, *J. Mol. Catal. A: Chem.* 177 (2002) 1.
- [12] A. Heckel, D. Seebach, *Helvetica Chem. Acta* 85 (2002) 913.
- [13] D.A. Annis, E.N. Jacobsen, *J. Am. Chem. Soc.* 121 (1999) 4147.
- [14] H. Zhang, S. Xiang, C. Li, *Chem. Commun.* (2005) 1209.
- [15] S. Xiang, Y. Zhang, Q. Xin, C. Li, *Chem. Commun.* (2002) 2696.
- [16] Y.R. de Miguel, *J. Chem. Soc., Perkin Trans. 1* (2000) 4213.
- [17] G.-J. Kim, S.-H. Kim, *Catal. Lett.* 57 (1999) 139.
- [18] L. Canali, D.C. Sherrington, H. Deleuze, *React. Funct. Polym.* 40 (1999) 155.
- [19] S.T. Regar, K.D. Janda, *J. Am. Chem. Soc.* 122 (2000) 6929.
- [20] B. Bahramian, V. Mirkhani, M. Moghadam, S. Tangestaninejad, *J. Mol. Catal. A: Chem.* 244 (2006) 139.
- [21] B. Bahramian, V. Mirkhani, M. Moghadam, S. Tangestaninejad, *Catal. Commun.* 7 (2006) 289.
- [22] V. Mirkhani, M. Moghadam, S. Tangestaninejad, B. Bahramian, *Appl. Catal. A: Gen.* 311 (2006) 43.
- [23] V. Mirkhani, M. Moghadam, S. Tangestaninejad, B. Bahramian, *Polyhedron* 25 (2006) 2904.
- [24] M.A. Kelkar, R.P. Gogate, A.B. Pandit, *Ultrason. Sonochem.* 13 (2006) 523.
- [25] N.N. Mahamuni, R.P. Gogate, A.B. Pandit, A.B. Ultrason. Sonochem. 14 (2007) 135.

[Mn(salophen)Cl] Supported on Modified Polystyrene

- [26] K. Bahrami, *Tetrahedron Lett.* 47 (2006) 2009.
- [27] D.A. Alonso, C. Najera, M. Varea, *Tetrahedron Lett.* 43 (2002) 3459.
- [28] A. Arcoria, F.P. Ballistreri, *J. Mol. Catal.* 18 (1983) 177.
- [29] G.J. Kim, D.W. Park, *Catal. Today* 63 (2000) 537.
- [30] a) D. Chan, A.E. Martell, *Inorg. Chem.* 26 (1987) 1026;
b) B.M. Trivedi, P.K. Bhattacharya, P.A. Ganeshpure, S. Satish, *J. Mol. Catal.* 75 (1992) 109.
- [31] J.P. Collman, L. Zeng, I.J. Brauman, *Inorg. Chem.* 43 (2004) 2672.
- [32] Z. Groos, S. Ini, *J. Org. Chem.* 62 (1997) 5514.
- [33] V. Mirkhani, S. Tangestaninejad, M. Moghadam, I. Mohammadpoor-Baltork, H. Kargar, *J. Mol. Catal. A: Chem.* 242 (2005) 251.