# Silica-supported cobalt(II) tetrasulfophthalocyanine catalyzed aerobic oxidation of thiols to disulfides under neutral conditions

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Abstract A very simple and mild reaction is described for the aerobic oxidative coupling of thiols to disulfides by silica-supported cobalt(II) tetrasulfophthalocyanine as the catalyst in non-aqueous media under neutral conditions at room temperature. The catalyst can be reused for the oxidative coupling of several thiols without any significant loss of catalytic activity.

**Keywords** Oxidation; Thiols; Disulfides; Cobalt(II) tetrasulfophthalocyanine.

#### Introduction

The oxidative coupling of thiols to disulfides is of interest from the point of view of the synthetic, biological, and petroleum industry [1–5]. For selective oxidation of thiols several methods have been developed. For example  $I_2/HI$  [6],  $Br_2$  [7],  $KMnO_4/CuSO_4$  [8],  $H_2O_2$  in trifluoroethanol [9] and *DMSO* [10], *N*-phenyltriazolinedione [11], manganese(III) *Schiff*-base complex [12], bromine on hydrated silica gel support [13], potassium dichromate [14], and enzymatic [15] and electrochemical [16] methods are used for this conversion. Most of these suffer from drawbacks, such as the use of stoichiometric amounts of reagents that generate undesirable waste materials.

To overcome these drawbacks, catalytic oxidation using oxygen as co-oxidant has been developed by several groups. One of the efficient oxidative couplings of thiols to disulfides has been reported by using transition metallophthalocyanines in basic aqueous media [17-19]. However, not only the aqueous bases always cause a problem of spent caustic materials, but the main drawbacks of these catalysts are the poor solubility in common organic solvents and the formation of  $\mu$ -oxo-dimers in the case of water soluble tetrasulfonated phthalocyanines, which decrease the reactivity in aqueous media [20]. Thus, metallophthalocyanines have been immobilized on a variety of solid supports for stability and easy catalyst recovery. However, not only the efficiency of these catalytic systems was lower than that obtained under homogenous conditions but they are used with H<sub>2</sub>O<sub>2</sub> or KHSO<sub>4</sub> as activator of metallophthalocyanines [21].

During the course of our studies on the development of new routes for the oxidation of sulfur compounds [22] and the synthesis of phthalocyanines [23], we now describe aerobic oxidative coupling of thiols





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Product	R	Yield/%	$mp/^{\circ}C$ or $bp/^{\circ}C$	
			Found	Reported
2a	PhCH <sub>2</sub>	98, 98, 98, 98,98,98ª	70	69–72 <sup>b</sup>
2b	Ph	98, 98 <sup>a</sup>	61	59–60 <sup>b</sup>
2c	4-MePh	97, 97 <sup>a</sup>	45	$45-46^{\circ}$
2d	3-ClPh	98	210-213	213-219 <sup>d</sup>
2e	4-ClPh	97	72	73–74 <sup>e</sup>
2f	4-MeOPh	98, 98 <sup>a</sup>	43	43-44 <sup>f</sup>
2g	2-furylmethyl	95	109-112	112–115 <sup>g</sup>
2h	2-naphthyl	96	136	139 <sup>c</sup>
2i	cyclohexyl	98	126	125-130 <sup>h</sup>
2k	$CH_3(CH_2)_{7-}$	92	71–73	74–75 <sup>i</sup>
21	$CH_{3}(CH_{2})_{3^{-}}$	95	111–113	114–115 <sup>f</sup>

Table 1 Selective oxidation of thiols (1 mmol) to disulfides with cobalt(II) tetrasulfophthalocyanine at room temperature

<sup>a</sup> The same catalyst was used for each of the five runs

<sup>b</sup> Ref. [24], <sup>c</sup> Ref. [25], <sup>d</sup> Ref. [26], <sup>e</sup> Ref. [27], <sup>f</sup> Ref. [28], <sup>g</sup> Ref. [29], <sup>h</sup> Ref. [30], <sup>i</sup> Ref. [31]

to disulfides using silica-supported cobalt(II) tetrasulfophthalocyanine as a reusable catalyst in nonaqueous media under neutral conditions at room temperature (Scheme 1).

### **Results and discussion**

Cobalt(II) tetrasulfophthalocyanine-silica is readily prepared by the addition of silica to an aqueous solution of cobalt(II) tetrasulfophthalocyanine at room temperature. The slurry is poured into a chromatography column, and the reaction is done by percolating of a solution of thiols in *EtOAc* through the column. The pure product is obtained by evaporation of the solvent. As indicated in Table 1, various alkyl and aryl thiols are converted into the corresponding disulfides in very high yields. This is a highly useful reaction for the oxidation of thiols, which are meager impurities in petroleum. A further set of experiments was carried out to examine the reusability of the silica-supported cobalt(II) tetrasulfophthalocyanine catalyst. After the oxidative coupling of benzylthiol (5 times, entry 2a, Table 1), the same column was used for the oxidations of benzenethiol (98% entry 2b, Table 1), 4-methylbenzenethiol (97%, entry 2c, Table 1), and 4-methoxybenzenethiol (98%, Entry 2f, Table 1) proving the high efficiency of the silica-supported cobalt(II) tetrasulfophthalocyanine catalyst.

In conclusion, we have shown that the silica-supported cobalt(II) tetrasulfophthalocyanine, which can be easily prepared from commercially available starting material, efficiently catalyzed the selectively synthesis of disulfide by aerobic oxidation of thiols in non-aqueous media under neutral conditions at room temperature. The reaction is clean and it allows easier product separation. The catalyst can be reused in further reactions or in continuous operations without loss of catalytic activity.

#### Experimental

Melting points were measured on an Electrothermal 9100 apparatus. IR and <sup>1</sup>H NMR spectra were recorded on a Shimadzu IR-470 spectrometer and a BRUKER DRX-300 AVANCE spectrometer at 300.13 MHz. <sup>1</sup>H NMR spectra were obtained using CDCl<sub>3</sub> solutions.

Cobalt(II) tetrasulfophthalocyanine was prepared according to Ref. [23c].

## *Typical experimental procedure for the preparation of 1,2-dibenzyldisulfide*

Preparation of silica-supported cobalt(II) tetrasulfophthalocyanine (CoTSPc/SiO<sub>2</sub>) was accomplished by dissolving 30 mg cobalt(II) tetrasulfophthalocyanine in 25 cm<sup>3</sup> water and adding 1 g silica. The suspension is stirred magnetically at room temperature for 30 min. The slurry is poured into a column of 15 cm length and 2.15 cm diameter. Then, the solution of 0.124 g benzylthiol (1 mmol) in  $2 \text{ cm}^3 \text{ EtOAc}$  was added to the column, it was eluated with EtOAc:n-hexane (15:1) through the column containing the silica-supported cobalt(II) tetrasulfophthalocyanine at a convenient flow rate  $(0.5 \text{ cm}^3/\text{min})$ , and the effluent solution of product was collected. After evaporation of solvent under reduced pressure, the product 2a (0.242 g, 98%) is obtained with high purity. All of the products are known and they were characterized by IR and <sup>1</sup>H NMR spectra and melting point which were compared with those obtained from authentic samples.

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#### References

- Ogawa A, Nishiyama Y, Kambe N, Murai S, Sonoda N (1987) Tetrahedron Lett 28:3271
- 2. Antebi S, Alper H (1985) Tetrahedron Lett 26:2609
- Bischoff L, David C, Martin L, Meudal H, Roques BP, Fournie ZMC (1997) J Org Chem 62:4848
- a) Bodanszky M (1984) Principles of Peptide Synthesis: Reactivity and Structure Concepts in Organic Chemistry. Springer Verlag, Hiderberg, p 307; b) Aida T, Akasaka T, Furukawa N, Oae S (1976) Bull Chem Soc Jpn 49:1441
- a) Jocelyn PC (1992) Biochemistry of the Thiol Groups. Academic Press, New York; b) Basu S, Satapathy S, Bhatnaga AK (1993) Catal Rev Sci Eng 35:571
- 6. Wu X, Reike RD, Zhu L (1996) Synth Commun 26:191
- 7. Drabowicz J, Mikolajczyk M (1980) Synthesis:32
- 8. Noureldin NA, Caldwell M, Hendry J, Lee DG (1998) Synthesis:1587
- 9. Kesavan V, Bonnet DD, Begue JP (2000) Synthesis:223
- a) Tam JP, Wu CR, Liu W, Zhang JW (1991) J Am Chem Soc 113:6657; b) Shad STA, Khan KM, Fecker M, Voelter W (2003) Tetrahedron Lett 44:6789
- 11. Christoforou A, Nicolaou G, Elemes Y (2006) Tetrahedron Lett 7:9211
- 12. Golchoubian H, Hosseinpoor F (2007) Catal Commun 8:697
- 13. Ali MH, Dermott MM (2002) Tetrahedron Lett 43:6271
- 14. Patel S, Mishra BK (2004) Tetrahedron Lett 45:32
- 15. Sridhar M, Vadivel SK, Bhalerao UT (1998) Synth Commun 28:1499

- 16. Leite SLS, Pardini VL, Viertler H (1990) Synth Commun 20:393
- 17. Sanz R, Aguado R, Pedrosa MR, Arnaiz FJ (2002) Synthesis:856
- Karimi B, Hazarkhani H, Zareyee D (2002) Synthesis:2513
- 19. Chatti I, Ghorbel A, Grange P, Colin JM (2002) Catal Today 75:113
- 20. Chauhan SMS, Kumar A, Srinivas KA (2003) Chem Commun:2348
- 21. Sanchez M, Chap N, Cazaux JB Meunier B (2001) Eur J Inorg Chem:1775
- a) Shaabani A, Rezayan AH (2007) Catal Commun 8:1112; b) Shaabani A, Mirzaei P, Naderi S, Lee DG (2004) Tetrahedron 60:11415; c) Shaabani A, Mirzaei P, Lee DG (2004) Catal Lett 97:3; d) Shaabani A, Tavasoli-Rad F (2005) Synth Commun 35:571; e) Shaabani A, Soleimani K, Bazgir A (2004) Synth Commun 34:3303
- 23. a) Safari N, Jamaat PR, Pirouzmand M, Shaabani A (2004) J Porphyrins Phthalocyanines 8:1209; b) Shaabani A, Rezayan AH (2005) J Porphyrins Phthalocyanines 9:617; c) Safari N, Jamaat PR, Shirvan SA, Shoghpour S, Ebadi A, Darvishi M, Shaabani A (2005) J Porphyrins Phthalocyanines 9:256
- 24. Field L, Lawson JE (1958) J Am Chem Soc 80:838
- 25. Wallace TJ (1964) J Am Chem Soc 86:2018
- 26. The Sadtler Standard Spectra, NMR, Sadtler Research Laboratories, INC, 12327M (1972) CA 52 4543 (1958)
- 27. Yiannios CN, Karabinos JV (1963) J Org Chem 28:3246
- 28. Huang M, Chan CC (1982) Synthesis:1091
- 29. Aldrich Handbook of Fine Chemicals 1996-97
- 30. Orito K, Hatakeyama T, Takeo M, Suginoma H (1995) Synthesis:1357
- 31. Dictionary of Organic Compounds, 6th edn., Chapman and Hall, London (1966)