

# Copper chloride/kieselguhr: an efficient catalyst for oxidation of thiols to disulfides by molecular oxygen or air

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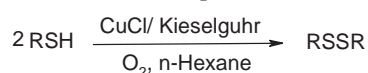
Kieselguhr supported copper chloride catalyses the oxidation of thiols to disulfides in the presence of oxygen or air.

**Keywords:** oxidation, thiols, disulfides, copper(I) chloride

The conversion of thiols to corresponding disulfides is an important reaction in biological and chemical processes<sup>1</sup> and many reagents such as cerium (IV) salts,<sup>2</sup> permanganates,<sup>3</sup> transition metal oxides,<sup>4</sup> chromium peroxide,<sup>5</sup> sodium perborate,<sup>6</sup> ferric chloride,<sup>7</sup> sodium chlorite,<sup>8</sup> copper (II) nitrate<sup>9</sup> and halogens<sup>10</sup> have been developed for the oxidation of thiols to disulfides.

The increasing environmental concern surrounding the use of toxic and dangerous oxidants has impelled organic chemists to develop catalytic oxidation methodologies using molecular oxygen as primary oxidant. In this context catalytic oxidation of thiols to disulfides by molecular oxygen using basic alumina,<sup>11</sup> Fe (III)/NaI,<sup>12</sup> cobalt phthalocyanine<sup>13</sup> and Co(II) and Mn(II) salts supported on silica gel<sup>14</sup> as catalysts have been reported.

During the course of our systematic study on catalytic oxidation of organic compounds with molecular oxygen,<sup>14–19</sup> we have recently developed a heterogeneous catalytic method base on copper chloride supported on silica gel that is an efficient and convenient catalyst for the oxidation of alkyl halides and alkyl tosylates to the carbonyl compounds<sup>18</sup> and oxidative cleavage of oximes and phenylhydrazones.<sup>19</sup> Here we report this method for oxidation of thiols to disulfides. This catalyst is stable, reusable and easily prepared by the addition of weighed amount of kieselguhr to an aqueous solution of CuCl, followed by evaporation of solvent to dryness. The oxidation of thiols is carried out in *n*-hexane as solvent and work-up is simply by extraction and separation of catalyst by filtration. After removal of solvent and purification of products disulfides are obtained in high yields (Table 1) without any evidence for the formation of corresponding sulfonic acid or other oxidation product.



The catalyst was recovered quantitatively after each experiment and can be reused. The reusability of the catalyst after four successive oxidations of thiophenol to diphenyl disulfide is shown in Table 2.

To evaluate the catalytic effects of CuCl/kieselguhr, experiments were carried out under similar condition but

**Table 1** Oxidation of thiols to disulfides by oxygen or air in presence of CuCl/ Kieselguhr

Entry	Substrate	Oxygen		Air	
		Time/h	Yield/% <sup>a</sup>	Time/h	Yield/% <sup>a</sup>
1	Thiophenol	0.5	98	2	92
2	Benzylmercaptan	0.5	94	2	90
3	4-methylthiophenol	0.5	95	2	90
4	4-chlorothiophenol	0.5	95	2	90
5	1-octanethiol	1	91	2	84
6	1-butanethiol	1	88	2	85

<sup>a</sup>Isolated yields

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**Table 2** Reusability of catalyst for the oxidation of thiophenol to diphenyl disulfide

Experimental trial	Yield/%
1	98
2	95
3	93
4	91

without catalysts. The results showed that there was no oxidation of 1-octanethiol to corresponding disulfide even after 24 h.

In summary we have extended successfully the application of CuCl/Kieselguhr for oxidation of thiols to disulfides by oxygen. This method offers some advantages in terms of simplicity of performance, reusability of catalyst and no side product formation or over oxidation. The greatest advantages of this procedure arise from its employment of molecular oxygen and air for oxidation.

## Experimental

Products were characterised by comparison of their physical and spectral data with those of authentic samples. All yields refer to isolated products after column chromatography. IR and NMR spectra were recorded on Perkin Elmer 781 and Bruker DPX500. Progress of the reaction was monitored by TLC. CuCl/kieselguhr was prepared according to Hashemi *et al.*<sup>18,19</sup>

*A typical procedure for the oxidation of thiols to disulfides:* To a stirring solution of thiophenol (110 mg, 1mmol) in *n*-hexane (25 ml) was added CuCl/ Kieselguhr reagent (5 g). The reaction mixture was refluxed for 0.5 h during which time oxygen was bubbled at the rate of 15 ml min<sup>-1</sup> into the solution. When the reaction was completed, the reaction mixture was cooled to room temperature and then filtered to recover the solid material. The residue was washed thoroughly with *n*-hexane (20 ml). Evaporation of *n*-hexane followed by recrystallisation from ethanol yielded pure diphenyl disulfide in 98% yield.

The above experiment was repeated using air instead of oxygen (see Table 1).

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