



Short communication

Solvent, metal and halogen-free synthesis of sulfoxides by using a recoverable heterogeneous urea-hydrogen peroxide silica-based oxidative catalytic system

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ABSTRACT

An efficient and green protocol was used for the selective oxidation of sulfides to sulfoxides by using silica sulfuric acid (SSA) as a recoverable heterogeneous solid acid catalyst in the presence of urea-hydrogen peroxide (UHP) under toxic transition metal-, solvent- and halogen-free conditions at room temperature. The present method offers several noteworthy advantages, such as high product yields, easy work-up, non-toxicity, easy preparation and reusability of the catalyst for at least six runs, which make this procedure the most convenient and attractive with low cost of catalyst and oxidant.

1. Introduction

The selective oxidation of organosulfur compounds such as sulfides to the corresponding sulfoxides has been a challenge for many years owing to the extensive application of sulfoxides in organic synthesis and their importance in various medical, biological and technological applications, including: drugs [1–3], flavors [4], germicides [5], chiral ligands [6,7] and molecular rearrangements [8,9].

For this reason, many methods have been developed over the years to increase the efficiency of these kinds of oxidation reactions. For example, oxidation of sulfides has been reported in the presence of various catalysts and oxidants (e.g. metal oxidants, organic oxidants, peroxides, halogens and air) [10]. Among a lot of different oxidants, aqueous hydrogen peroxide has been one of the most important “green oxidants”, offering the advantages of safety in storage and operation, being cheap, readily available, having highly effective oxygen content and environmentally-benign with the formation of water as the only by-product [11–15].

Although different catalysts, such as polyoxometallates and transition-metal Schiff-base complexes, have been used for H₂O₂-based oxidation of sulfides, most of them suffer from one or more limitations such as high cost, the requirement of a promoter or co-catalyst, high temperatures, long reaction times, chlorohydrocarbon solvents and excessive use of H₂O₂. Furthermore, there are several disadvantages for the metal-catalyzed methods such as the use of toxic transition metal compounds, the preparation of complex catalysts and remaining metals

in products [16–20]. In spite of all the advantages of H₂O₂, the handling of its concentrated solutions is not desirable because of safety problems. Therefore, urea-hydrogen peroxide (UHP), as an urea-adduct compound has attracted much attention since it is inexpensive, commercially available, stable solid and anhydrous source of H₂O₂ [21]. In addition, most of the catalysts are required to use a solvent in the reaction, while it is highly favorable to expand a process in the absence of any solvent, which this aspect is very important from the viewpoint of green chemistry.

Due to environmental, economic and industrial aspects and based on green chemistry principles, recoverable heterogeneous catalysts play important roles in the development of organic functional group transformations and are suitable alternatives for transition metals and liquid acid catalysts [22–28]. Owing to the numerous privilege of inexpensive and non-hazardous reusable heterogeneous catalysts, silica sulfuric acid (SSA) has been considered as a powerful catalyst for a variety of organic reactions under facile circumstances [27,28].

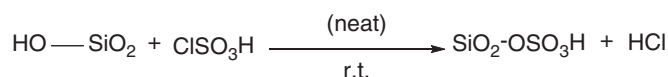
2. Experimental

2.1. General

All chemicals were purchased from Merck and Aldrich chemical companies. Melting points were measured on a Buchi B-540 apparatus. Infrared spectra were recorded on ABB FT/IR 2000 Bruker FT-IR spectrophotometer. ¹H and ¹³C NMR spectra were recorded in CDCl₃ as the

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Scheme 1. Preparation of SSA.

solvent and TMS as the internal standard on a Bruker AQS 300 Avance spectrophotometer at 300 and 75 MHz, respectively. Preparative TLC was performed using silica gel kieselgel 60 PF₂₅₄ + 366. All yields refer to isolated products.

2.2. Preparation of silica sulfuric acid (SSA)

A 500 mL suction flask was equipped with a constant pressure-dropping funnel containing chlorosulfonic acid (23.3 g, 0.2 mol) and a gas inlet tube for conducting HCl gas over an absorbing solution, i.e. H₂O. Then, 60.0 g of silica gel was charged into the flask. Chlorosulfonic acid was added drop wise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately. After the addition was complete, the mixture was shaken for 30 min and SSA was obtained (76 g) as a white solid (Scheme 1) [27]. Synthesized catalyst was characterized with FT-IR spectroscopy.

2.3. General procedure for the oxidation reactions catalyzed by UHP/SSA

The solid reaction mixture containing the sulfide (1 mmol), UHP (2 mmol) and SSA (0.1 g) were thoroughly mixed and the resulting mixture was stirred magnetically. The progress of the reaction was followed by TLC (eluent: *n*-hexane/ethyl acetate: 2:1). After completion of the reaction, CHCl₃ (20 mL) was added and the solid catalyst was removed by filtration. The filtrate was washed with water (15 mL) and the extract was dried over MgSO₄. After evaporation of the solvent, the crude product was purified by chromatography on silica gel (25–30 mesh), eluting with ethyl acetate/*n*-hexane to give pure sulfoxides.

2.4. Spectral data of a selected product

2.4.1. 4-(Bromo phenyl) benzyl sulfoxide

Colorless crystals. M.p.: 138–139 °C (139–140 °C) [32]. IR (KBr) ν : 3060, 2961, 1454, 1067, 1038, 766 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ : 4.01 (d, 1H, *J* = 12.4 Hz), 4.1 (d, 1H, *J* = 12.4 Hz), 6.96–6.99 (d, 2H, *J* = 6 Hz), 7.18–7.33 (m, 5H), 7.52–7.56 (d, 2H, *J* = 8.4 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 63.44, 125.62, 126.03, 128.43, 128.55, 128.63, 130.36, 132.02, 141.89.

3. Results and discussion

Current demand for environmentally friendly processes requires the

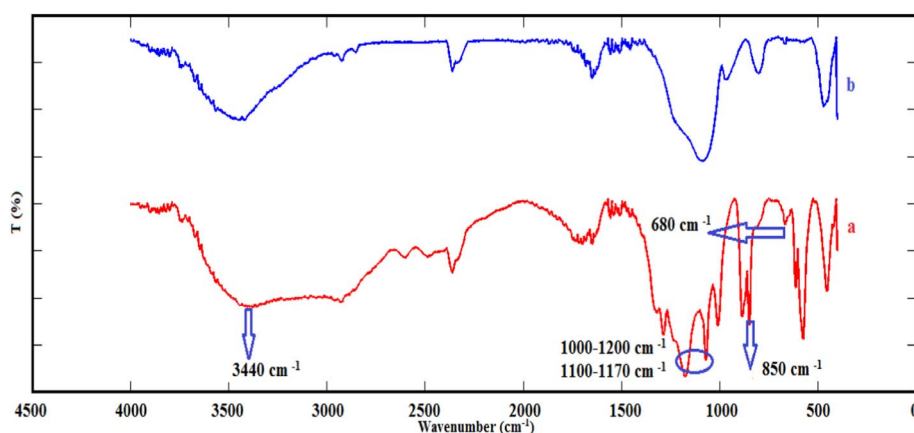


Fig. 1. FT-IR spectra of silica sulfuric acid (a) and silica gel (b).


Table 1
Optimization of the relative amounts of reagents under solvent-free conditions.^a

Entry	UHP (mmol)	SSA (g)	Time (min)	Yield ^b (%)
1	1	0.05	300	33
2	1	0.1	120	40
3	1	0.15	90	52
4	1.5	0.05	90	65
5	1.5	0.1	65	85
6	2	0.1	35	95
7	2	0.15	40	95
8	2.5	0.1	40	95

^a 4-(Bromo phenyl) benzyl sulfide (1 mmol), r.t.

^b Isolated yields.

Table 2
Oxidation of sulfides to sulfoxides in the presence of SSA/UHP.^a

Entry	R ¹ R ²	Time (min)	Yield ^a (%)	M.p.(°C) Found	Reported
1	Ph PhCH ₂	35	95	122–123	124 [30]
2	4-Cl-C ₆ H ₄ PhCH ₂	40	93	127–129	126–127 [31]
3	4-Br-C ₆ H ₄ PhCH ₂	35	95	138–139	139–140 [32]
4	<i>n</i> -Octyl PhCH ₂	35	90	69–70	71–71.5 [33]
5	Ph Ph	65	69	71–72	72 [30]
6	4-Me-C ₆ H ₄ PhCH ₂	40	93	122–124	121–122 [31]
7	PhCH ₂ PhCH ₂	30	95	135–136	136 [30]
8	4-Cl-C ₆ H ₄ CH ₃	35	91	42–44	45–46 [30]
9	<i>n</i> -Butyl <i>n</i> -Butyl	30	88	Colorless oil	Oil [31]
10	Ph CH ₃	30	96	Colorless oil	Oil [31]
11	4-Br-C ₆ H ₄ CH ₃	35	94	74–76	72–75 [34]
12	4-Br-PhCH ₂ PhCH ₂	35	94	139–140	139–140 [20]
13	Ph Allyl	30	95	Colorless oil	Oil [30]
14		25	93	Colorless oil	Oil [35]

^a Isolated yields.

synthesis of new catalysts and the development of green oxidation methods that use clean oxidants, such as hydrogen peroxide, without any solvent. Because of the importance of solid-phase-assisted reaction systems in green chemistry, as well as to overcome the above-mentioned limitations, such as over-oxidation to sulfones, low selectivity, low yields, toxicity and expensive reagents or catalysts, and also as part

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