

Cellulose Sulfuric Acid: As an Efficient Bio Polymer Based Catalyst for the Selective Oxidation of Sulfides and Thiols by Hydrogen Peroxide

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ABSTRACT: Cellulose sulfuric acid as a bio-polymer based solid catalyst efficiently catalyzes the selectively oxidation of sulfides to sulfoxides and thiols to disulfides using hydrogen peroxide as a green oxidant with good yields at room temperature. The developed method offers a number of advantages such as high selectivity, mild reaction conditions, simple operation, cleaner reaction profiles, low cost and biodegradability of the catalyst.

KEY WORDS: Cellulose sulfuric acid, Oxidation, Sulfide, Thiol, Hydrogen peroxide.

INTRODUCTION

The oxidation of organosulfurs is of a great importance in synthesis of drug, drug metabolism and the preparation of bioconjugates compounds [1,2]. In addition, the removal of sulfur from fuels, and industrial products and wastes is important in chemical industry. In this regard, several new methods were recently proposed for the removal of sulfur by oxidation [1-3].

Heterogeneous solid acid catalysts for the synthesis of fine chemicals have attracted considerable attention from both environmental and economic points [4]. Majority of the reported supports for catalytic applications is based on inorganic materials or functional synthetic polymers in which the synthesis of the supports involves high temperature calcinations or polymerization of petrochemical base feed stocks [6,7]. Biopolymers, especially cellulose and its derivatives [8] which have some unique properties are attractive and alternative supports for catalytic process in synthesis of conventional organic or inorganic compounds. Cellulose is one of

the most abundant natural bio-polymers in the world and has been widely studied during the past decades because of it is a biodegradable material and a renewable resource.

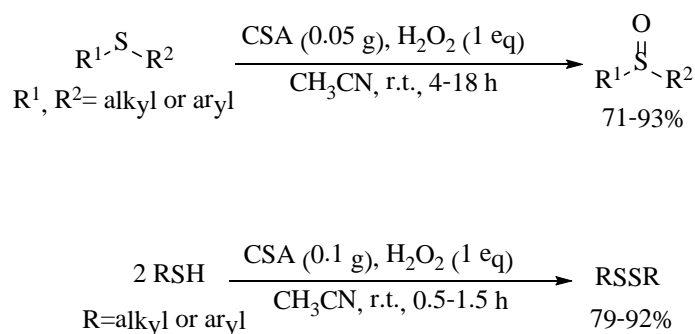
In this context, Cellulose Sulfuric Acid (CSA) is one of the useful heterogeneous catalysts which has a good performance as an inexpensive biopolymer-based catalyst and can be easily separated without contaminating the products [9]. The aim of this study is to utilize cellulose supported sulfuric acid as a catalyst for the selective oxidation of sulfides to sulfoxides and thiols to disulfides using hydrogen peroxide (H_2O_2) as a green oxidant. Over other traditional oxidants, H_2O_2 has many advantages. The major benefit of using H_2O_2 is its environmental concern in view of effective-oxygen content (47%) and more importantly, entire process is very clean since water is the only side product [10-13]. Furthermore, H_2O_2 has acceptable safety in storage and operation [14, 15]. Hydrogen peroxide is a mild oxidizing agent, and often activated by homogeneous [16-19] or heterogeneous [20-22] catalysts.

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Scheme 1: Selective oxidation of thiols and sulfides by hydrogen peroxide in the presence of a catalytic amount of CSA.

In connection with our studies on the development of new routes for the oxidation of organic compounds [23-29] and exploring CSA as a solid acid catalyst [9,30-33], we wish to report herein the selective oxidation of alkyl and aryl sulfides to sulfoxides and thiols to disulfides, in good yields with aqueous hydrogen peroxide in the presence of CSA as an efficient solid acid catalyst (Scheme 1).

EXPERIMENTAL SECTION

Apparatus

Melting points were measured on an Electrothermal 9200 apparatus. The chemicals used in this work were purchased from Merck and Fluka chemical companies. Conversion of the sulfides and selectivity for the sulfoxides was determined by GC by using Agilent GC with FID detector.

General experimental procedure for the oxidation of sulfides and thiols

In a round bottom flask, to a solution of sulfide or thiol (1 mmol) in CH₃CN (5 ml), 30% (w/w) H₂O₂ (1mmol) and the CSA catalyst (0.05 g for oxidation of sulfides and 0.1 g for oxidation of thiols) was added successively and the mixture was stirred magnetically at room temperature for the indicated time in Table 3. The progress of the reaction was monitored by TLC or GC. After completion of the reaction, the reaction mixture was filtered and the excess of solvent was removed under reduced pressure to give the corresponding pure sulfoxide or disulfide (Table 3, Entries 1-15). All the products are

known and they were characterized by melting point which were compared with those obtained from authentic samples [34-41].

RESULTS AND DISCUSSION

Cellulose sulfuric acid is readily prepared by the dropwise addition of chlorosulfonic acid to cellulose in CHCl₃ at 0°C, as our previously reported method [9]. It is important to note that, this reaction is easy and clean without any further work-up due to the release of HCl gas from the reaction vessel immediately. The white homogeneous and nonhygroscopic solid acid is very stable under reaction conditions.

To study the catalytic oxidation of sulfides mediated by CSA, thioanisole was chosen as a model compound and reaction conditions were optimized. The yield and rate of the reaction were also found to be dependent on the amount of the catalyst (Table 1). The optimum molar ratio of sulfide:H₂O₂ (1:1) in the presence of CSA (0.05 g) is found to be ideal for complete conversion of sulfides to sulfoxide with no observation of sulfone. The catalyst is very active, stable to air and moisture, nontoxic and inexpensive.

The choice of the organic solvent is of particular importance. The reaction was carried out in different solvents and the results are tabulated in Table 2. The reaction gave very good yields in acetonitrile. It is comparatively slower in non-polar solvents such as toluene. In water, it affords lower yield.

To indicate the scope of reaction, a series of sulfides were chosen and subjected to the oxidation reaction.

Table 1: Effect of amount of catalyst on the oxidation of thioanisole in CH₃CN.

Entry	CSA (g)	t (h)	Isolated Yield (%)
1	0	30	35
2	0.015	24	73
3	0.025	7.5	81
4	0.35	6	89
5	0.05	4.5	92
6	0.075	4.5	93

Table 2: Influence of different solvents on oxidation of thioanisole.

Entry	Solvent	t(h)	Isolated Yield (%)
1	Acetonitrile	4.5	92
2	Acetone	6	81
3	Methanol	5	84
4	Ethanol	9	73
5	Toluene	14	66
6	Chloroform	9	68
7	Water	15	45

The results summarized in Table 3 (Entries 1-9) and they clearly indicated the generality of the reaction with respect to variety of alkyl and aryl sulfides.

In an effort to expand CSA efficiency within the family of organosulfur species, we turned our attention toward exploring the oxidation of thiols to their respective disulfides. In the first step, we carried out a set of initial experiments on benzothiol as a model substrate using 30% H₂O₂ in the presence of different amounts of catalyst (Table 4) in various solvents (Table 5) at room temperature. The best result was obtained by carrying out the reaction with molar ratios of thiol:H₂O₂(1:1) in the presence of 0.1 g of CSA in acetonitrile as solvent for 30 min.

The oxidative couplings of other thiols were then examined using the optimized reaction conditions and oxidation performed almost in excellent yields (Table 3,

entries 10-15).

CONCLUSIONS

In summary, we have developed an efficient and simple procedure for the selective oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides with using H₂O₂ in the presence of CSA as an environmentally friendly bio-supported proton source catalyst. Inexpensive nature and availability of the reagents, easy and clean workup process and the ability to be operated at room temperature are features of this new procedure to selective oxidation of sulfides and thiols.

Acknowledgement

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Table 3: Oxidation of sulfides to sulfoxides and thiols to disulfides with H₂O₂ in the presence of CSA at room temperature in CH₃CN.

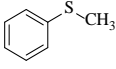
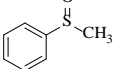
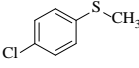
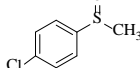
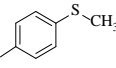
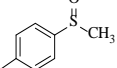
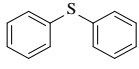
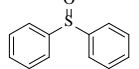
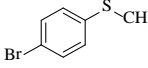
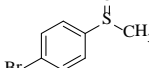
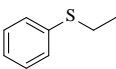
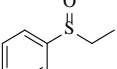
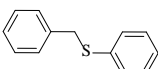
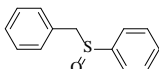
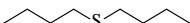
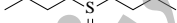


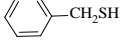
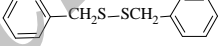
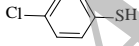
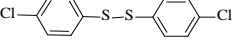
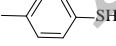
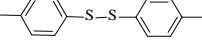
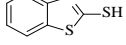
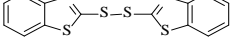
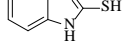
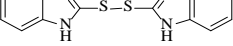
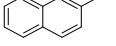
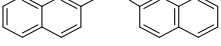
Entry	Substrate	Product	t (h)	Isolated Yield (%)	M.p.(°C)	
					Found	Reported[Ref.]
1			4.5	92	28-30	30-30.5 [34]
2			5.5	87	135-138	136-137[35]
3			6	85	136-138	138-140 [35]
4			8	79	70-73	72-73 [34]
5			5	93	71-73	74-76 [36]
6			9	74	145-147	146 [36]
7			4	87	41-44	43-45 [36]
8			12	71	27-29	29-32 [34]
9			18	78	100-103	103-106 [37]
10			0.5	90	70-73	69-72[38]
11			1.5	89	68-70	70-71[39]
12			1.25	92	43-46	45-46[40]
13			0.75	82	175-177	177-179[41]
14			0.5	79	200-203	202-204[41]
15			1	88	137-139	139[40]

Table 4: Effect of amount of catalyst on the oxidation of benzothiol in CH₃CN.

Entry	CSA (g)	t (h)	Isolated Yield (%)
1	0	8	77
2	0.025	5	81
3	0.05	2.5	85
4	0.075	2.5	87
5	0.1	0.5	90
7	0.12	0.5	91

Table 5: Influence of different solvents on oxidation of benzothiol.

Entry	Solvent	t (h)	Isolated Yield (%)
1	Acetonitrile	0.5	90
2	Acetone	3	86
3	Methanol	2	79
4	Ethanol	7	66
5	Toluene	10	62
6	Chloroform	5	78
7	Water	10	55

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