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Zeolite nanoparticles (H-ZSM5) as a highly efficient, green, and reusable heterogeneous catalyst for selective oxidation of sulfides to sulfoxides under mild conditions

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ABSTRACT

H-ZSM5 is applied as an efficient, highly reusable, and heterogeneous catalyst for the oxidation of sulfides to sulfoxides using 30% H_2O_2 under solvent-free conditions at room temperature. A variety of aromatic and aliphatic sulfides with different functional groups were successfully oxidized with good to excellent yields in short reaction times. The catalyst can be easily recovered by simple filtration and recycled for several consecutive runs without any significant loss of its catalytic activity.

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1. Introduction

The selective oxidation of sulfides to sulfoxides is an important reaction in organic chemistry, because sulfoxides play an important role as versatile and synthetic intermediates for the production of various chemically and biologically active molecules, and also activation of enzymes [1–4]. Therefore, various oxidizing agents (e.g., metal oxidants, organic oxidant, halogens, peroxides, and air) have been proposed for this type of transformation [5–7], but some of these methods have limitations such as the use of stoichiometric toxic reagents, low atom efficiency, tedious work up of products, and the formation of large amounts of toxic waste [8]. Among oxidizing agents, hydrogen peroxide is the most attractive oxidant, because of its environmental implications, lower costs, and is readily available and produces water as the only byproduct [9–11], but major drawback of hydrogen peroxide is its poor oxidizing power; hence extensive studies have been undertaken to develop new catalysts (homogeneous and heterogeneous catalysts) for this reaction [12–14]. Although these methods have partly addressed problem of the stoichiometric reagents, some of these methods require the transition metal catalyst for the selective oxidation of sulfides, which have a number of disadvantages such as preparation of complex catalyst, using toxic transition metal compounds, and removing or recovery of the expensive catalyst and remaining metals in products [15–19].

In recent years, one of the main objectives of modernizations in catalytic processes is the development of new and efficient technologies to improve environmental conditions and industries related to fine chemicals. Porous solids are particularly attractive, because they were reported for potential applications such as catalysts, catalyst supports, and as adsorbents [20–23].

Zeolites are porous crystalline materials that are defined as aluminosilicates with discrete uniform particle with high internal surface area, small pore size, and flexible frameworks [24,25], which are useful catalysts in petroleum cracking, petrochemical industry, reforming processes, and chemical reactions [26–28]. Also, zeolites can have both

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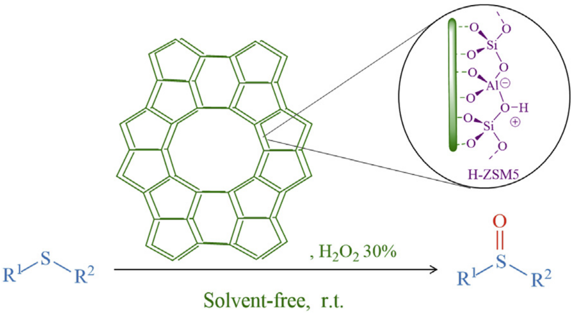


Scheme 1. H-ZSM5 catalyzed the oxidation of sulfides to sulfoxides using H_2O_2.

Brønsted and Lewis acid sites and can be used as a solid acid to activate oxygenated molecules containing carbonyl and hydroxyl groups, that is noncorrosive, and as a stabile, low-cost, and commercially available reagent [29–31].

2. Experimental section

2.1. Materials and physical measurements

Sulfides, solvents (such as ethyl acetate and *n*-hexane), and H_2O_2 (30%) were purchased from Merck chemical company and used without further purification. H-ZSM5 is commercially available from Zeolyst International. Melting points were recorded using an Electrothermal 9100 apparatus. ^{1}H NMR spectra were recorded using a Bruker 400 MHz spectrometer in $CDCl_3$ as solvent. Chemical shifts are reported in ppm with Tetramethylsilane (TMS) as an internal standard.

2.2. General procedure for the oxidation of sulfides to sulfoxides using 30% H_2O_2 in the presence of H-ZSM5 as a catalyst

H-ZSM5 (12 mg) was added to a mixture of sulfide (1 mmol) and 30% H_2O_2 (2.4 equiv), then the mixture was stirred at room temperature under solvent-free conditions and the progress of the reaction was monitored by Thin-layer chromatography (TLC) (EtOAc/*n*-hexane, 1/2). After completion of the reaction, EtOAc (5 mL) was added, the catalyst was separated by filtration, and washed with additional EtOAc (5 mL). The organic layer was washed with brine (5 mL) and dried over anhydrous Na_2SO_4. Finally, the organic solvent was evaporated, and products were obtained in good to high yield. All the products are known and were characterized by comparing their spectral and physical data with those of authentic samples.

2.3. Selected spectra data

2.3.1. Methyl phenyl sulfoxide

^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.70–7.62$ (m, 2H), 759–7.48 (m, 3H), 2.72 (s, 3H) ppm; IR (KBr); 3030, 1488, 1451, 1296, 1128, 1029, 696 cm^{-1}.

2.3.2. Didodecyl sulfoxide

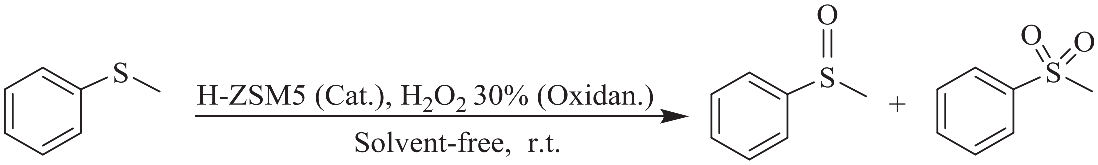
^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.75–261$ (m, 4H), 1.85–1.75 (br, 4H), 1.45–1.29 (m, 36H), 0.91 (t, $J = 4$ Hz, 6H) ppm; IR (KBr); 2920, 2849, 1466, 1011.

3. Results and discussion

In continuation of our studies on environmentally benign chemical processes [32–34], we report our results about H-ZSM5 zeolite as a recyclable and effective heterogeneous catalyst for selective oxidation of sulfides to sulfoxides using 30% H_2O_2 (Scheme 1).

To optimize the reaction conditions, the oxidation reaction of methyl phenyl sulfide to methyl phenyl sulfoxide was selected as a model reaction. The effect of different amounts of hydrogen peroxide and catalyst was investigated on the model reaction under solvent-free conditions at room temperature (Table 1). The oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide was not completed using H_2O_2 (4.8 equiv) as an oxidant in the absence of H-ZSM5 as a catalyst even after 24 h (Table 1, entry 1). When 50 mg of H-ZSM5 catalyst and 4.8 equiv of 30% H_2O_2 were used both sulfoxide and sulfone were obtained with 65% and 35%, respectively, within 24 h (Table 1, entry 2). To control selectivity, the amounts of both catalyst and oxidant were reduced. When the amount of catalyst

Table 1
Optimization of the reaction conditions with respect to the effect of the amount of H-ZSM5 and 30% H_2O_2 on the oxidation reaction of methyl phenyl sulfide.[a]



Entry	H-ZSM5 (mg)	H_2O_2 (equiv)	Time	Conversion (%)[b]	Yield of sulfoxide (%)	Yield of sulfone (%)
1	–	4.8	24 h	80	70	0
2	50	4.8	24 h	100	65	35
3	25	4.8	60 min	100	98	0
4	25	2.4	60 min	100	98	0
5	**12**	**2.4**	**60** min	**100**	**98**	**0**[c]

[a] Reaction conditions unless stated otherwise: sulfide (1 mmol), solvent-free, rt.
[b] Conversion was determined by GC.
[c] The bold values represent the most effective reaction conditions.

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