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Selective Oxidation of Sulfides to Sulfoxides Using 30% Hydrogen Peroxide Catalyzed with a Recoverable Silica-Based Tungstate Interphase Catalyst

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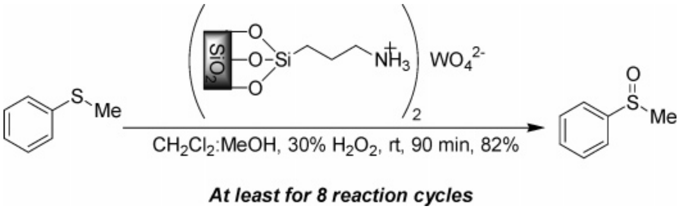
ABSTRACT



Various types of aromatic and aliphatic sulfides are selectively oxidized to sulfoxides and sulfones in good to excellent yields using 30% H_2O_2 in the presence of catalytic amounts of a novel recoverable silica-based tungstate interphase catalyst at room temperature. The catalyst can be recovered and reused for at least eight reaction cycles under the described reaction conditions without considerable loss of reactivity.

The selective oxidation of sulfides to sulfoxides is an attractive and important method in organic chemistry, since sulfoxides are useful building blocks especially as chiral auxiliaries in organic synthesis[1] They also play key roles in the activation of enzymes.[2] However, this transformation is conventionally achieved using stoichiometric amounts of both organic[3] and inorganic[3h,4] reagents, most of which are not suitable for medium to large scale operations and which also lead to large a volume of toxic wastes. Moreover, over-oxidation of the sulfoxides to their sulfones is a common problem during the oxidation of sulfides. In recent years, the newly coined term "green chemistry" has become increasingly important, with the objective to create new products, industrial and laboratory processes, and services that achieve social and economic progress without environmental detriment.[5] The use of H_2O_2 as final oxidant offers the advantages that it is a cheap, environmentally benign, and readily available reagent and produces water as the only

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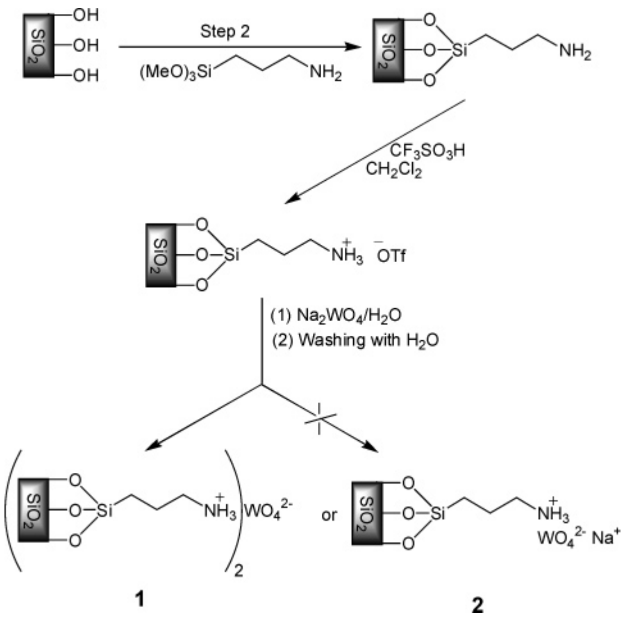
byproduct.[6] This feature has stimulated the development of useful procedures for H_2O_2 oxidation, especially with the use of various types of tungsten-based catalyst systems.[7] Very recently, the elegant work of Noyori and co-workers has shown that a combination of $Na_2WO_4/C_6H_5PO_3H_2$ and a quaternary ammonium hydrogen sulfate as an acidic phase transfer catalyst can be effectively applied for selective oxidation of sulfide to sulfoxides or sulfones using 30% H_2O_2 under halide-free conditions.[8] Although using this protocol represents a considerable progress, the protocol needs homogeneous reaction conditions, and therefore the catalyst is difficult to recover and reuse. Since the replacement of current homogeneous oxidation procedures for the production of fine chemicals by environmentally acceptable protocols based on recoverable catalysts is one of the major tasks in green chemistry, solid oxidation catalysts are called to play a crucial role to accomplish this issue.[9] One way to attain this goal is to immobilize one or more components of the catalytic systems onto a large surface area solid carrier to create new *organic−inorganic hybrid* (interphase) catalysts.[10] An interphase is defined as a *region* within a material in which a stationary (organic−inorganic hybrid catalyst) and mobile component (solvent and reactants) penetrate each other on a molecular level. According to the definition, an interphase catalyst is composed of three parts. An inert matrix (support), a flexible organic spacer, and an active center.[8b] In contrast to traditional physisorbed heterogeneous catalysts, in the interphase counterparts the organic spacer provides sufficient mobility of the reactive center and diminishes undesired steric effect of the matrix over the accessibility of the reactive center. Therefore, these systems are able to simulate homogeneous reaction conditions, and at the same time they have the advantage of easy separation and recovery of the heterogeneous catalysts. Owing to the relative mobility of the reactive center in the interphase catalyst, we hypothesized that it might be possible to replace the phase transfer catalyst in Noyori's protocol with a silica matrix having a quaternary organic spacer. In the present work we wish to report the results obtained with a novel silica-functionalized ammonium tungstate as a recoverable heterogeneous catalyst for selective oxidation of sulfide to sulfoxides using 30% H_2O_2. The catalyst is simply prepared by building up an aminopropyl group on the surface of commercially available mesoporous silica followed by acidification of amino groups using triflic acid and ion exchange of triflate ion by tungstate (Scheme 1).

Scheme 1



Typically, a surface-bound amino group at a loading ca. 0.31 mmol·g^{-1} (by TGA/DTG analysis) was obtained. However, from the simultaneous XRF analysis of the catalyst for tungsten and sodium it was calculated that the loading of the former in the solid was 0.15 mmol·g^{-1}, while a trace amount (less than 0.4 ppm) of the latter was detected. The major weight loss at high temperature in TGA is characteristic of chemisorbed materials and confirmed that the aminopropyl group is covalently bound on the surface of silica.[11] From this result, in combination with those obtained from TGA and XRF analyses, we can clearly conclude that the catalyst corresponds to a 2:1 ratio between the surface-bound ammonium group and WO_4^{2-} anion (Scheme 1, compound **1**).

To test the catalytic activity of **1** we selected the oxidation of sulfides using 30% H_2O_2 as the model reaction. To increase accessibility of the H_2O_2 to the catalyst we chose a solvent mixture CH_2Cl_2/MeOH (1:1). We first examined the oxidation of methyl phenyl sulfide (2 mmol) using 30% H_2O_2 (3 equiv) and **1** (1 mol %, 0.133 g) in CH_2Cl_2/MeOH (10 mL) at room temperature. We observed that the reaction was sluggish and only low yields of the corresponding sulfoxide were formed after 18 h. However, when a similar oxidation reaction was conducted in the presence of **1** (2 mol %, 0.266 g), methyl phenyl sulfoxide was efficiently formed in excellent yields within 1.5 h (Table 1, entry 1).

In a blank experiment no considerable oxidation was observed under similar reaction conditions in the absence

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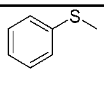
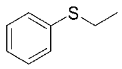
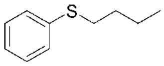
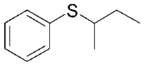
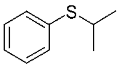
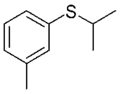
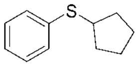
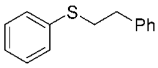
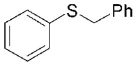
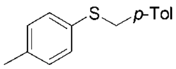
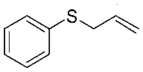
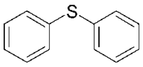
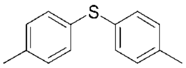
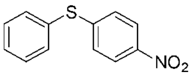
(11) See Supporting Information for details.

Table 1. Oxidation of Aryl Sulfides to Sulfoxide Using 30% H_2O_2 Catalyzed by Silica-Based Ammonium Tungstate Interphase Catalyst **1**

entry	sulfide	H_2O_2(equiv.)	time(h)	yield(%)[a, b]
1		3	1.5	82
	1st	3	1.5	82[c]
	2nd	3	1.5	90[c]
	3rd	3	1.5	87[c]
	4th	3	1.5	80[c]
	5th	3	1.5	85[c]
	6th	3	1.75	89[c]
	7th	3	2	87[c]
	8th	3	3	84[c]
2		3	1.5	80
3		3	2	89
4		3	2.5	79
5		3	2.5	91
6		3	3	84
7		4	2	80
8		4	3	85
9		4	4	83
10		6	5	90
11		4	2	90[d]
12		8	6.5	80
13		7	7	60[e]
14		8	8	65[e]

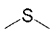
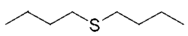
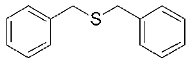
[a] Isolated yields. [b] All reactions were completed with >99% GC conversion unless otherwise stated. [c] Recycling experiment. [d] No epoxidation products was detected. [e] The reaction was not completed within the indicated time, yields after column chromatography.

of **1** within 1.5 h and the reaction required 24 h time to reach a reasonable conversion. In a similar way, various types of structurally diverse aryl alkyl sulfides underwent smooth oxidation to selectively afford the corresponding sulfoxides in good to excellent yields (entries 2−10). Another useful feature of the presented protocol can be seen in the selective oxidation of allyl phenyl sulfide to the corresponding sulfoxide. Neither overoxidation to the sulfone nor epoxidation of the double bond was observed, and the corresponding sulfoxide was obtained in excellent yields (Table 1, entry 11).

The formation of sulfoxides from diaryl sulfides is difficult to achieve under standard oxidation procedures using 30% H_2O_2. Interestingly, under the described reaction conditions even hindered diaryl sulfides furnished the corresponding sulfoxides in good to excellent yields (Table 1, entries 12−14). It is also worth mentioning that even the strong withdrawing NO_2 group in the phenyl ring of diaryl sulfides does not affect the synthetic efficiency (Table 1, entry 14).

On the other hand, when using the protocol for the oxidation of dialkyl sulfides, the formation of the corresponding sulfones was observed along with sulfoxides almost simultaneously. Decreasing the amount of either catalyst **1** or H_2O_2 did not affect the concomitant formation of sulfoxides and sulfone. Therefore, we decided to pursue the oxidation of dialkyl sulfides directly to the corresponding sulfones. We found that under the optimum reaction condition by using dibutyl sulfide (2 mmol) and 30% H_2O_2 (10 mmol) in the presence of **1** (2 mol %) the corresponding dibutyl sulfone was obtained in excellent yield after 5 h at room temperature (Table 2, entry 2). In the same way dibenzyl sulfide and dimethyl sulfide both furnished the corresponding sulfones in high yields (Table 2, entries 1 and 3).

Table 2. Oxidation of Alkyl Sulfides to Sulfones Using 30% H_2O_2 Catalyzed by Silica-Based Ammonium Tungstate Interphase Catalyst **1**

entry	sulfide	H_2O_2(equiv.)	time(h)	yield(%)[a]
1		4	4	>99[b]
2		5	5	92
3		5	4.5	88

[a] Yields refer to isolated yield of sulfones unless otherwise stated. [b] GC yields of sulfones.

Catalyst reuse studies were carried out by recycling the catalyst without further conditioning. Recycling experiments were examined for the oxidation of methyl phenyl sulfide on a 5 mmol scale. This was done by decanting the liquid from the reaction mixture and charging the reaction vessel with fresh substrate and 30% H_2O_2 and then repeating the experiment. Interestingly, the recycled catalyst could be used for at least eight reaction cycles, corresponding to a overall turnover number of 340 (Table 1, entry 1). These results clearly show the practical reusability of the present tungstate intephase catalyst under the described reaction conditions.

In conclusion, we have shown that the novel silica-based tungstate interphase catalyst **1** can be easily prepared from commercially available starting materials. This catalyst efficiently affects the selective oxidation of a variety of sulfides to sulfoxides or sulfones. The catalyst **1** can be considered as a heterogeneous version of Na_2WO_4, and therefore it is possible to easily recover and reuse for several reaction cycles without considerable loss of activity. The oxidation procedure using **1** is free from additives such as soluble phase transfer catalysts and cocatalysts such as C_6H_5-PO_3H_2, which makes it a reasonably environmentally benign chemical process in terms of potential industrial application for this transformation. The work on other applications of **1** is currently underway in our laboratories.

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Supporting Information Available: Experimental procedures and TGA for catalyst **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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