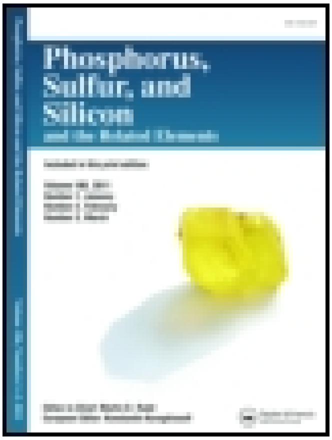

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Simple and Friendly Sulfones Synthesis Using Aqueous Hydrogen Peroxide with a Reusable Keggin Molybdenum Heteropolyacid, Immobilized on Aminopropyl-Functionalized Silica

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Simple and Friendly Sulfones Synthesis Using Aqueous Hydrogen Peroxide with a Reusable Keggin Molybdenum Heteropolyacid, Immobilized on Aminopropyl-Functionalized Silica

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Keggin molybdenum heteropolyacid ($H_3PMo_{12}O_{40}$), immobilized on aminopropyl-functionalized silica catalysts, were made using two immobilization methods: incipient wetness and equilibrium adsorption. The material prepared for the equilibrium adsorption technique was found to be a highly efficient, ecofriendly, and recyclable heterogeneous catalyst for the selective oxidation of sulfides to sulfones in excellent yields, under mild reaction condition using 35% w/v aqueous hydrogen peroxide as the oxidant.

Keywords Functionalized silica; hydrogen peroxide; Keggin heteropolyacid; sulfide oxidation

INTRODUCTION

Sulfones and their derivatives are widely applied. They can be used as intermediates for pharmaceuticals and pesticides and for the modification of polymers.[1] 1,1-Diiodomethyl sulfone, heterocyclic sulfones, and α-sulfonyloximes[2] have been described as plant fungicides. Certain sulfones are effective herbicides,[3] and others act as insecticides and acaricides.[4] Dihydropyridine sulfone derivatives are calcium

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antagonists,[5] fluorosulfones are very effective leukotriene antagonists with antiallergic and anti-inflammatory activity,[6] and aryl- or heteroaryl-substituted sulfones exhibit activity against retroviruses.[7] Piperidinyl sulfones are used as light stabilizers in polymers, particularly polyolefins,[8] and certain heterocyclic sulfones can be used as corrosion protection agents for metals.[9]

Sulfones are generally synthesized by oxidation of sulfides via sulfoxides as intermediates. The oxidizing agents used include potassium permanganate,[10] sodium perborate,[11] dimethyldioxirane,[12] and periodic acid in the presence of ruthenium tetroxide as a catalyst.[13] In industrial processes, wet clays such as kaolin or montmorillonite are used in the oxidation of various sulfides in dichloromethane to give the corresponding sulfone in excellent yields.[14] A common oxidizing agent in the laboratory is hydrogen peroxide in acetic acid. It is also often used in industry, but requires reaction temperatures of 70°C and up to reflux in many cases.[15,16] In the presence of various metal catalysts, oxidation with hydrogen peroxide proceeds at 20°C and 1 atm of pressure. The sulfides can be oxidized selectively with good yield to the corresponding sulfones by using titanium, vanadium, molybdenum, or tungsten salts[17] or oxides,[18] and heteropolyacids as catalysts.[19]

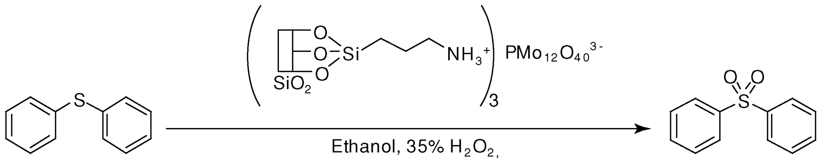
On the other hand, oxidation reactions are some of the most useful chemical transformations, despite the fact that they are among the most problematic processes, due to the production of large amounts of pollutant materials. Significant efforts have been devoted to substituting the stoichiometric oxidant, such as Cr (VI) and Mn (VII), with a cleaner catalytic system.[20] In this context, hydrogen peroxide is an ideal oxidant for liquid-phase reactions because it produces only water in the reaction, is safe to store and use, and is cheap and readily available.[21] During the last several years, very useful procedures involving polioxometalatos (POM) and heteropolyacids (HPA) catalysis and hydrogen peroxide as oxidant have been developed to promote the oxidation of organic substrates, but the application of POM catalyst still suffers from some drawbacks related to the nature of polyoxometalates, particularly their low area and the high solubility, which makes recycling difficult and causes environmental problems.

A further step in the development of environmentally benign chemical processes is the replacement of current homogeneous oxidation procedures for heterogeneous processes. Immobilized catalysts have been of great interest due to their advantages, such as simplified product workup, separation, isolation, and catalyst reuse. Previous studies of Keggin-type HPAs supported on silica by the incipient wetness method have shown that the leaching of HPA is rather significant, but in recent papers it has been reported that the anchoring of heteropolyacids onto the amine groups–modified silica surface minimizes the leaching of the cluster during the different reaction cycles.[22]

In the present work, we report the results obtained with a $H_3PMo_{12}O_{40}$ Keggin heteropolyacids supported on silica-amine functionalized as a recoverable heterogeneous catalyst for the oxidation of sulfide to sulfone using 35% w/v aqueous hydrogen peroxide.

RESULTS AND DISCUSSION

To test the catalytic activity of Keggin molybdenum heteropolyacid immobilized on an aminopropyl-functionalized silica catalyst, we selected the oxidation of sulfides using 35% w/v H_2O_2 as oxidizing agent. We first screened the oxidation of diphenylsulfide using different catalysts, solvents, and reaction conditions (Table I). In a blank experiment, no sulfone was detected in the absence of the catalyst (for 7 h) at 65°C using an excess of hydrogen peroxide (35% w/v, 0.75 mL) and acetonitrile or ethanol as solvent (Table I, entries 1 and 2). However, when a commercial HPA sample such as $H_3PMo_{12}O_{40}$ (PM_{12}) was used (Table I, entry 3), a yield of 89% is observed at 3 h of reaction using acetonitrile as solvent at 65°C. As can be observed (Table I, entry 4), upon increasing the temperature (80°C), the conversion rate increases and the yield is 91% at 1 h. The replacement of acetonitrile by a more friendly solvent such as ethanol increases the catalytic activity of PM_{12}. A 92% yield of sulfone is observed at 0.5 h and at a temperature of 78°C (Table I, entry 5). This protocol needs homogeneous reaction conditions, and therefore the catalyst is difficult to recover and reuse. Scheme 1



SCHEME 1

Since the replacement of current homogeneous oxidation procedures by environmentally acceptable protocols based on recoverable catalysts is one of the major tasks in green chemistry, solid oxidation catalysts play an important role.[22] Therefore, we prepared three catalyst types: (i) the immobilization of PM_{12} on the inner surface of the silica [as prepared in the Experimental section ($PM_{12}SiO_2$)] and (ii) the immobilization of PM_{12} of the amino-functionalized silica. In this context, two methods, incipient wetness ($PM_{12}NH_2SiO_{2i}$) and equilibrium

TABLE I Oxidation of Diphenylsulfide to Sulfone Employing Different Reaction Conditions[a]

Entry	Catalyst (mg)	Solvent	Time (h)	Temp (°C)	Isolated yields[b](%)
1	None	CH_3CN	7	65	—
2	None	Ethanol	7	65	—
3	PM_{12} (50 mg)	CH_3CN	3	65	89
4	PM_{12} (50 mg)	CH_3CN	1	80	91
5	PM_{12} (50 mg)	Ethanol	0.5	78	92
6	PM_{12} (50 mg)	Ethanol	1.5	65	90
7	SiO_2	Ethanol	6	78	—
8	NH_2SiO_2	Ethanol	6	78	—
9	$PM_{12}SiO_2$ (50 mg)	Ethanol	0.75	78	91, 10[c]
10	$PM_{12}NH_2SiO_{2i}$ (50 mg)	Ethanol	1	78	90, 10[c]
11	$PM_{12}NH_2SiO_{2i}$ (50 mg)	Ethanol	2.5	65	93, 40[c]
12	$PM_{12}NH_2SiO_{2e}$ (50 mg)	Ethanol	3	65	92, 90[c], 88[d]
13	$PM_{12}NH_2SiO_{2e}$ (100 mg)	Ethanol	20	25	87
14	$PM_{12}NH_2SiO_{2e}$ (50 mg)	Ethanol	6	65	10[e]

[a] H_2O_2: 0.75 mL, except Entry **13**: 1 mL and Entry **14**: 0.20 mL.
[b] Yield% of pure product.
[c] First reuse.
[d] Second reuse.
[e] Conversion of sulfide, 100%.

adsorption techniques were employed ($PM_{12}NH_2SiO_{2e}$). As previously reported, strong interaction of HPA acidic proton with amine groups results in the highest HPA retention on silica surface when used as a catalyst in polar media.[22b]

In order to demonstrate that the supports do not contribute on the catalytic activity, experiments with SiO_2 and amino group–modified support, NH_2-SiO_2, were carried out. No sulfone was detected under the same reaction conditions (Table I, entries 7 and 8).

The diphenylsulfide oxidations using the three supported PM_{12} catalysts are summarized in Table I, entries 9–14. As can be observed (Table I, entry 9), the $PM_{12}SiO_2$ gives a high conversion and 91% yields of the corresponding sulfide at 78°C, using 0.75 mL of 35% w/v aqueous hydrogen peroxide in 45 min. Similarly, $PM_{12}NH_2SiO_{2i}$ gives 90% in 1 h (Table I, entry 10).

In addition, one of the main advantages of using a supported solid catalyst in the liquid phase reaction is the ease of separation and reuse of the catalyst in the catalytic cycles. In this way, the catalysts were separated by filtration, washed with ethanol, dried, and then reused in the second cycle with a fresh reaction mixture. The procedures were repeated using the same conditions (Table I, entries 9 and 10). In both cases the yields of sulfone were only of 10%. These results confirm the important leaching of both catalysts ($PM_{12}SiO_2$ and $PM_{12}NH_2SiO_{2i}$, respectively). For this reason, the effect of leaching was studied by varying the reaction temperature. For the use of $PM_{12}NH_2SiO_{2i}$ as catalyst and a temperature of 65°C, the results obtained for the use and the first reuse are 93% and 40%, respectively (Table I, entry 11). This result confirms a decrease in the leaching for a lower reaction temperature. Under similar conditions, the catalyst obtained by the equilibrium adsorption technique ($PM_{12}NH_2SiO_{2e}$) was tested. A yield of 92% was observed at 3 h of reaction time using ethanol as solvent and a temperature of 65°C (Table I, entry 12). The first and the second reuse give 90% and 88% of diphenylsulfone, respectively. Under this condition, we confirm the absence of considerable leaching using the Keggin molybdenum heteropolyacid immobilized on aminopropyl-functionalized silica ($PM_{12}NH_2SiO_{2e}$).

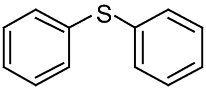
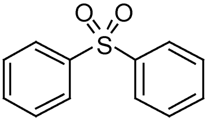
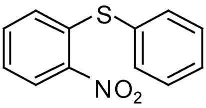
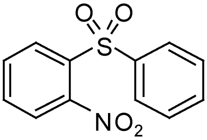
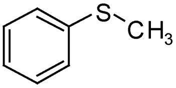
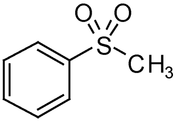
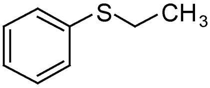
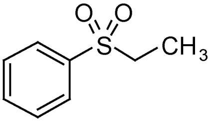
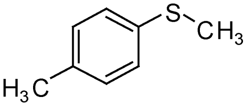
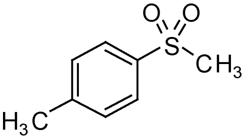
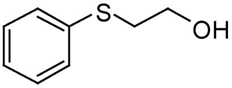
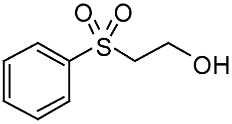
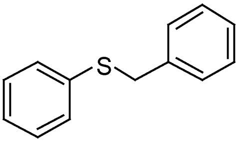
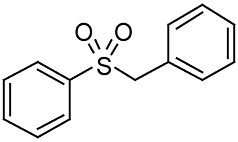
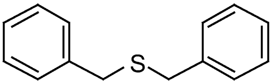
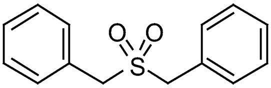
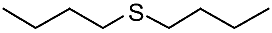
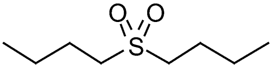
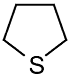
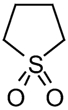
The same reaction was carried out at 25°C using 100 mg of catalyst and 1 mL of 35% w/v H_2O_2, (Table I, entry 13). In this condition, 87% of diphenylsulfone was obtained after 20 h of reaction. When the amount of hydrogen peroxide was reduced to 0.2 mL, under the same reaction conditions, conversion of diphenylsulfide was 100%, but the yield of sulfone only of 10%. In this case, the reaction was selective to obtain diphenylsulfoxide (Table I, entry 14).

Once the reaction conditions for the selective oxidation of diphenylsulfide to diphenylsulfone had been optimized, the reaction was extended to other starting substrates. Table II shows the results for the selective oxidation of different sulfides to sulfones. All the reactions were run within a short time, and the sulfones were obtained in very good yields as practically the only oxidation product. For example, in Table II entry 13, it is shown that the formyl group was not affected by the reaction conditions.

It was observed that the reaction rates of sulfide oxidation with diaryl and aryl alkyl groups were lower than those of other aryl alkyl or dialkylsulfides (see Table II, entries 1, 3, 8, and 9, respectively). Finally, it was also observed that the reaction rates for the sulfides with an electron-withdrawing group at the ortho position of diphenylsulfide was lower than those of diphenylsulfide (see Table II, entries 1 and 2), which indicates that the electron-withdrawing group and the diaryl group produced a deactivating effect in the oxidation process.

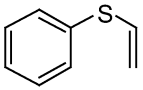
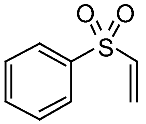
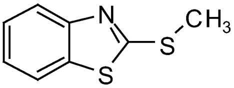
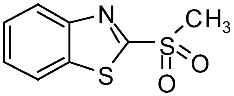
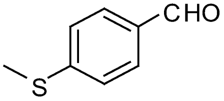
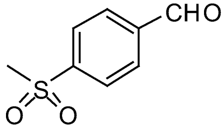
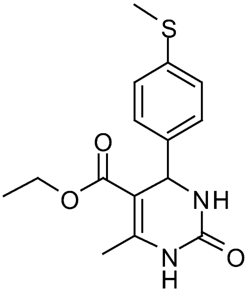
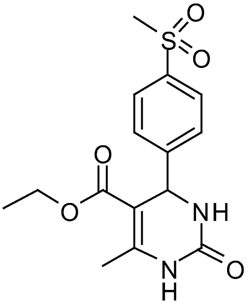
As reported by Gregori et al.[17d] a plausible mechanism of this reaction involves the formation of peroxo species and the subsequent nucleophilic attack of the sulfur atom in the thioether on the peroxo species. Indeed, it is well known that thioethers are oxidized to sulfones by electrophilic oxidants, which explains the lower reactivity of

TABLE II General Procedure of Oxidation of Sulfides to Sulfones[a,b]

Entry	Substrate	Time	Product	Isolated yields (%)[c]	TOF[d]
1		3		92	4860
2		4		88	3492
3		2		93	7344
4		2		94	7452
5		2		90	7128
6		2		86	6804
7		2		96	7596
8		1.5		92	9684
9		1		83	13140
10		1		81	12813

(Continued on next page)

TABLE II General Procedure of Oxidation of Sulfides to Sulfones[a],[b] *(Continued)*

Entry	Substrate	Time	Product	Isolated yields (%)[c]	TOF[d]
11		20[e]		77	609
12		1		70	11073
13		2.5		89	5616
14		3		62	3276

[a] See Experimental section for reaction conditions.

[b] We performed also the oxidation reaction at 25 °C with substrates sensitive to the oxidation. Double and triple bonds, alcohols, amines, aldehydes and esters as styrene, phenyl acetylene, undecene, phenyl allyl ether, 1-decanol, aniline and ethyl acetate are not oxidized if the reaction is carried out for 20 h at 25 °C. In this condition sulfide was oxidized selectively to sulfone using 1 mL of 35% w/v H_2O_2.

[c] Pure product yields.

[d] Turnover frequency (product mols × $H_3PMo_{12}O_{40}$ mols^{-1} × h^{-1}).

[e] At 25°C.

aromatic thioether due to delocalization of the electron density on the sulfur.

This protocol also represents a clear alternative to preparing more sophisticated molecules. For example in Table II, entry 14, Biginelli derivatives can be oxidized to the corresponding sulfones using these catalysts.

The characterization of commercial PM_{12} and supports were previously carried out.[23] The FT-IR spectra of $PM_{12}NH_2SiO_{2e}$ show that the undergraded Keggin structure is presented. Nevertheless, the band near to 1100 cm^{-1} is masked by the support. The band next to 900 cm^{-1} indicates a good interaction between silanols and HPA protons. The diffraction lines of the bulk heteropolyacid, corresponding to crystalline structures, were not observed in the patterns of supported catalyst. The potentiometric titration curve showed that the acid strength of $PM_{12}NH_2SiO_{2e}$ is lower than the HPA, due the acid characteristic of the amino-functionalized silica.

CONCLUSION

In summary, we have reported a new, versatile, and efficient methodology for the rapid oxidation of sulfides to sulfones with aqueous 35% w/v hydrogen peroxide as a clean oxidant, in the presence of catalytic amounts of Keggin molybdenum heteropolyacid immobilized on aminopropyl-functionalized silica. The catalyst prepared by the equilibrium adsorption technique was recovered and reused without loss of its catalytic activity. The main advantages of this procedure are the operational simplicity; the use of a noncorrosive, reusable catalyst in mild, clean oxidation; and the very good yields attained. The use of an insoluble catalyst instead of soluble inorganic acids contributes to waste reduction. Further investigations about the use of this catalyst for the selective oxidation of sulfides in sulfoxides are in progress.

EXPERIMENTAL

Chemicals were purchased from Fluka, Merck, and Aldrich. The products were characterized by comparison of their spectral (^{1}H and ^{13}C-RMN), TLC, and physical data with the authentic samples.

Preparation of Catalysts

Silica Preparation

Silica preparation by sol–gel technique was made using tetraethylorthosilicate (34 mL), absolute ethanol (14 mL), and glacial acetic acid (30 mL) with a molar ratio TEOS/EtOH/AcOH equal to 1:1.6:3.5. The reactants were mixed in a glove box under nitrogen atmosphere at 20°C. Then the mixture was removed from the controlled atmosphere, and ethanol (30 mL) was added and gelation of the sols took place. The wet gel was then aged in the same medium until dry silica particles were obtained. This solid was dried at 40°C. The solid was labeled SiO_2.

Functionalized Silica as Support

The catalyst was synthesized by addition of 3-aminopropyltrimethoxysilane (6.4 mL) to a suspension of silica (4 g) previously prepared in refluxing toluene (128 mL). The mixture was then stirred at this temperature for 24 h. The solid was filtered, washed in a Soxhlet apparatus with diethyl ether and dichloromethane, and then dried at 40°C according to the literature.[22b]

Immobilization of $H_3PMo_{12}O_{40}$ on Functionalized Silica

The immobilization of $H_3PMo_{12}O_{40}$ (PM_{12}) on functionalized silica was achieved by two methods: incipient wetness and equilibrium adsorption techniques.

Incipient wetness. The functionalized support was impregnated by means of the incipient wetness method with a solution of 22% (w/v) PM_{12} in acetonitrile, in order to obtain 23% (w/w) PM_{12} in the final catalyst. Then it was dried at 70°C for 24 h. The catalyst prepared was named $PM_{12}NH_2SiO_{2i}$.

Equilibrium adsorption technique. The impregnated solution was prepared by dissolution of PM_{12} in absolute ethanol [4% (w/v)]. The solution was contacted with functionalized silica, and then H_2O was added dropwise, obtaining 23% (w/w) in the final catalyst. The impregnated solid was left without stirring for 24 h. After that, the obtained solid was shaken for 3 h and then was kept undisturbed overnight. Then it was shaken for 7 h, and the impregnated solid was allowed to stand for 24 h. Finally, the impregnating solution was separated from the solid and dried at 20°C for 12 h. The catalyst prepared was named $PM_{12}NH_2SiO_{2e}$.

Characterization of Samples

The characterization of catalysts was performed by different techniques: FT-IR, XRD, SBET, and potentiometric titration although not all of them are presented in this work.

General Experimental Procedure for the Preparation of Sulfones

A mixture of Keggin molybdenum heteropolyacid immobilized on aminopropyl-functionalized silica catalyst (50 mg), sulfide substrate (1 mmol), hydrogen peroxide (35% w/v, 7.7 mmol), and ethanol (4 mL) was refluxed for the specified reaction times (Tables I and II). After completion of the reaction, the catalyst was removed by filtration, and the resulting solution was concentrated under reduced pressure. The reaction mixture was directly charged on a small silica gel (Grace Davison, Grade 62, 70 × 200 Mesh) column and eluted with ethyl acetate–hexane, to obtain pure compounds in good yields (Tables I and II).

Recycling of Catalyst

After reaction, the catalyst was filtered, washed thoroughly with ethanol, dried under vacuum, and reused for the oxidation reaction, following the procedure described above.

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