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Tungstate Supported on Periodic Mesoporous Organosilica with Imidazolium Framework as an Efficient and Recyclable Catalyst for the Selective Oxidation of Sulfides

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A catalyst based on immobilization of tungstate ions (WO_4^{2-}) inside the mesochannels of periodic mesoporous organosilica comprising bridged ionic liquid (1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride) has been synthesized and characterized. This catalyst was then employed for the selective oxidation of organic sulfides to the corresponding sulfoxides or sulfones. The final synthesized catalyst was characterized by various techniques such as nitrogen sorption analysis, transmission electron microscopy, and thermogravimetric analysis. The catalyst was also applied to the selective oxidation of sulfides containing readily oxidizable functional groups such as hydroxyl, allylic, and even challenging aliphatic sulfides. Interestingly, it was found that on changing the reaction medium from aqueous methanol to aqueous acetonitrile, the product selectivity was changed successfully from sulfoxide to sulfone with good to excellent yields. Moreover, the catalyst can also be recovered and reused efficiently in nine subsequent reaction cycles without any remarkable decrease in the catalyst activity and selectivity.

Introduction

Since the discovery of ordered mesoporous silica (OMS),[1] a variety of organic–inorganic hybrid mesoporous materials with high specific surface area, available pore volume, and tunable pore size have been developed extensively in view of their potential applications in various fields from catalysis[2] and adsorption[3] to nanoelectronics[4] and controlled drug delivery.[5] These surfactant-derived organo-functionalized ordered mesoporous materials are typically synthesized either by terminally bonded siliceous organic groups [$(R'O)_3Si{-}R$] through co-condensation or post-grafting of surface silanol groups in the parent OMS.[2d,6] Moreover, these materials have attracted great interest from the viewpoints of academia and industry, because many of their characteristics, such as hydrophilicity/hydrophobicity, mechanical/hydrothermal stability, and other chemical or physical properties, can be adjusted intelligently and simply by varying the nature of the immobilized organic group (R).[7] In this way, a large number of successful incorporations of various sophisticated organosilanes into the nanospace of OMS have been reported by applying post-grafting and/or co-condensation, but it has been proven that this approach could potentially lead to a dramatic pore-blocking effect and inhomogeneous distribution of organic functional groups throughout the surface of these materials.[8] In addition, in many circumstances, the long-range order of the resulting material could be reduced dramatically if an organic content (organosilane precursors) greater than 25% was employed during the co-condensation methods.[9]

To overcome these limitations, periodic mesoporous organosilicas (PMOs), which were built by the self-assembly of bridged organosilane precursors [$(R'O)_3SiRSi(OR')_3$] in the presence of surfactants as structure-directing agents (SDAs), were developed.[10] Because PMOs often exhibit large internal surface areas and open pore structures, the organic bridging groups inside the pore wall of mesochannels are readily accessible to molecules diffusing through the porous matrix,[11] a feature that makes these materials a unique platform in preparing advanced functionalized catalysts for important liquid-phase organic transformation.[12] Compared with functionalized OMSs, the PMO surface reactivity, hydrophilicity/hydrophobicity balance, structural rigidity, and mass-transfer rate as well as its surface, optical, electronic, magnetic, and charge-transport properties, can be readily tuned for specific applications in a more sophisticated way.[13]

In recent years, many catalytic systems based on PMOs comprising simple groups, such as sulfonic acids, Brønsted or Lewis bases, and phenylene, as well as bulky organic functional groups, such as phosphine complex, 1,1′-bi-2-naphthol (BINOL), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP),

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bis[(salicylidene)ethylenediaminato] (salen), phorphyrin, guanine, and also some metal complexes such as copper, cobalt, and palladium, have been employed extensively in a variety of important organic transformations.[14] Along this line, we have recently demonstrated the synthesis and characterization of a series of PMOs with ionic liquid (IL) framework and studied their applications as an efficient support for immobilization of several types of transition-metal catalysts through an anion-exchange technique. In this way, we have recently introduced the novel functionalized material called PMO-IL, which was successfully employed as a competent support for the immobilization and stabilization of Pd nanoparticles in C–C bond formation reactions,[15] aerobic oxidation of alcohols,[16] for RuO_4^{-} [17] in aerobic alcohol oxidation, as well as for Au nanoparticles in the synthesis of propargylamines through the A^3 coupling reaction.[18] Quite recently, we also found that tungstate ions supported on a PMO with IL framework (WO_4^{2-}@PMO-IL) is a recoverable catalyst system for the highly selective oxidation of various primary or secondary alcohols to the corresponding aldehydes or ketones by 30% H_2O_2.[18g]

Selective oxidation of sulfides into the corresponding sulfoxides is a promising process from both a laboratory and industrial point of view, since they are important synthetic intermediates and/or products in the synthesis of pharmaceuticals and agrochemicals, and are particularly useful building blocks as chiral auxiliaries in asymmetric organic syntheses.[19] Although a significant number of traditional oxidants, such as high-valence metal salts, concentrated HNO_3, *m*-chloroperoxybenzoic acid, sodium metaperiodate, halogens, and nitrogen pentoxide, have been widely used for this transformation, many of them suffer from the use of hazardous reagents, generate unwanted toxic waste, and also show overoxidation of sulfoxides to the expected sulfones during relatively harsh or harmful reaction conditions.[20] To address these limitations and consider the eco-sustainability, green chemistry, and especially atom economy, a substantial amount of research has been directed toward developing new and efficient catalytic systems based on the use of aqueous 30% H_2O_2 as a final green oxidant because its remarkable benefits include low cost, environmentally benign properties, high atom economy, and water as a byproduct.[21] For this reason, various heterogeneous/homogeneous catalytic systems based on organic material and metal as well as self-supported catalysts were used successfully for the activation of hydrogen peroxide in this transformation.[22] Although these reports provided significant advances in the field, some of the processes described suffer from low selectivity for sulfoxide or sulfone production. Meanwhile, a number of versatile and efficient catalysts based on oxotungstates have received considerable attention for the oxidation of sulfides, which feature high functional compatibilities and the possibility to control the selectivity of this reaction toward formation of either sulfoxide or sulfone.[23] To deliver more viable "green" protocols for sulfoxidation reactions, several strategies for the immobilization of tungsten-based catalyst into/onto inorganic supports, organic–inorganic hybrid materials, and organic polymers with the hope of improving the recyclability and durability of the employed catalyst systems have subsequently been developed.[24] On the other hand, the use of supported IL phases[25] has also been considered as a platform for tungstate ion immobilization for the activation of 30% H_2O_2 in several oxidative transformations.[26] Although these approaches have provided substantial improvements to some extent, the catalyst efficiency and selectivity, especially in the case of sulfide oxidations, remain a challenging research area.

We have presented for the first time a new catalytic protocol composed of tungstate ions inside the hydrophobic channels of the OMS SBA-15, as a novel catalyst system for the selective preparation of sulfoxides or sulfones by adjusting the hydrophobicity of starting sulfides and/or the solvent polarity.[27] Encouraged by this interesting observation and finding, we were keen to investigate whether the catalyst comprising WO_4^{2-} ion immobilized in the interior of nanospaces of PMO-IL (WO_4^{2-}@PMO-IL, see Figure 1) could be employed in the same way for the selective oxidation of sulfide into sulfoxide or sulfone with 30% H_2O_2 as a safe oxidant by adjusting the reaction conditions.

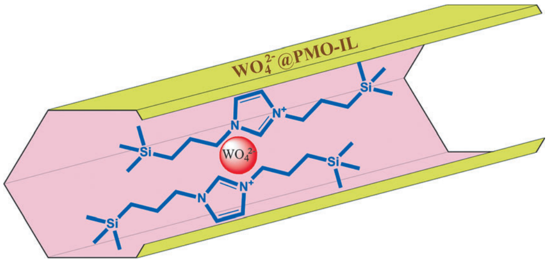


Figure 1. Schematic representation of the WO_4^{2-}@PMO-IL.

Results and Discussion

First, the preparation of PMO-IL was performed by hydrolysis and condensing of silica precursors, such as the IL 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride (BTMSPI) and tetramethyl orthosilicate (TMOS), in the presence of an acidic solution of Pluronic P123, which acted as a SDA according to our previous reports.[15–18,28] The resulting PMO-IL was then allowed to react with an aqueous solution of Na_2WO_4 to replace some of the chloride ions with tungstate ions through a direct ion-exchange approach following our recent protocol.[29] Then, the presence of bridged IL and tungstate ions and structural uniformity were concomitantly investigated by employing well-known techniques such as nitrogen physisorption, transmission electron microscopy (TEM), and thermogravimetric analysis (TGA).

Figure 2 shows the N_2 adsorption–desorption isotherms and pore size distributions (Barrett–Joyner–Halenda, BJH) for the synthesized materials. In particular, N_2 sorption analysis provides useful information on the textural properties and mesoscopic quality of the presented materials. The PMO-IL itself displays a type IV isotherm, with an H1 hysteresis loop, which indicates the formation of mesoporous materials with cylindrical pores of relatively uniform pore size and shape.[29] Further-

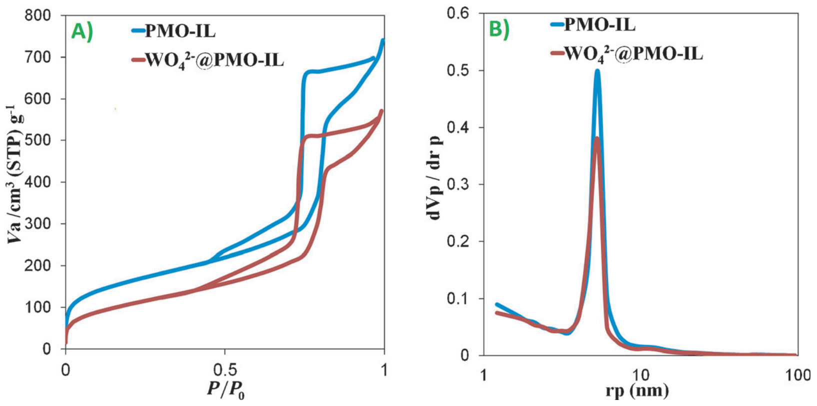


Figure 2. N_2 adsorption–desorption isotherms (A) and BJH pore size distributions (B) for PMO-IL and WO_4^{2-}@PMO-IL.

more, a sharp capillary condensation step around $P/P_0 \approx 0.7$–0.8 is evidence for the formation of well-ordered mesoporous solid materials with narrow pore size distribution, despite the flexible precursor (BTMSPI) that has been inserted into the PMO wall networks. This is made possible by the structural rigidity imported to these materials by the siloxane linkages. The data of BET surface area (S_{BET}) derived from the linear part of adsorbed nitrogen around $P/P_0 \approx 0.05$–0.3 and the amount of total pore volume (V_t) of $P/P_0 \approx 0.99$ show successive formation of PMO-IL with high surface area of 563 $m^2 g^{-1}$, which contains open mesoporous channels with total volume 1.12 $cm^3 g^{-1}$ (Table 1).[30] Interestingly, a narrow pore size distribution derived from the absorbance branch of the isotherm for PMO-IL centered around 10.6 nm indicates a highly ordered structure in the synthesized PMO-IL, which is also in agreement with N_2 physisorption data (Figure 2 and Table 1).[31] In addition, the specific surface area and pore volume of WO_4^{2-}@PMO-IL in comparison with the parent PMO-IL were decreased significantly from the initial amounts to 391 $m^2 g^{-1}$ and 0.88 $cm^3 g^{-1}$, respectively; this result clearly demonstrates that the tungstate ions have been successfully immobilized inside the pores of the PMO-IL. Interestingly, a sharp capillary condensation step in the isotherms and narrowed pore size distribution (BJH) indicate that structurally ordered and available mesochannels also remained intact after modification of the parent PMO-IL with tungstate ions (Figure 2).

Table 1. Textural properties of the synthesized materials determined from nitrogen physisorption.

Material	S_{BET}[a] [$m^2 g^{-1}$]	V_t[b] [$cm^3 g^{-1}$]	D_{BJH}[c] [nm]
PMO-IL	563	1.12	10.6
WO_4^{2-}@PMO-IL	391	0.88	10.6

[a] S_{BET} = specific surface area. [b] V_t = total pore volume. [c] D_{BJH} = average pore diameter.

TEM images of the catalyst also provided further evidence that the ordered organizations of the mesopores were retained after surfactant extraction and/or immobilization of tungstate ions. Hence, TEM images of WO_4^{2-}@PMO-IL along the [001] and/or [110] directions also demonstrate a highly ordered structure with 2D hexagonal symmetry in the mesoporous channels, which is in good agreement with the results of N_2 physisorption (Figure 3).

The TGA of WO_4@PMO-IL catalyst was performed at temperatures that ranged from 20 to 600 °C under an air flow (Figure S3 in the Supporting Information). This TG pattern shows two main weight losses; the first one of about 5% below 100 °C may be a result of the desorption of solvent molecules such as water, ethanol, and methanol that remained from the solvent extraction processes, whereas a major weight loss of about 16 wt% observed from 350 to 600 °C could be attributed to the loss of the organic fragments such as IL precursors from the final catalyst. From these data, estimated IL amounts were determined as approximately 1 $mmol g^{-1}$. Finally, the amount of exchanged tungstate ions in the catalyst was found to be 0.07 $mmol g^{-1}$ by using inductively coupled plasma

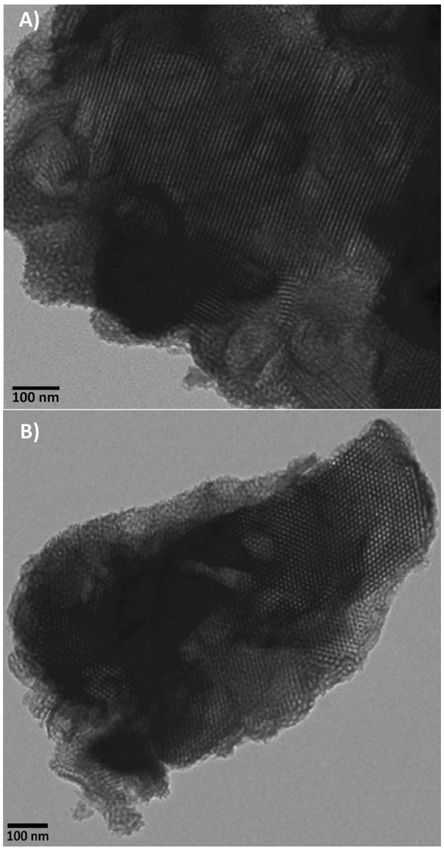


Figure 3. TEM images of WO_4^{2-}@PMO-IL along the A) [110] and B) [001] directions (scale bars: 100 nm).

atomic emission spectroscopy (ICP-AES) of its acid-washed solution.

After the initial characterization of the WO_4^{2-}@PMO-IL, its catalytic activity was studied in the oxidation of organic sulfides to the corresponding sulfoxides and/or sulfones with aqueous 30% H_2O_2 as terminal green oxidant. Thus, the oxidation of methyl phenyl sulfide (1 mmol) as a test model was first investigated in various solvents and at different temperatures, to find the optimum reaction conditions (Table 2). Initially, the oxidation of methyl phenyl sulfide with 30% H_2O_2 (1.2 equiv) in the presence of 1 mol% of catalyst in pure water at room temperature afforded the corresponding methyl phenyl sulfoxide in 50% yield after 30 minutes (Table 2, entry 1). Our preliminary investigation showed that the solvent has a crucial role in this transformation.[27] With this promising result, we then switched our attention to the use of a mixture of water with organic solvent. In this context it was found that, in an equal mixture of water and acetonitrile (1:1), which was recently selected as the optimum solvent system according to our previous tungstate-based catalyst system,[27] the oxidation of thioanisole proceeded much better and furnished the corresponding sulfoxide in 81% yield within 1 hour under the same reaction conditions (Table 2, entry 2). Encouraged by these results, the effect of temperature was then examined (Table 2, entry 3). Although no significant improvement in both sulfoxide yield and reaction conversion was achieved upon increasing the reaction temperature to 35 °C, when employing either a higher temperature (50 °C) or larger amount of 30% H_2O_2 (1.5 equiv) a gradual selectivity changeover toward the formation of the corresponding sulfone was observed (Table 2, entries 3–5). Consistent with these results, it was found that the use of only 2 equivalents of 30% H_2O_2 was sufficient for providing excellent selectivity for the corresponding sulfone, although somewhat longer reaction times were necessary to ensure complete substrate conversion (Table 2, entries 6 and 7). The fact that the oxidation of methyl phenyl sulfide in water afforded the corresponding sulfoxide (Table 2, entry 1) and that the same reaction in H_2O/CH_3CN (1:1) furnished the respective sulfone (Table 2, entry 8) highlights the notion that in order to adjust the selectivity of the reaction toward sulfoxide or sulfone the solvent composition needs to be respected. Therefore, to gain better insight into the impact of solvent composition on the selectivity of this catalyst process, we performed additional experiments. Along this line, it was found that when water was replaced by methanol under otherwise the same reaction conditions, the conversion was noticeably improved whereas the selectivity toward sulfoxide did not vary significantly and still remained around the excellent value of 96% at 83% conversion (Table 2, entry 9). Surprisingly, the same reaction when methanol/H_2O (10:1) was used as the solvent system instead of pure water or methanol gave an excellent yield of 92% of methyl phenyl sulfoxide as major product within 30 minutes (Table 2, entry 10). These data indicate that on changing the solvent system from aqueous methanol to aqueous acetonitrile, the reaction selectivity varies from sulfoxide to sulfone with retention of the high yield and selectivity (Table 2, entries 8 and 10). These preliminary results indicate that there is a distinctive relationship between the solvent composition and the catalyst activity–selectivity for the selective formation of either sulfoxide or sulfone using the present catalyst system. More information about this issue is provided later.

Table 2. Optimization of the solvent, temperature, and amount of hydrogen peroxide during oxidation of methyl phenyl sulfide.

Entry[a]	Solvent	T [°C]	t [h]	Sulfoxide [%][b]	Sulfone [%][b]
1	H_2O	RT	0.5	50	5
2	H_2O/MeCN (1:1)	RT	1	81	2
3	H_2O/MeCN (1:1)	35	1	84	5
4[c]	H_2O/MeCN (1:1)	50	1	75	25
5[d]	H_2O/MeCN (1:1)	50	0.5	30	70
6[d]	H_2O/MeCN (1:1)	50	1	23	77
7[d]	H_2O/MeCN (1:1)	50	1.5	10	90
8[d]	**H_2O/MeCN (1:1)**	**50**	**2**	**4**	**96**
9	MeOH	RT	0.5	80	3
10	**H_2O/MeOH (1:10)**	**RT**	**0.5**	**92**	**8**
11[d]	H_2O/MeOH (1:10)	50	2	55	45

[a] Reaction conditions: methyl phenyl sulfide (1 mmol), WO_4^{2-}@PMO-IL (1 mol%), 30% H_2O_2 (1.2 equiv), and solvent (2 mL). [b] Yield determined by GC analysis using the standard addition method. [c] 1.5 equiv 30% H_2O_2 was used. [d] 2 equiv 30% H_2O_2 was used.

Kinetic experiments were also performed for oxidation of methyl phenyl sulfide under the optimized reaction conditions (Table 2, entries 8 and 10). Although in H_2O/CH_3OH solvent mixture the oxidation of methyl phenyl sulfide furnishes the corresponding sulfoxide in high yield and selectivity (up to 92%, 30 min), the yield of methyl phenyl sulfones was less than 10% (Figure 4A). On the other hand, in H_2O/CH_3CN mixture, the reaction kinetic profile indicates that both sulfone and sulfoxide were concomitantly produced from almost the beginning of the reaction with very close reaction rates to afford the same approximately 50:50 ratio within 25 minutes (Figure 4B). Interestingly, a gradual selectivity changeover toward the formation of the corresponding sulfone was observed when the reaction was allowed to proceed for an additional reaction time up to 120 minutes. Considering these interesting results, it is believed that the concomitant formation of both sulfoxide and sulfones in the latter case might be the result of in situ generation of proxamidic acid ($CH_3CNHOOH$) through the reaction of CH_3CN and 30% H_2O_2. It is therefore reasonable to speculate that the in situ generated $CH_3CNHOOH$ may contribute to and to some extent be responsible for the enhanced reactivity in H_2O/CH_3CN relative to those obtained in H_2O/CH_3OH using our catalyst system.

On having the optimized reaction conditions, we then extended the scope of the present catalytic system to the selective oxidation of a range of sulfides to the corresponding sulfoxides or sulfones (see Scheme 1). As shown in Table 3, various types of sulfides including aryl, alkyl, diaryl, and dialkyl sulfides furnished the corresponding sulfoxide in moderate to excellent yields (52–98%) and good to excellent selectivities (83–98%) under the conditions demonstrated in entry 10 of Table 2. Notably, this method was equally applicable to the oxidation of

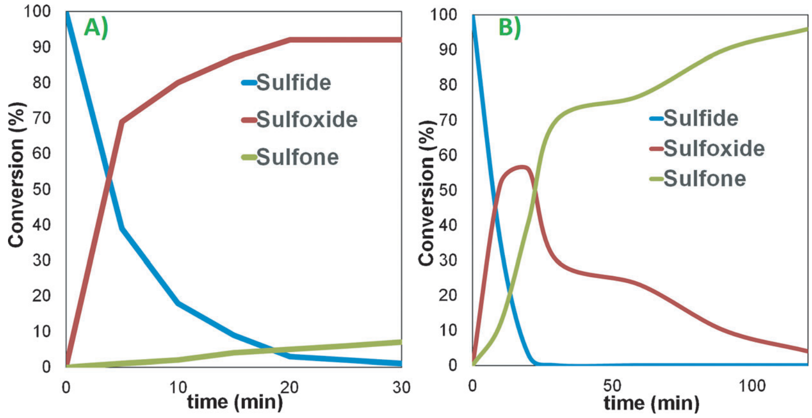
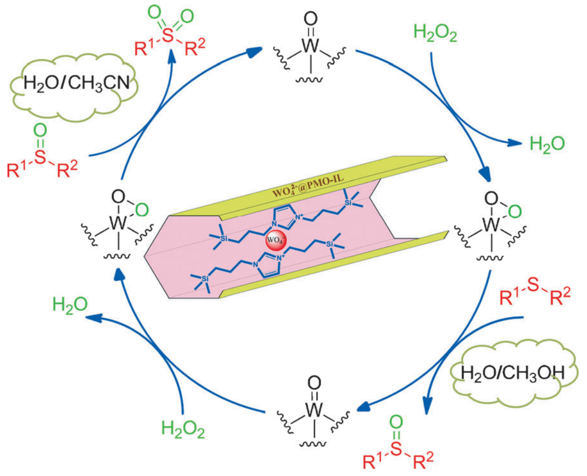


Figure 4. Reaction progress as a function of time in the oxidation of methyl phenyl sulfide using 30% H_2O_2 in A) water/MeOH and B) water/MeCN.

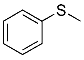
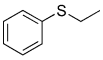
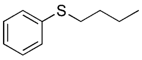
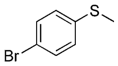
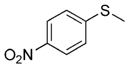
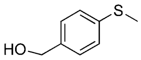
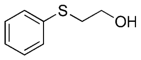
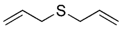
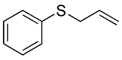
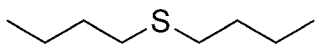
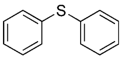
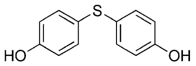
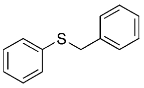


Scheme 1. A possible mechanism for catalytic oxidation of sulfide using WO_4^{2-}@PMO-IL.

sulfides with electron-withdrawing functional groups such as bromide and nitro, which gives the respective sulfoxide compounds in good to excellent yields with a high level of selectivity under the same reaction conditions (Table 3, entries 4 and 5). Even in the case of more challenging sulfides comprising sensitive functional groups, such as olefin and hydroxyl functionalities, the corresponding sulfoxides were obtained in good to excellent yields and selectivities. In the case of allylic sulfides neither the epoxidation of the double bond nor the overoxidation of sulfoxide to sulfone were observed (Table 3, entries 8 and 9) even after prolonged reaction times. It is also worth mentioning that under essentially identical reaction conditions, highly selective sulfoxidation of sulfides such as 4-(methylthio)benzyl alcohol and 2-(phenylthio)ethanol that bear an oxidizable primary alcohol unit can also be achieved without formation of any measurable amount of the respective carbonyl compound (Table 3, entries 6 and 7). Even in the case of less reactive substrates such as diaryl sulfides, the corresponding sulfoxides were obtained in moderate yields and high chemoselectivity (Table 3, entries 11 and 12). In addition, dibutyl sulfide as a model for aliphatic sulfide can be converted into the corresponding sulfoxide in excellent yield and selectivity (Table 3, entry 10).

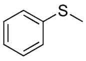
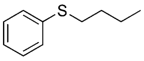
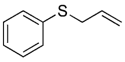
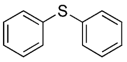
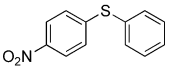
As already mentioned, in the equal mixture of water and acetonitrile (1:1) in the presence of two equivalents of hydrogen peroxide and 1 mol% of our catalyst, methyl phenyl sulfide was oxidized to the corresponding sulfone in excellent yield and selectivity (Table 2, entry 8). Considering these initial promising results and with the aim to study the generality of this procedure, selective oxidations of various challenging sulfides were explored under identical reaction conditions (Table 4, entries 1–5). The butyl phenyl sulfide as relatively sluggish substrate was oxidized selectively to the corresponding sulfone in quantitative yield and excellent selectivity (Table 4, entry 2). Interestingly, under the same reaction conditions, allyl phenyl

Table 3. Oxidation of various sulfides to the corresponding sulfoxides catalyzed by WO_4^{2-}@PMO-IL in H_2O/CH_3OH (1:10).

Entry[a]	Sulfide	t [h]	Sulfoxide [%]	Selectivity [%]
1		0.5	92[b]	92
2		0.5	79[b]	92
3		0.5	57[b]	89
4		1.5	93[c]	95
5		2	94[c]	96
6		1	91[c]	91
7		1	85[c]	85
8		0.5	94[b]	98
9		1	70[b]	98
10		1	98[b]	98
11[d]		2	52[c]	84
12		2	70[c]	89
13[e]		5	60[c]	83

[a] Reaction conditions: sulfide (1 mmol), 30% H_2O_2 (1.2 equiv), WO_4^{2-}@PMO-IL (1 mol%), and H_2O/CH_3OH (1:10, 2 mL) at room temperature (25 °C). [b] Yield determined by GC analysis using the standard addition method. [c] Yields referred to isolated pure products after column chromatography. [d] 3 equiv 30% H_2O_2 was used. [e] 3 equiv 30% H_2O_2 and 2 mol% of catalyst were used.

Table 4. Oxidation of various sulfides to the corresponding sulfones catalyzed by WO_4^{2-}@PMO-IL in H_2O/CH_3CN (1:1).

Entry[a]	Sulfide	t [h]	Sulfoxide [%]	Selectivity [%]
1		2	96[b]	100
2		1.5	100[b]	100
3		1	100[b]	100
4[d]		6.5	89[c]	100
5[e]	 O_2N	9	87[c]	100

[a] Reaction conditions: sulfide (1 mmol), 30 % H_2O_2 (2 equiv), WO_4^{2-}@PMO-IL (1 mol %), and H_2O/CH_3CN (1:1, 2 mL) at 50 °C. [b] Yield determined by GC analysis using the standard addition method. [c] Yields referred to isolated pure products after column chromatography. [d] 3 equiv 30 % H_2O_2 and 2 mol % of catalyst were used. [e] 4 equiv 30 % H_2O_2 and 2 mol % of catalyst were used.

sulfide was completely converted to the expected sulfone within 1 hour without any oxidation of double bonds to epoxide or diols (Table 4, entry 3). Furthermore, relatively less reactive diphenyl sulfide and 4-nitrodiphenyl sulfide were carefully oxidized to their sulfones with good yield and excellent selectivity (Table 4, entries 4 and 5).

An important feature of the heterogeneous catalyst is its recyclability and stability after the reaction process through simple filtration and separation of the catalyst from the reaction medium for use several times. Hence, the recyclability of WO_4^{2-}@PMO-IL was examined for the selective oxidation of methyl phenyl sulfide (1 mmol) to the corresponding sulfoxide under optimized reaction conditions. At this point, after each run the catalyst was isolated through simple filtration, then washed with dichloromethane (3 × 10 mL) and subsequently dried under vacuum overnight (12 h). Interestingly, the described catalyst was carefully reused for a subsequent nine cycles and resulted in 92, 92, 92, 93, 92, 90, 94, 94, and 81 % yields, respectively, without any significant decrease in its efficiency and selectivity. For evaluating the effect of reaction conditions on the catalyst structure, a sample of the separated catalyst from the last cycle was characterized by N_2 sorption analysis, TEM, and TGA. Data from N_2 adsorption–desorption analysis indicate that the recovered catalyst shows a typical type IV isotherm with hysteresis loop H1, which demonstrates that the recovered catalyst is still characterized as an ordered mesoporous material (Figure S4). A particularly sharp capillary condensation step indicates that the nanostructural uniformity of the catalyst did not change after ten reaction cycles. The BET data show a surface area of 290 $m^2 g^{-1}$ and pore volume of 0.7 $cm^3 g^{-1}$. Moreover, the pore size distribution was estimated as 10.6 nm according to the BJH method derived from the adsorbed branch. On considering the pore size distribution (10.8 nm) for the catalyst and recovered catalyst, it is clearly indicated that the pore regularity and uniformity remains intact and it especially shows hydrothermal stability of the catalyst during the recycling process (Figure S5). Moreover, the TG pattern of the recovered catalyst indicated that the catalyst compositions were stable under the reaction conditions (Figure S6). In addition, TEM images of the recovered WO_4^{2-}@PMO-IL after the tenth reaction cycle indicate the presence of a two-dimensional ordered structure with estimated pore size of 10 nm, which is in good agreement with nitrogen physisorption data, and predominantly confirms the stability and robustness of the catalyst under the described reaction conditions and recycling procedure (Figure 5). The high recyclability of the catalyst can also be understood from the low leaching of tungstate species, which was found to be less than 0.5 ppm by ICP-AES.

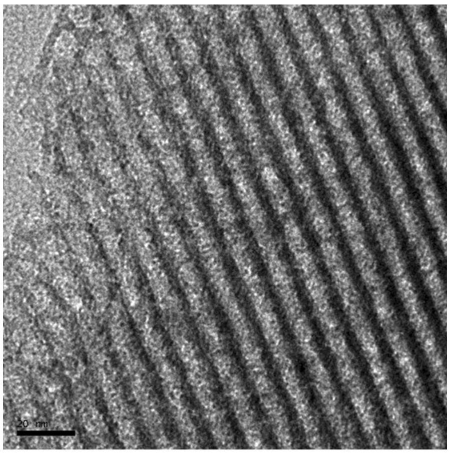


Figure 5. TEM image of the recovered WO_4^{2-}@PMO-IL after the tenth reaction cycle in the oxidation of methyl phenyl sulfide to the related sulfoxide by using 30 % H_2O_2 (scale bar: 20 nm).

We were also very interested to compare the catalytic performance of our system with the ones already reported in the literature in terms of the observed turnover frequencies (TOFs). At this point, selective oxidation of methyl phenyl sulfide to the related sulfoxide in the presence of 30 % H_2O_2 was selected (Table 5). As can be clearly seen, the TOF in our protocol is superior to those of the W-supported catalysts on silica gel, layered double hydroxide (LDH), MCM-41, as well as SBA-15 (Table 5, entries 1–6) under nearly the same reaction conditions, whereas it is inferior to those obtained from either decatungstate or peroxotungstate catalysts supported on SiO_2 or polymer, respectively (Table 5, entries 7 and 8). This might be owing to higher loading and thus a higher number of active sites in the catalyst systems comprising either decatungstate or peroxotungstate species. In particular, the superior catalytic performance of the present catalyst system in comparison with the W-supported catalysts on nonfunctionalized silica materials, such as silica gel, MCM-41, and SBA-15, clearly highlights the advantage of imidazolium motifs inside the framework of PMO-IL in achieving the observed superior catalytic activity. Considering the short reaction times, good recyclability, excellent yields, and great selectivities as well as high TOFs obtained at room temperature for our catalyst system in the oxi-

Table 5. Oxidation of methyl phenyl sulfide to the related sulfoxide by using 30 % H_2O_2 in the presence of various supported tungsten-based catalysts.

Entry	Catalyst	Cat. amount [mol %]	Solvent	T [°C]	t [h]	Conv. [%]	Select. [%]	TOF [h^{-1}][a]	Ref.
1	WO_4^{2-}@LDH[b]	4.4	H_2O	RT	0.5	35	88	43	[22a]
2	$W_2O_3(O_2)_4^-$MIL@SiO_2[c]	1.5	CH_2Cl_2/CH_3OH (1:1)	RT	1.5	98.6	98.6	43.5	[23j]
3	$W_2O_3(O_2)_4$@SiO_2	1.5	CH_2Cl_2/CH_3OH (1:1)	8	2.5	92	86	24.5	[23h]
4	WO_4^{2-}@SiO_2	1	CH_2Cl_2/CH_3OH (1:1)	RT	1.5	82	100	54.6	[23d]
5	WO_3@MCM-41	1	CH_3OH	RT	4	97	94	25	[24a]
6	WO_4^{2-}@SBA-15	1	H_2O	35	1	93	97	101	[27]
7	$W_{10}O_{32}^{4-}$@SiO_2	0.1	CH_3OH	RT	1.5	92	92	666.6	[23e]
8	W(O)(O_2)(CN)@polymer	0.5	CH_3OH	RT	0.58	>99	>99	1235	[23j]
9	**WO_4^{2-}@PMO-IL**	**1**	**CH_3OH/H_2O** (10:1)	**RT**	**0.5**	**100**	**92**	**200**	this study

[a] Turnover frequency determined using (conversion) ÷ [(cat. mol %) × (reaction time)]. [b] LDH = layered double hydroxide. [c] MIL = multilayer ionic liquid.

dation of various organic sulfides, it is reasonable to consider this system as a high-performance alternative for this purpose.

Conclusion

In summary, we have reported the synthesis and characterization of periodic mesoporous organosilica with ionic liquid framework (PMO-IL), as an efficient support for the immobilization of tungstate ion catalysts through a simple ion exchange technique. At first, the designed catalyst was characterized by various techniques such as nitrogen physisorption, TEM, and TG analysis. The mentioned WO_4^{2-}@PMO-IL was carefully checked in the selective oxidation of organic sulfides into the corresponding sulfoxide or sulfone derivatives. Our studies showed that various aliphatic or aromatic sulfides comprising readily oxidizable groups such as hydroxyl and allylic functional groups were selectively converted into the corresponding sulfoxide with good to excellent yields under the same reaction conditions. Moreover, by changing the reaction medium from aqueous methanol to aqueous acetonitrile, the substrates were completely oxidized to sulfones instead of sulfoxides. Furthermore, the presented catalyst could be effectively recovered and reused at least nine times without remarkable loss in the catalytic activity. Finally, embedding of the flexible ionic liquid along with active catalyst in the PMO wall network allows the catalysis to act as an interphase catalyst during reaction progress. Further works on the practical applications of PMO-IL as heterogeneous ionic liquid and also as an innovative support for the immobilization of other types of transition-metal catalysts through anion-exchange is underway in our laboratories.

Experimental Section

Materials

Sodium hydride 95 %, Pluronic P123 (MW_{av}≅5800, Aldrich), and tetramethyl orthosilicate (TMOS) were obtained from Aldrich. Imidazole, 3-chloropropyltrimethoxysilane (CPTMS), potassium chloride, concd HCl (37 %), and $Na_2WO_4\cdot 2H_2O$ were purchased from Merck. Imidazole was first recrystallized in distilled CH_2Cl_2 and then dried in a desiccator under vacuum over dry P_2O_5 for 3 days at room temperature.

Syntheses

Synthesis of ionic liquid precursor:[15] The IL BTMSPI precursor was prepared by a few modifications of our last synthesis report.[28] In a typical experiment, a suspension of sodium imidazolide in dry tetrahydrofuran (THF) was prepared from the direct reaction of freshly dried imidazole (2 g) and NaH (95 %, 0.77 g) in a flame-dried two-necked flask containing dry THF (60 mL) under an argon atmosphere. CPTMS (5.4 mL) was added to the mentioned stirred suspension and the resulting mixture was heated at reflux for 30 h. Then, the reaction mixture was allowed to cool to room temperature followed by solvent removal under reduced pressure until an oily mixture containing NaCl was obtained. To this end, CPTMS (5.4 mL) and dry toluene (60 mL) were added and the resulting mixture was heated at reflux for 48 h until a two-phase mixture comprising toluene and IL (BTMSPI) was obtained. Then, the toluene phase was removed and dry CH_2Cl_2 (60 mL) was added to remove the precipitated NaCl. In the next stage, the CH_2Cl_2 phase was transferred into a well-dried two-necked flask and the volatiles removed by reduced pressure until the IL (BTMSPI) and unreacted starting materials were obtained. Finally, the IL was washed by dry toluene (5 × 50 mL) for removal of unreacted starting materials to give almost pure BTMSPI in 78 % yield of isolated product. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.00$ (s, 1H; NC**H**N), 7.46 (d, $J = 1.7$ Hz, 2H; C**H**C**H**), 4.32 (t, $J = 7.1$ Hz, 4H; NC**H**$_2$), 3.60 (s, 18H; 6OC**H**$_3$), 2.00 (m, 4H; CH_2C**H**$_2$$CH_2$), 0.62 ppm (t, $J = 8.1$ Hz, 4H; SiC**H**$_2$); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 136.08$ (N**C**HN), 122.20 (**C**H**C**H), 51.76 (N**C**H$_2$), 50.77 (O**C**H$_3$), 24.12 (CH_2**C**H$_2$$CH_2$), 5.81 ppm (Si**C**H$_2$).

Synthesis of PMO-IL: PMO-IL was also synthesized according to our previously reported methods.[15–18] In a typical procedure, Pluronic P123 (1.67 g) was dissolved in a mixture of H_2O (10.5 g), HCl (2 M, 46.14 g), and KCl (8.8 g), and the mixture was stirred at 40 °C until a homogeneous solution was obtained. To this end, a premix of BTMSPI (2 mmol, 0.86 g) and TMOS (18 mmol, 2.74 g) in dried methanol was added immediately to the above-mentioned solution and stirred at 40 °C for 24 h. The resulting mixture was exposed to hydrothermal treatment without stirring at 100 °C for 72 h. The obtained solid material containing surfactant was isolated by filtration and carefully washed with deionized water. The surfactant residue was then extracted from the material through a Soxhlet apparatus by using ethanol (100 mL) and concd HCl (37 %, 3 mL). In a typical extraction, as-synthesized PMO (1 g) was washed four times with acidic ethanol over 12 h and then dried under vacuum for 24 h, to afford PMO-IL as a bright yellow powder.

Preparation of WO_4^{2-}@PMO-IL: WO_4^{2-}@PMO-IL was synthesized by a simple ion-exchange technique according to our previous procedure with slight modifications.[23d] In a typical method, PMO-IL (0.5 g) was added to deionized water (20 mL) and the mixture was sonicated for at least 10 min. Then $Na_2WO_4{\cdot}2H_2O$ (0.090 g, 0.26 mmol) in deionized water (3 mL) was added gradually to the aforementioned suspension and stirred at room temperature for 5 h. The excess of tungstate solution was filtered, washed with deionized water (3×30 mL), and dried under vacuum at 65 °C overnight (12 h). The total tungstate loading of the materials was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to be approximately 0.07 mmol g^{-1}.

Oxidation

General procedure for the selective oxidation of sulfides to the corresponding sulfoxides in water/CH_3OH: WO_4^{2-}@PMO-IL (0.143 g, 1 mol%) was added to a solution of sulfide (1 mmol) and 30% H_2O_2 (1.2 mmol; exceptionally 3 mmol in the case of phenyl benzyl sulfide) in H_2O/CH_3OH (2 mL, 1:10), and the solution was stirred at room temperature for the requisite time. The progress of the reaction was monitored by TLC or GC. After completion of the reaction the product was first extracted with CH_2Cl_2 (3×10 mL) and finally purified by using column chromatography (*n*-hexane/ethyl acetate, 8:1).

General procedure for the selective oxidation of sulfides to the corresponding sulfones in water/CH_3CN: WO_4^{2-}@PMO-IL (0.143–0.286 g, 1–2 mol%) was added to a solution of sulfide (1 mmol) and H_2O_2 (2–4 mmol, depending on sulfide) in H_2O/CH_3CN (1:1), and the solution was stirred at 50 °C for the requisite time. The progress of the reaction was monitored by TLC or GC. After completion of the reaction the product was first extracted with CH_2Cl_2 (3×10 mL) and finally purified by using column chromatography (*n*-hexane/ethyl acetate, 8:1).

General procedure for recycling of WO_4^{2-}@PMO-IL in the oxidation of methyl phenyl sulfide to the corresponding sulfoxide: After the first run, the catalyst was isolated by centrifugation and subsequently washed with CH_2Cl_2 (3×10 mL) and dried under vacuum for 12 h. The recovered catalyst was then used in several runs in same manner reported for the first run.

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Keywords: ionic liquids · oxidation · supported catalysts · sustainable chemistry · tungsten

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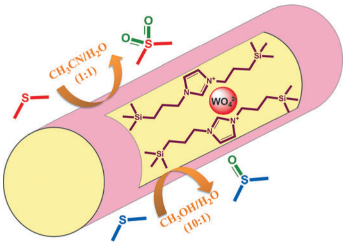
Interior design: The tungstate ion supported on periodic mesoporous organosilica with an ionic-liquid framework (see figure) has been used as an efficient and recoverable catalyst in the selective oxidation of organic sulfides into the related sulfoxides or sulfones, according to the choice of reaction solvent. The use of 30 % H_2O_2 as a green oxidant was also achieved.



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Tungstate Supported on Periodic Mesoporous Organosilica with Imidazolium Framework as an Efficient and Recyclable Catalyst for the Selective Oxidation of Sulfides