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Babak Karimi, and Mojtaba Khorasani

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Selectivity Adjustment of SBA-15 Based Tungstate Catalyst in Oxidation of Sulfides by Incorporating a Hydrophobic Organic Group inside the Mesochannels

BabakKarimi and Mojtaba Khorasani*

Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), PO-Box 45195-1159, Gava-zang, Zanjan 45137-6731, Iran

Fax: (+98-241-4214949)

Keywords: Supported Catalyst, SBA-15, Mesoporous Materials, Sulfoxides, Hydrogen Peroxideand Tungstate.

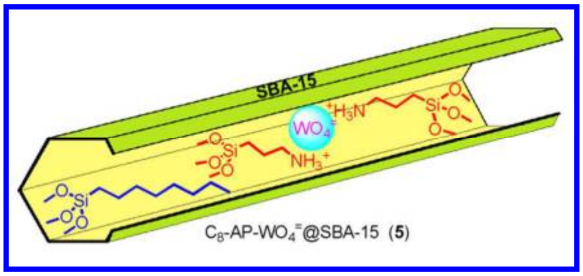
ABSTRACT: A novel heterogeneous catalyst system comprising tungstate ions embedded into the hydrophobic mesochannels of SBA-15 was found to exhibit significant selectivity enhancement in oxidation of sulfides in water or water/CH_3CN using 30% H_2O_2. Our studies demonstrated that the presence of *n*-octyl group in the interior of nanospaces of our catalyst system provides a hydrophobic/hydrophilic region in the mesochannels of the catalyst where the active tungstate species are located and in turn results in at least three distinct important features. First of all, the catalyst comprising *n*-octyl group shows much better water tolerance than the catalysts not having hydrophobic organic moieties. Moreover, the non-productive decomposition of H_2O_2 was significantly inhibited in the present catalyst system. The present catalyst system also offers an unprecedented selectivity changeover depending to the hydrophobic nature of the initial sulfides and/or the utilized solvent mixture. While high yields and excellent selectivities toward the corresponding sulfoxide were obtained in the oxidation of less hydrophobic sulfides in H_2O as reaction solvent, the selectivity pattern was shifted toward sulfones in the case of using more hydrophobic sulfides as substrates. On the other hand, in CH_3CN/H_2O (1:1) as reaction solvent almost all of the studied sulfides were selectively oxidized to the corresponding sulfoxide in high yields. Based on several compelling observation we have proposed a synergistic model to explain the origin of the observed selectivities. The catalyst was respectively recovered and reused in 5 and 7 successive reaction runs in water and water/CH_3CN, respectively, with only slight decrease of reactivity.

INTRODUCTION

Since the discovery of ordered mesoporous materials,[1] a variety of inorganic-organic hybrid mesoporous materials with high specific surface area, has been extensively used as adsorbent, catalyst, and support in the chemical, biochemical and petrochemical applications.[2] The distinct order of the channels ranging from 2-50 nm as well as the ease with which pore size, pore structure, physical properties, and chemical functionalities of these materials can be uniformly tailored, make them promising platform in designing novel sophisticated materials possessing desired properties in a typical application. In the catalyst design context, better understanding of the aforementioned characteristics and their relationship to the reaction profile may effectively result in the possibility to enhance (or adjust) the product selectivity whilst keeping high catalytic activity.

In particular, for the reactions in which a desired product could subject to further reaction on the catalyst surface, its longer retention inside the nanospaces of such catalysts may drastically alter product selectivity. On the other hand, considering the hydrophilic nature of mesoporous silica framework, for the reactions which contain both aqueous phase and hydrophobic starting materials the major problem is the mass transfer phenomena since the activity of these catalysts can often decline by physical adsorption of water. Therefore, the hydrophobic/hydrophilic balance of the solid catalysts could significantly influence on their catalytic performance, durability, and product selectivity.There are several reports pointing to the design and applications of hydrophobic mesoporous silica in different reactions such as esterification and biodiesel production,[3] oxidation of alkyl benzenes,[4] Pechmann coumarine synthesis[5] and Strecker reactions[6] and so on. It is also worthy of note that hydrophobic titanosilica based on MCM-41 has been also used for the efficient epoxidation of alkenes.[7] It was well-documented that the hydrophobization of nanospaces of the mesoporous support could markedly influence the stability and/or the performance of a certain catalyst system especially in the reactions in which water participates as one of the reaction partners.

In this work, we try to address this issue by designing a novel catalyst system consisting tungstate ion immobilized in the interior of hydrophobic nanospace of SBA-15 (Scheme 1) for selective oxidation of sulfides using 30% H_2O_2 to their corresponding sulfoxide or sulfones by choosing appropriate reaction solvent.



Scheme 1. A schematic illustration of catalyst **5**

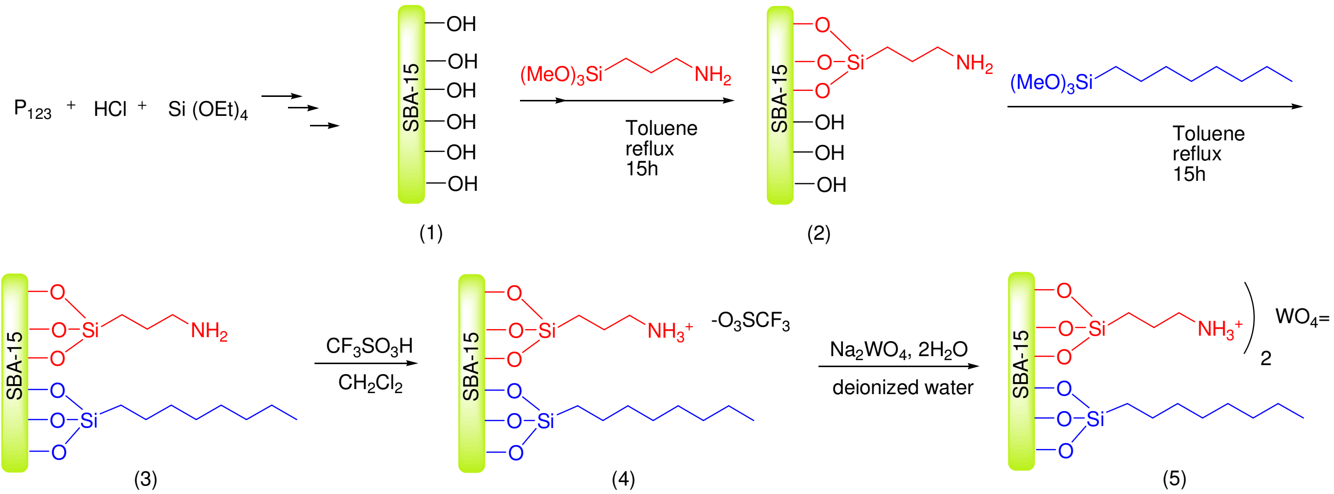
The selective oxidation of sulfides into the correspondingsulfoxides is one of the most important processes within both laboratory and industrial setting,[8] since they are versatile intermediates and products in the synthesis of pharmaceuticals, agrochemicals and other fine chemicals.[9] However, frequently such oxidation reactions have traditionally been relied upon environmentally damaging oxidant, many of which are extremely hazardous to use or toxic.[10] Moreover, sulfoxides can often undergo over-oxidation to their corresponding sulfones and therefore, it is very important that the catalyst has a high selectivity toward sulfoxide and/or sulfone. In view of higher polarity of sulfoxides in comparison with the pristine sulfides, we reasoned that designing a catalyst system having suitable surface hydrophobicity might indeed provide a mean to expel the sulfoxide molecules as soon as they formed from the catalyst surface, thus suppressing their further oxidation to the corresponding sulfones.

Therefore we have chosen the oxidation of sulfide as a probe to exemplify whether it would be possible to control the selectivity of this reaction by employing our novel hydrophobic SBA-15 immobilized tungstate catalyst.

RESULTS AND DISCUSSION

The route for the preparation of the catalyst is schematically illustrated in Scheme 2. The pristine SBA-15 was initially prepared by hydrolysis and condensation of $(EtO)_4Si$ in the present of Pluronic P123 under acidic condition according to the reported procedure with slight modification.[1d] The resulting SBA-15 was then successively functionalized with terimethoxysilyl derivatives of 3-aminopropyl (AP) and *n*-octyl (C_8) moiety through two step silylation to yield the corresponding hydrophobic aminopropyl SBA-15 denoted as C_8-AP@SBA-15 (**3**). The final catalyst which is denoted as C_8-AP-$WO_4^=$@SBA-15 (**5**) was obtained by neutralization of amino groups in **3** with fresh CF_3SO_3H followed by ion-exchange by tungstate ions according to our previously developed protocol.[11] The process for preparing the catalyst and its intermediates was first monitored by N_2 adsorption-desorption analysis and the structural parameters for these materials are presented in Table 1. N_2 sorption diagrams for all materials exhibited type IV isotherms with relatively sharp hysteresis loop, which are characteristics of mesoporous structure with narrow pore size distributions (Figure 1). It can be also clearly seen that the nitrogen gas adsorption uptake decreased as the AP, C_8, and $WO_4^=$ functions were successively incorporated into the nanospaces of the parent SBA-15. Notably, a clear capillary condensation step was even observed for **5**, which provided clear evidence for the preservation of open-up mesopore structure, implying that the channels and thus immobilized tungstate species are still accessible. According to BJH and BET plots, specific surface area, pore size distributions and total pore volume of the materials were all decreased after the post-grafting and tungstate ion immobilization stage (Table 1). TEM images of **5** along 001 and 110 directions also provided further evidence that the 2D-hexagonal mesostructures of the material were well retained during the catalyst preparation processes, a result consistent with N_2 sorption diagrams (Figure 2).

Both elemental and thermogravimetric analysis (TGA) (Figure S2) were concomitantly employed in each stage to estimate the loading of individual organic groups in **5** (Table1). Finally, the amounts of loaded $WO_4^{=}$ in the catalyst were found to be 0.22 mmol/g using polarography a value which further confirmed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) of its acid washed solution.



Scheme2. A schematic presentation for the preparation of catalyst **5**

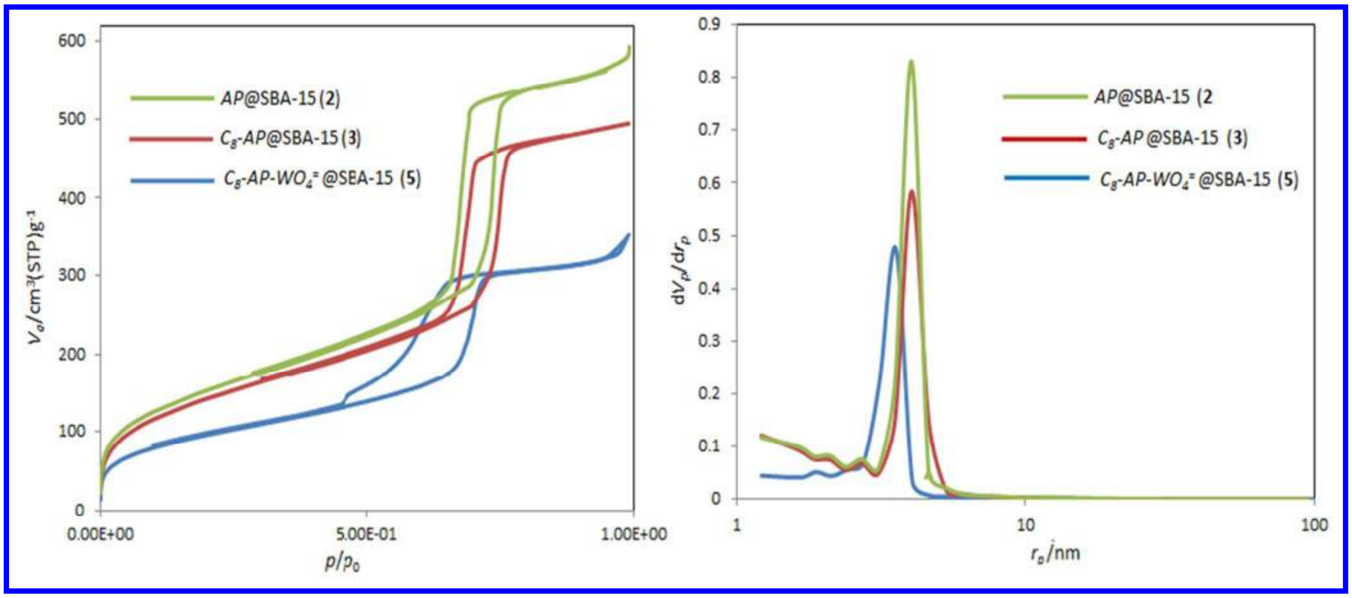


Figure 1. Nitrogen adsorption-desorption isotherms (left) and pore size distributions (right) of the synthesized materials.

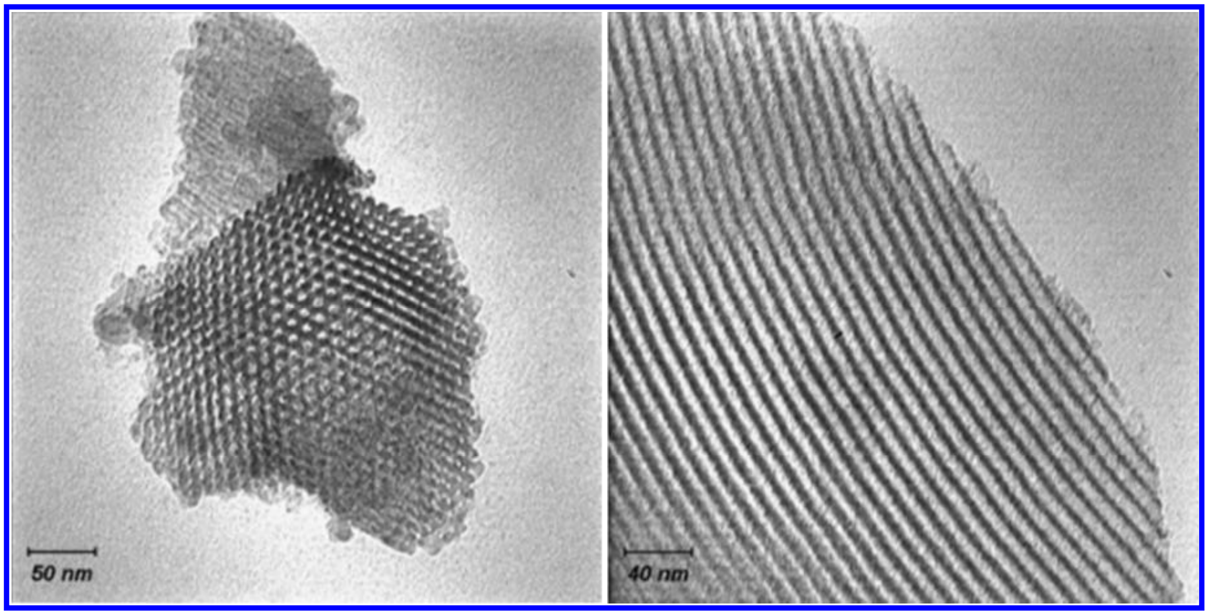


Figure2. TEM images of **5** along [001] (left) and [110] (right) directions

Table1.Textural properties and the loading of functionalized organic groups and tungstate in the materials

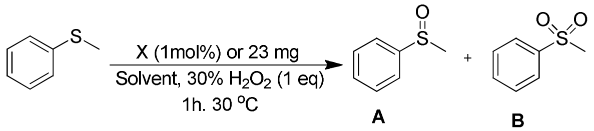
Material	S_{BET}[a] $m^2.g^{-1}$	V_t[b] $m^3.g^{-1}$	D_{BJH}[c] nm	C[d] %	N[d] %	Loading of FunctionalGroups mmol. g^{-1}
1	820	1.03	7.7			
2	554	0.91	8.06			
3	517	0.67	8.06			
5	339	0.51	7.1	6.5	1.2	0.86 (AP)[e], 0.35 (C_8)[e], 0.22 ($WO_4^{=}$)[f]

a) S_{BET} = specific surface area, b)V_t = total pore volume, c) D_{BJH} = pore size distribution calculated from the adsorption branch using BJH methods, d)calculated from elemental (CHN) analysis, e)Estimated by elemental (CHN) analysis and TGA,f)Determined using polarography and further confirmed using ICP-AES of a sample of acid washed solution of **5**

The catalytic activity of **5** was then examined in selective oxidation of sulfide using 30% H_2O_2 by emphasizing to preferably employ water as a green solvent. The reaction was first tested in the oxidation of phenyl methyl sulfide at the ambient temperature (25-30 °C). In our earlier study, we showed that silica-based tungstate catalyst (AP-$WO_4^{=}$@SiO_2 2-5 mol%) was an effective catalyst for the selective oxidation of sulfides to the corresponding sulfoxides or sulfones in CH_3OH/CH_2Cl_2 solvent mixture.[11] we found that this catalyst showed a completely disappointing catalytic activity and selectivity in aqueous media under otherwise the some reaction condition (Table 2, entry 1). To our great delight, when as little as 1 mol% of **5** and only 1 equivalent of 30% H_2O_2 was employed, a significant yield improvement was observed affording phenyl methyl sulfoxide in 94% and remarkably excellent selectivity of >97% (Table 2, entry 2).

Further studies also revealed that the use of a number of selected catalysts such as **4** alone and in combination with un-supported Na_2WO_4 (Table 2, entries 3 and 4), AP-$WO_4^{=}$@SBA-15 (Table 2, entry 4) C_8-AP@SBA-15 (**3**) (Table 2, entry 6), AP@SBA-15 (**2**) (Table 2, entry 7) and SBA-15 (**1**) (Table 2, entry 8) under the same reaction conditions and with essentially the same $WO_4^{=}$ loading, if any, resulted in much inferior yields of phenyl methyl sulfoxides. These data imply that the presence of both *n*-octyl groups and tungstate ion in immobilized form is indispensable in attaining high activity in water by employing the present catalytic system. In particular, the much prominent catalytic activity of **5** with regard to AP-$WO_4^{=}$@SBA-15 may be attributed to appropriate hydrophilic-hydrophobic balance arising from *n*-octyl unit inside the mesochannels of SBA-15, which would favor smooth diffusion of both starting sulfide as well as H_2O_2 into the nanospace of the catalyst and thus enhancing the catalytic activity of **5**. Encouraged by these promising results, we next proceeded to exemplify further the scope and feature of our catalyst system by applying the given reaction condition for the oxidation of various types of structurally divergent sulfides in water. The initial results were rather interesting and revealed that the hydrophobic property of the sulfides has also some marked effects on the reaction selectivity in water. Although high yield of 94% with excellent selectivity (>97%) toward sulfoxide was obtained for the oxidation of thioanisole in water (Table 3, entry1), the behavior of phenyl ethyl sulfide and phenyl *n*-butyl sulfide having a little bit more hydrophobic aliphatic part was completely different (Table 3, entries 2, 3). As can be clearly seen by increasing the size of aliphatic part and thus to some extent the hydrophobic property of the pristine sulfide, the selectivity pattern of the reaction was gradually shifted toward the higher sulfone/sulfoxide ratio (Table 3, entries 2, 3). It is also very important to note that in these cases both sulfoxide and sulfone were concomitantly generated from the beginning of the reaction.

Table2. The Oxidation of Phenyl Methyl Sulfide in the Presence of Various Possible Catalyst Systems Including **1-5** using H_2O_2 30% in Water



Run	**X**	Solvent	A^a (%)	B^a (%)	TON^b
1	$AP\text{-}WO_4^{=}@SiO_2$	H_2O	-	-	-
2	**5**	H_2O	94	3	100
3	**4** +Na_2WO_4(1mol%)	H_2O	33	-	33
4	**4**	H_2O	17	-	-
5	$AP\text{-}WO_4^{=}$@SBA-15	H_2O	59	2	63
6	**3**	H_2O	5	-	-
7	**2**	H_2O	8	-	-
8	**1**	H_2O	10	-	-
9	Leaching test	H_2O	5	-	-
10	**5**	$CH_3OH:CH_2Cl_2$	51	-	51

a) GC yield using internal standard method. b) TON = (substrate/catalyst)×conversion (%).

In light of the above finding and based on the observation that the catalyst system not possessing *n*-octyl group exhibited much lower activity in water (Table 3, entry 4 and 5), it appears that the presence of *n*-octyl group in the interior of nanospaces of **5** in the vicinity to the catalytic center not only improved its water resistivity but it might also provide a means of *longer retention* of more hydrophobic organic substrates inside the mesochannels, thus resulting in a gradual changeover of the product selectivity to sulfone. To our great delight in two separated experiments when only two equivalents of 30% H_2O_2 and 2 mol% of catalyst were employed for the oxidation of phenyl ethyl sulfide and phenyl butyl sulfide, a significant selectivity refinement was observed in each case affording the corresponding sulfone within 4 h in 98% and 99% yields, respectively (Table 3, entries 6 and 7).

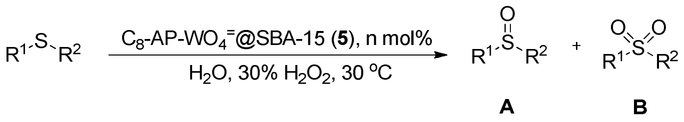
To assess whether the aforementioned proposed model could be generalized or not, the oxidation of a range of sulfides having different hydrophobic nature depending on their size and/or additional functional groups has also been investigated under essentially identical reaction conditions. As indicated by the two additional examples summarized in entries 8 and 9 of Table 3, similar to phenyl methyl sulfide (Table 3, entry 1), highly selective sulfoxide formation can be also achieved in water in the case of aryl sulfides such as 4-thiomethylbenzyl alchohol and 2-(phenylthio)ethanol that bear an additional polar hydroxyl unit (Table 3, entries 8, 9). Interestingly, under identical reaction conditions, highly selective oxidation of diallyl sulfide also proceeded smoothly within 1h and diallyl sulfoxide was remarkably the only product detected in water (Table 3, entry 10). Neither over-oxidation to diallyl sulfone nor epoxidation of double bonds was observed in this case even after prolonged reaction time. To this end, if the observed high selectivities could be indeed related to the hydrophobic/hydrophilic balance between the reaction partners and the solvent, it would be a very important advance and thus we sought to further verify this issue. In order to better probe how much the hydrophobic nature of starting sulfide could participate the selectivity pattern of the described reaction, the oxidation reaction of a series of selected organic sulfide with more hydrophobic character have been screened under our optimal reaction conditions.

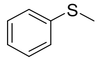
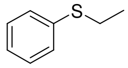
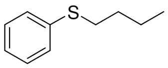
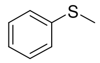
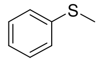
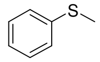
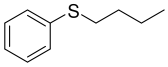
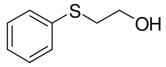
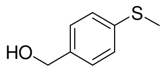
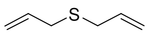
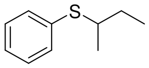
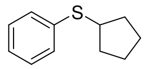
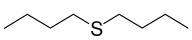
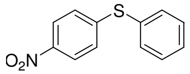
As can be clearly seen, these substrates were also oxidized effectively and affording the corresponding sulfone in quantitative conversion and with excellent selectivities (Table 3, entries 11-14). However, a slight decrease in the conversion (but not selectivity) was observed in the case of 4-nitrodiphenyl sulfide, which may be caused by strong electron-withdrawing of substitute nitro group on the aromatic ring (Table 3, entry 14).

These results again imply that the hydrophobic nature of the starting sulfides might be mainly contributed to the observed selectivities toward the corresponding sulfones. This unprecedented observation offers the possibility of achieving high degree of selectivity to either sulfoxide or sulfone by adjusting the polarity of initial sulfide.

Since the nature of solvent system could also effectively influence the retention of the reaction products inside the system pores of our catalyst, we speculate that increase in partitioning of the sulfoxide product into the reaction solvent will possibly decrease the over-oxidation arising from extended sulfoxide residence on the catalyst surface, thus improving the sulfoxide selectivities particularly in the case of more hydrophobic starting sulfide. Therefore, we next planned to determine whether the product selectivities of the present oxidation protocol using **5** might be affected by reaction solvent or not. Among different solvents and solvent combinations we tested, it was proved that the use of a mixture of water and CH_3CN (1:1) as reaction solvent resulted in the optimum catalyst performances in comparison with those obtained using pure water (Table S1). Interestingly, we also found that the presence of water was indispensable to ensure satisfactory conversion using this catalytic system. Once again, our studies showed that among the materials listed in Table 2, **5** exhibited the highest catalytic performance in water/CH_3CN (1:1) as it did the same in pure water (Table S2, entry 2).

Table 3. Highly Selective Oxidation of Sulfide to Sulfoxide or Sulfones with 30% H_2O_2 Catalyzed by **5** in Water



Run	Sulfide	n	H_2O_2 (eq)	Time (h)	A (%)[a]	B (%)[a]	TON[b]
1		1	1	1	93	4	101
2		1	1	1.5	60	12	84
3		1	1	2.5	18	44	106
4		1	1	2.5	-	-[c]	-
5		1	1	2.5	59	2[d]	63
6		2	2	4	2	98	102
7		2	2	4	-	>99	100
8		1	1	1	94[e]	6[e]	106
9		1	1	1	97[e]	3[e]	103
10		1	1	1	97	3	103
11		2	2	4	-	>99	100
12		2	2	4	-	>99	100
13		1	2	2	-	>99	200
14		2	4	10	-	86[e]	86

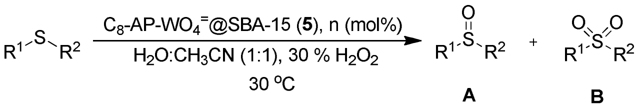
[a] GC yield using internal standard method, [b]TON = (substrate/catalyst) × conversion (%).[c] The reaction was performed in the presence of AP-$WO_4^=$@SiO_2, 1mol%,[d] The reaction was performed in the presence of AP-$WO_4^=$@SBA-15, 1mol%, [e] Isolated yield.

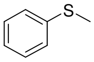
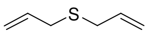
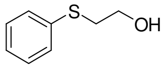
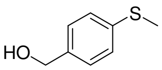
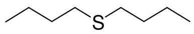
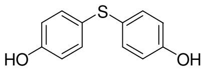
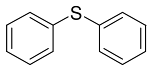
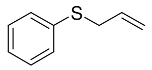
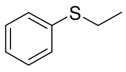
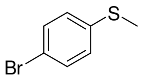
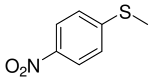
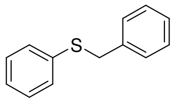
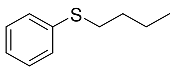
With these initial results in hand, we then started to investigate whether this new solvent system could alter or influence the product selectivity in the oxidation of a relatively wide range of sulfides. The results are collected in Table 4. As can be seen, the catalyst worked well for various aryl alkyl sulfides by employing only 1 equivalent 30% H_2O_2, giving good to excellent isolated yields of the sulfoxide product with excellent selectivities (Table 4, entry 1-5). These results are remarkable since the quest for selective as well as economic oxidation of sulfides using stoichiometric amount of H_2O_2 remains a great challenge.[12]In a similar way, even diaryl sulfides were converted to the corresponding sulfoxide in moderate yield and still excellent selectivity up to 90% (Table 4, entries 6-7).

Interestingly, sulfides with additional functional groups susceptible to over oxidation such as phenols (Table 4, Entry 6), alkenes (Table 4, entries 2 and 8) and alcohols (Table 4, entries 3-4) were found to selectively afford the corresponding sulfoxide without affecting the sensitive functionalities. Remarkably, no epoxidation of double bond and only a slight over-oxidation of sulfoxide to their sulfone were observed during the oxidation of allylic sulfide (Table 4, entries 2 and 8). Dibutyl sulfide as a model for dialkyl sulfides also underwent rapid oxidation to selectively furnish dibutyl sulfoxide in excellent yield (Table 4, entry 5). Once again no detectable sulfone products were ever seen in this case, a feature not observed for the oxidation of the same substrate using our previously developed catalyst AP-$WO_4^{=}$@SiO_2.[11]

At this point, one question arose: how could the observed product selectivities is related to the matching between the surface physicochemical properties of our supported catalyst and the hydrophobic character of the starting sulfide? Considering the reaction pathway profile of sulfide oxidation using H_2O_2, it is obviously clear that during the reaction the reactants (sulfide and H_2O_2) should first diffuse into the mesopores of the catalyst where they got reacted at available tungstate active site to produce the corresponding sulfoxide**.**

Table 4. Highly Selective Oxidation of Sulfide to Sulfoxide with 30% H_2O_2 Catalyzed by **5** in water:CH_3CN Solvent System



Run	Sulfide	n	Time (h)	A (%)[a]	B (%)[a]	TON [b]
1		1	1.5	93	3	99
2		1	1.5	84	6	96
3		1	1.5	85[c]	5[c]	95
4		1	1.5	85[c]	5[c]	95
5		1	1	97	2	101
6		2	5	60[c]	10[c]	45
7[d]		4	6.5	55[c]	5[c]	16
8		2	2	84	5	47.5
9		2	2	93	4	50.5
10		2	2	77[c]	5[c]	42.5
11		3	2	70[c]	5[c]	26.6
12		3	4	57[c]	5[c]	22
13		2	2.5	90	9	54.5

a) GC yield using internal standard method. b) TON = (substrate/catalyst)×conversion (%). c) Isolated yield. d) 3 eq 30% H_2O_2 was used.

This should be followed by the departure of generated sulfoxide from the system pore which leaves the reaction site for the next available reactant in order to attain high selectivity toward sulfoxide formation; otherwise it would further expose to the active site and thus over oxidized to the corresponding sulfone. Considering the surface hydrophobic character of the catalyst and based on the assumption that sulfide oxidation reduces their hydrophobicity, it would be generally expected that the favorable interaction of the hydrophilic corona of the sulfoxide molecules with water (or water/CH_3CN mixture) provides a driving force for its faster departure from the hydrophobic mesopores of the catalyst, thus improving the selectivity of process toward sulfoxide formation. However, when the starting materials become more hydrophobic, the resulting sulfoxide would settle inside the hydrophobic pore channels to a much greater extent, which inevitably can undergo further oxidation using H_2O_2 at the available active site, thus yielding the corresponding sulfone as the final product. This model may also explain the consistent higher selectivity toward sulfone in the oxidation of more hydrophobic sulfides in water in comparison with those obtained in water/CH_3CN solvent mixture. In fact, the use of organic co-solvent increases the departure rate of the sulfoxides (preliminary oxidation product) as soon as they produce from the catalyst system pore, thereby minimizing its over-oxidation arising from extended residence in the close proximity to the active site. In the same way, the reason that sulfoxide formations are more prominent in water in case of substrates bearing an additional polar hydroxyl substituent (Table 4, entries 8-9) is possibly due to the more favorable hydrophilic-hydrophilic interaction of the sulfoxide products and water, which facilitates their departure from the hydrophobic catalyst nanospaces, thus strongly preventing their over-oxidation to the corresponding sulfones. This proposed cooperative mechanism also emphasizes the critical role of grafted *n*-octyl groups inside the nanospaces of the catalyst in attaining enhanced activity with concomitant improved selectivities, since much inferior activity and selectivity have been observed by employing AP-$WO_4^=$@SBA-15 bearing any capped *n*-octyl group (Table 4, entry 4). Once again, the lower activity of AP-$WO_4^=$@SBA-15 compared **5** may also be explained in terms of rapid surface saturation of the former by the excess of water, which prevents non-polar starting sulfide from diffusing into the pores and blocks the active site. Our studies also showed that the presence of *n*-octyl functional groups has at least two additional advantages beside the above-mentioned synergistic benefits. Obviously, the catalyst system having hydrophobic *n*-octyl functionalized group shows much better water tolerance than both our previous silica based tungstate catalyst[6] and AP-$WO_4^=$@SBA-15 which rapidly lose their catalytic activity under our optimal aqueous conditions. Moreover, another advantage is that the non-productive decomposition of H_2O_2 was inhibited to a great extent in our catalyst system. This can be clearly understood from the data embodied in Table 3 and 4. Almost in all cases, the reactions proceeded well with 1 or 2 equivalents of H_2O_2 with respect to the starting sulfides, giving excellent yields of the corresponding sulfoxides or sulfones, respectively, under the described optimal reaction conditions.

In order to explore the extent of recyclability of our catalyst system, the catalyst was recovered by microfiltration from the oxidation of thioanisol in both water and water/CH_3CN and reused in subsequent runs (Figure 3). The catalyst was found to retain its activity for a minimum of five reaction cycles in water and seven reaction runs in water/CH_3CN and displayed almost high catalytic performance with over 94% conversion of the substrate and excellent selectivities all over the studied recycling experiment. It was found that the reason for inferior recovery behavior of the catalyst in water is most likely owed to the slight loss of the catalyst body during the recycling stages. TEM image of the recycled catalyst after the 7th reaction cycle in water/CH_3CN revealed that two dimensioned ordered mesoporous structures of the catalyst were mostly retained both catalysis and recycling step (Figure S5). N_2 sorption diagrams of the recycled catalyst which is denoted as Re-C_8-AP-$WO_4^=$@SBA-15 showed also a distinct type IV isotherms with sharp hysteresis loop, further highlighting the notion that ordered mesoporous structure were well preserved during the catalytic reactions and recycling stages (Figure S4). ICP analysis of the reaction solution in the first run revealed that the leaching of $WO_4^=$ was less than 10 ppb.

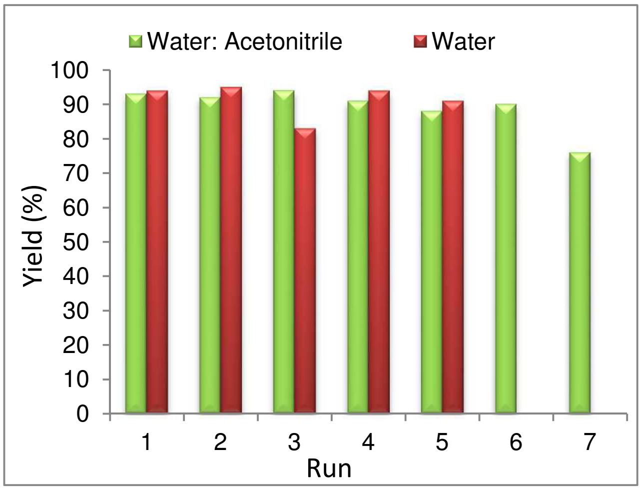


Figure 3. The reusability of catalyst (**5**) in oxidation of phenyl methyl sulfide to the corresponding sulfoxide.

CONCLUSION

Although, many efforts have been devoted to the development of novel protocol for the selective oxidation of sulfides to their corresponding sulfoxides and sulfones, to our knowledge there has been no report regarding the influence of hydrophobic/hydrophilic balance of reaction partners (starting sulfide, catalyst, and reaction solvent) on the selectivity pattern of the reaction. We present, herein, the preparation and characterization of a novel heterogeneous catalyst system comprising tungstate ions immobilized into the hydrophobic nanospaces of SBA-15. The material was then successfully employed in the selective oxidation of sulfides in water or water/CH_3CN using 30% H_2O_2 to their corresponding sulfoxide or sulfone depending on either the nature of the substrate or solvent. Our studies demonstrated that the presence of *n*-octyl group in the interior of mesochannels of our catalyst system provides a hydrophobic/hydrophilic region where the active tungstate species are located and in turn results in at least three distinct important features. First of all, the catalyst comprising *n*-octyl group shows much better water tolerance than the catalysts not having hydrophobic organic moieties. Moreover, the non-productive decomposition of H_2O_2 was significantly inhibited in the present catalyst system. The present catalyst system also offers an unprecedented selectivity changeover depending to the hydrophobic nature of the initial sulfides and/or the utilized solvent mixture. While high yields and excellent selectivities toward the corresponding sulfoxide were obtained in the oxidation of less hydrophobic sulfides in H_2O as reaction solvent, the selectivity pattern was shifted toward sulfones in the case of using more hydrophobic sulfides as substrates. On the other hand, in CH_3CN/H_2O (1:1) as reaction solvent almost all of the studied sulfides were selectively oxidized to the corresponding sulfoxide in high yields. Based on several compelling observation we have proposed a synergistic model to explain the origin of the observed selectivities. The catalyst was respectively recovered and reused in 5 and 7 successive reaction runs in water and water/CH_3CN with only slight decrease of reactivity. It was found that the reason for inferior recovery behavior of the catalyst in water is most likely owed to the slight loss of the catalyst body during the recycling stages.

EXPERIMENTAL SECTION

Preparation of 1.[1d] Typically, 24 g Pluronic P123 ($MW_{av} \cong 5800$, Aldrich) as structure directing agent was dissolved in a solution containing 101 mL HCl (*c*) and 505 mL distilled water. Then 54.2 ml TEOS was added and resulted mixture vigorously stirred at 35 °C for 18-20h. Then, the resulting mixture was aged without stirring at 80 °C for 24h. The obtained mesoporous silica with surfactant was filtered and washed with deionizer water, and dried at room temperature. The surfactant was extracted from the SBA-15 channels by a Soxhlet apparatus by using ethanol for 72h.

Preparation of 2.[13] AP@SBA-15 (**2**) was synthesized according to literature procedure. In a typical procedure, to a suspension of SBA-15 (2 g) in dry toluene, 3-aminoterimethoxy silan (0.35 mL, 2 mmol) was added and the resulting mixture was refluxed for 15 h under inert atmosphere. The resulted material was then filtered and unreacted 3-aminoterimethoxy silan were washed using a Soxhlet apparatus overnight by employing ethanol. The material was then dried at 80 °C for 12h and used in the next stage.

Preparation of 3.[13] *n*-octyl modified AP@SBA-15 (denote as C_8-AP@SBA-15, **3**) was prepared *via* a refluxing process, too. In a typical procedure, to a suspension of **2** (2 g) in dry toluene, *n*-octylterimethoxysilan (3.3 mL, 10 mmol) was added and resulting mixture was refluxed for 15 h under inert atmosphere. Then, the resulting material was filtered and unreacted *n*-octylterimethoxysilan was washed with ethanol overnight using a Soxhlet apparatus. The resulting material was then dried at 80 °C for at least 12h and directly used in the next step.

Preparation of 4.[11] C_8-AP-OTf@SBA-15 (**4**) was synthesized according to our previously reported protocol. Typically, 0.5 g of **3**obtained from previous stage was dispersed in freshly distilled CH_2Cl_2, and trifluoromethanesulfonic acid (CF_3SO_3H, 0.3 mL, 4 mmol) was added and the resulting mixture stirred for 8 h. Finally, the material was filtered and was successively washed with ethanol (2×50 mL) and diethyl ether (2×25 mL). The resulted material was dried at the room temperature in vacuum over P_2O_5.

Preparation of 5.[11] C_8-AP-$WO_4^{=}$@SBA-15 (**5**) was prepared using a simple ion exchange technique according to our previously developed procedure with slight modification.[6] Typically, **4** (0.5g) was added to 20 mL of deionized water and sonicated for at least 10 min. Na_2WO_4, $2H_2O$ (0.073 g, 0.21 mmol) was separately dissolved in deionized water (3 mL) and gradually added to the above-mentioned suspension and stirred at room temperature for 24 h. The resulted ion-exchanged solid was filtered and washed with acetonitrile (2×30 mL) and acetone (2×40 mL), respectively. The material was then dried at room temperature under vacuum over P_2O_5.

General Procedure for the Selective Oxidation of Sulfide to the Corresponding Sulfoxide in Water/CH_3CN. To a solution of 0.5 mmol sulfide and 0.5-1.5 mmol H_2O_2 (depending on sulfide) in H_2O:CH_3CN (1:1), was added 0.023-0.092 g (depending on sulfide) **5** (1-4mol%) and above solution was stirred at 30 °C for requisite time. The progress of the reactions was monitored by TLC or GC. After completion of the reaction the product was first extracted using CH_2Cl_2 (2×25 mL), then evaporated solvent and purified product using column chromatography (*n*-hexane: ethyl acetate (8:1)) if necessary.

General Procedure for the Selective Oxidation of Sulfide to the Corresponding Sulfoxide and/or Sulfone in Water. To a solution of 0.5 mmol sulfide and 1-2 mmol30% H_2O_2 (depending on sulfide) in H_2O, was added 0.023-0.046 g (depending on sulfide) **5** (1-4mol%) and above solution stirred at 30 °C for requisite time. The progress of the reactions was monitored by TLC or GC. After completion of the reaction the product was first extracted using CH_2Cl_2 (2×25 mL), then evaporated solvent and purifiedproduct usingcolumn chromatography (*n*-hexane: ethyl acetate (8:1)) if necessary.

Typical Procedure for Recycling of 5 in Oxidation of Phenyl Methyl Sulfide to the Corresponding Sulfoxide. After the first reaction run, the catalyst was isolated with centrifugation followed by washing with CH_2Cl_2 (3 ×10 mL) and dried under vacuum for 12h at room temperature. The recovered catalyst was used in the subsequent procedure in the same manner as reported in the first run.

AUTHOR INFORMATION

Corresponding Author:

***E-mail :Karimi@iasbs.ac.ir**

Present Address:

Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), PO-Box 45195-1159, Gava-zang, Zanjan 45137-6731, Iran Fax: (+98-241-4214949)

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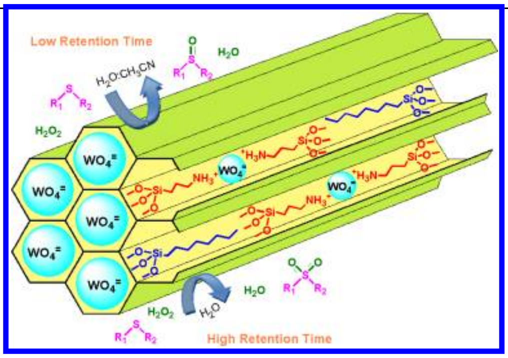
Low Retention Time
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H2O
R1 S R2
H2O2
WO4=
WO4-
+H3N
NH3+
Si
O
H2O
H2O2
High Retention Time

Graphical Abstract