Selective hydrogen peroxide oxidation of sulfides to sulfones with caroxylated Multi-Walled Carbon Nano Tubes (MWCNTs-COOH) as heterogenous and recyclable nanocatalyst under organic solvent-free conditions

Journal:	*RSC Advances*
Manuscript ID:	RA-ART-11-2014-014964.R1
Article Type:	Paper
Date Submitted by the Author:	19-Dec-2014
Complete List of Authors:	Veisi, Hojat; Payame Noor University, Hemmati, Saba; Bu-Ali Sina University, Baghayeri, Mehdi; University of Mazandaran, Hosseini, Fereshteh; PNU,

Selective hydrogen peroxide oxidation of sulfides to sulfones with caroxylated Multi-Walled Carbon Nano Tubes (MWCNTs-COOH) as heterogenous and recyclable nanocatalyst under organic solvent-free conditions

Hojat Veisi,*[,a] Fereshteh Hosseini Eshbala,[a] Saba Hemmati,[a] Mehdi Baghayeri[b]

[a]*Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran*
[b]*Department of Chemistry, Faculty of Science, Hakim Sabzevari University, P.O. Box 397, Sabzevar, Iran.*
Fax +98(838)4227463; E-mail: hojatveisi@yahoo.com

Abstract: This study deals with oxidation of sulfides to sulfones via using a heterogenous and recyclable nanocatalyst. Alkyl and aryl sulfides were directly oxidized to the corresponding sulfones in excellent yields with 30% H_2O_2 under organic solvent-free conditions, in the presence of carboxylated Multi-walled Carbon Nano Tubes (MWCNTs-COOH) as the efficient and heterogeneous nanocatalyst. The oxidation of alkyl and aryl sulfides was proceded at room temperature, and the corresponding sulfones were selectively obtained. The catalyst is recyclable for at least 8 cycles, and the only byproduct is water.

Keywords: Oxidation, Sufide, Sulfone, Hydrogen peroxide, Nanocatalyst

---

Organosulfur compounds, such as sulfoxides and sulfones, are useful synthetic reagents in organic chemistry. Sulfones represent an important class of the compounds due to their properties and reactivity. The strong inductive effect of sulfones moiety and the broad possibilities of the subsequent transformations make them very attractive in the field of asymmetric organocatalysis.[1] Numerous sulfones and their derivatives exhibit different biological activities and have been a subject of an extensive investigation.[2] Phenyl- and heteroaryl-substituted sulfones are important reactants in the Julia-type olefination reaction [3]; in addition, the Grignard reagents of sulfones are useful intermediates for the synthesis of variously functionalized sulfones.[4] 1,2-Diarylethenyl sulfones serve as masked diarylethynes, intermediates for carbon-rich materials and molecular wires.[5] Good hydrolytic stability in basic and acidic media, resistance to oxidation and corrosion, excellent thermal stability and good electrical properties make polymeric sulfones as attractive functional materials. The selective oxidation of sulfides to sulfoxides or sulfones is a useful transformation in organic chemistry.[6] There are many reported methods for the oxidation of sulfides, and therein many reagents are available for the oxidation of sulfides.

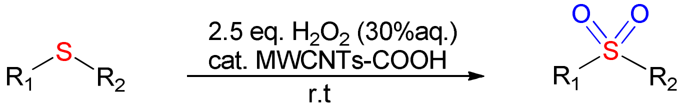
Considering an effective oxygen content, cleanness that leaves water as the only byproduct,[7] safety in storage and operation and the low cost of production transportation, [8, 9] aqueous H_2O_2 is a moderate inorganic ideal green oxidant. Because of the low standard redox potential of H_2O_2 in neutral media, it has been usually used in the presence of acids such as CH_3CO_2H,[10] $HClO_4$,[11] $H_2Mo_2O_7$,[12] and peracids.[13] However, in spite of their potential utility, these homogenous catalysts show some limitations due to the use of toxic and corrosive reagents, the tedious work-up procedure, the necessity of neutralization of the strong acidic media; producing undesired washes, and long reaction times. Furthermore, in these types of reactions, which the catalyst is inherently dissolved in organic phase, it is required to separate the catalyst from the product and a chromatographic procedure for recovery of the catalyst is invariably needed.[14]

Being H_2O_2 a relatively weak electrophile, the sulfide oxidation requires a catalyst such as Mo, Fe, V, W, Re, Ru, Sc, Zr, Mn, Zn and Se acid metal oxides,[15-19] For example, $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)].H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ were reported by Kumar Chand et al.[20], Cp′Mo(CO)$_3$Cl by A. Gamelas et al.[21], and Ce(OTf)$_4$.xH$_2$O by K. Saikia et al.,[22]. However, one of the problems frequently encountered in metal-catalyzed oxidation with H_2O_2 is the concomitant decomposition of H_2O_2, which makes necessary the use of a large excess of H_2O_2 to reach full conversion. In addition, there are several disadvantages for those methods such as: using toxic transition metal compounds, preparation of complex catalyst, removing or recovery of the expensive catalyst and remaining metals in the products.

These reactions, however, require large amounts of hazardous organic solvent, and/or high temperature. when a homogeneous catalyst is used, it is also difficult to separate and reuse it after the reaction. On the other hand, although solid catalyst is more easily removed and reused after the reaction.[23-26]

Carbon nanotube (CNT), as a new type of carbon material among the solid supports, is cylindrically shaped and has appropriate pore-size distributions favoring maximum metallic dispersion. Their morphology, special and steady structural characteristics are quite suitable for their use as hybrid catalysts, which could be regarded as a novel system being able to combine the advantages and to overcome the drawbacks of homogeneous and heterogeneous catalysis. Especially, their surface properties can be modified through various treatments to satisfy special needs. They can represent a new class of advanced materials for catalytic applications, owing to specific metal support interactions given by their graphitic structure, which can improve the catalytic selectivity/activity, as well as their specific surface area. CNTs exhibit extraordinary chemical, electrical, thermal and mechanical strength characteristics, rendering several potential applications in biological materials catalysts.[27-29] Lately, Fe(TPP)Cl-MWCNT has been reported by A. Rezaeifard and M. Jafarpour as the catalyst in the oxidation of sulfides to sulfones.[30]

Due to our interest in the synthesis of organic compounds,[31] herein, in this study, the oxidation of sulfides is investigated. We now report the selective oxidation of sulfides to sulfones with H_2O_2 in the presence of carboxylated Multi-walled Carbon Nano Tubes (MWCNTs-COOH) as a heterogenous and recyclable nano catalyst under organic solvent-free conditions at room temperature (Scheme 1).



Scheme 1.

The surface structure of the materials was confirmed using fourier transform infrared (FTIR) spectroscopy. Figure 1 shows the FT-IR spectra obtained for (a) MWCNT, and (b) MWCNTs-COOH. As it is seen in the curve **b**, the band at 1701 cm^{-1} is corresponding to carbonyl stretch of the carboxylic acid group.

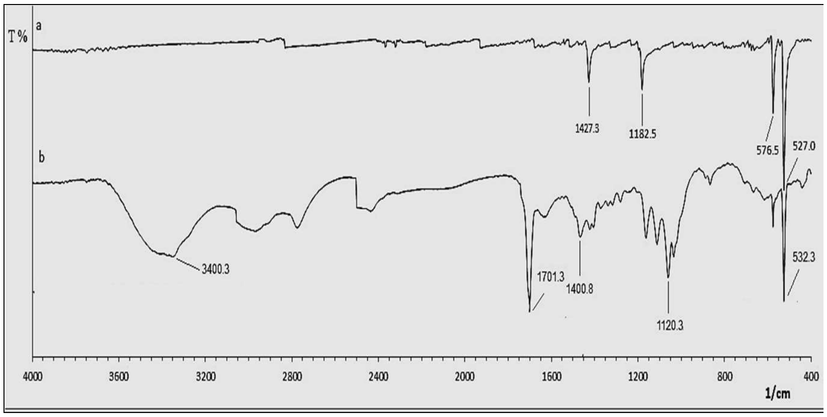


Fig. 1. FTIR spectra of (a) MWCNT, and (b) MWCNT-COOH.

Transmission electron microscopy (TEM) and the scanning electronic microscopy (SEM) investigations are carried out to observe the morphology of the prepared catalyst. Fig. 2 presents SEM images of the pristine MWCNTs (Fig. 2a) and the MWCNTs-COOH (Fig. 2b). One can see the cylindrical cross-section of MWCNTs. The interspaces between functionalized MWCNTs are lower than that of the pristine MWCNTs. This higher entangled configuration could be attributed to functionalization of MWCNTs.[32] In fact the aggregated structure may be due to an enhanced interaction between the functionalized MWCNTs. In fact, the carboxylic acid groups act cross-links adjacent MWCNTs. In addition, pristine MWCNTs are shows low entanglement in compare with functionalized samples.

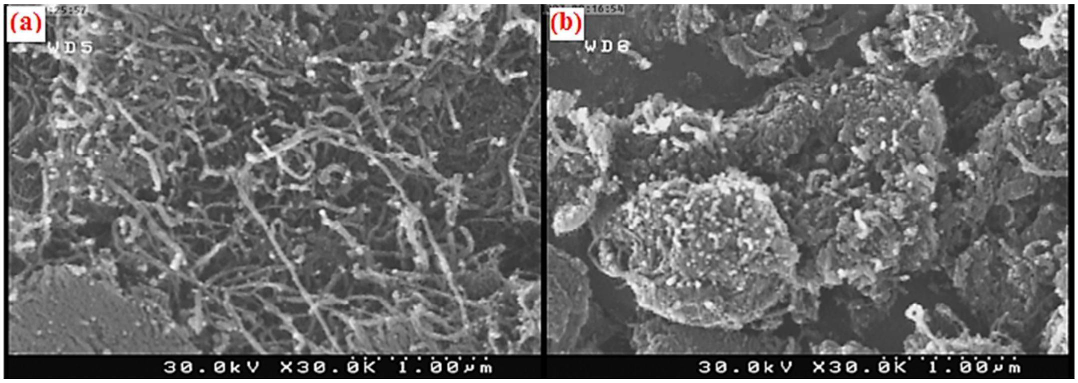


Fig 2. SEM images of (a) MWCNTs, and (b) MWCNTs-COOH.

This may also be evidenced by the TEM observation as shown in Fig. 3. The uniform surfaces of raw MWCNTs have been observed, owing to the perfect lattice structure of carbon-carbon bonds, while the modified MWCNTs have showed some defects in the carbon-carbon bonding associated with the formation of carboxylic acid groups on the surface. Again, the cross-linking phenomenon could be seen for some adjacent functionalized MWCNTs (Fig. 3b). As discussed earlier in SEM section, the carboxylic acid groups could act as bridges between adjacent MWCNTs. In a big picture, such bridge moieties could assist in CNT agglomeration.

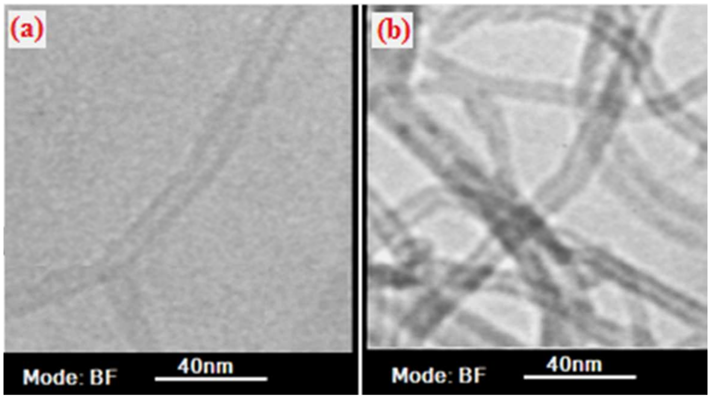
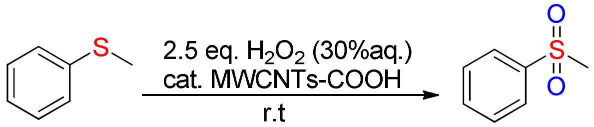


Fig 3. TEM images of (a) MWCNTs, and (b) MWCNTs-COOH.

In continuation of our interest in the development of a highly expedient methodology for the synthesis of fine chemicals compounds of biological importance, we report here the generation of MWCNTs-COOH as a catalyst for the synthesis of sulfone derivatives under solvent-free conditions at room temperature (Scheme 1).

The influence of different reaction parameters on the efficiency of the oxidation process is evaluated in the model reaction depicted in Table 1. The exploratory experiments started using methyl phenyl sulfide as the model substrate. Thus, we have studied the solvent effect, and the results are shown in Table 1. After much experimentation on optimizing solvent, it was found that the use of a less-polar solvent like toluene and 1,4-dioxane afforded phenylmethyl sulfone in low yields (Table 1; entries 1 and 2). Other aprotic solvents such as ethyl acetate, acetone, propylene carbonate, ethylene carbonate, dimethoxy ethane, and 1,2-dichloroethane are demonstrated to be inefficient (entries 3-8). High polar DMF and protic solvents like methanol and acetic acid gave good conversions (entries 9-11). The reaction in acetonitrile and ethanol showed a good reactivity (entries 12, 13), but interestingly, excellent conversion and selectivity were achieved under solvent-free conditions (entry 14). However, a recoverable catalyst requires a sustainable reaction media for application in scale-up procedures in practical goals. Therefore, a new challenge is to make innovative, “clean” methods by using non-toxic solvents in particularly aqueous media. In other words, solvent could have a remarkable influence on the reaction outcome. As a consequence, solvent-free conditions were employed for the formation of the sulfone by H_2O_2 with MWCNTs-COOH.

Table 1. Solvent effect on oxidation of sulfides.



Entry	Solvent	Conv. (%)	Yield (%)
1	Toluene	13	11
2	1,4-Dioxane	42	24
3	Ethyl acetate	22	13
4	Acetone	18	15
5	PC	50	36
6	EC	20	17
7	DME	37	23
8	DCE	23	19
9	CH_3COOH	89	59
10	DMF	91	70
11	CH_3OH	88	82
12	CH_3CN	83	75
13	C_2H_5OH	93	86
14	No Solvent	99	99

We examined the oxidation of methyl phenyl sulfide (1 mmol) using 30% H_2O_2 (2.5 equiv) and MWCNTs-COOH (0.01 g) under solvent-free conditions at room temperature. We observed that the reaction was sluggish and only low yields of the corresponding sulfone were formed after 18 h. By changing the amount of the catalyst, the best performance showed 99% yield. However, when a similar oxidation reaction was conducted in the presence of MWCNTs-COOH (0.02 g), methyl phenyl sulfone was efficiently formed in excellent yields within 10 h (Table 2, entry 13). It is noteworthy that in a blank experiment no significant oxidation was observed in the absence of MWCNTs-COOH.

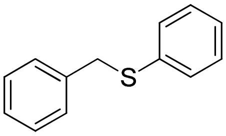
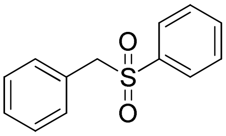
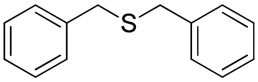
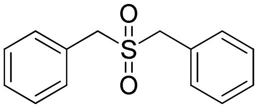
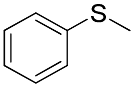
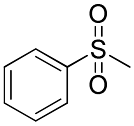
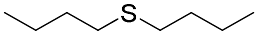
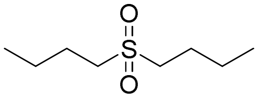
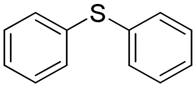
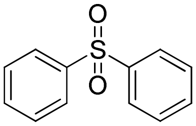
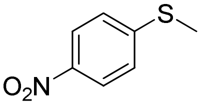
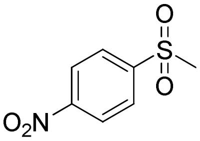
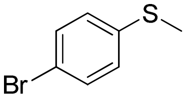
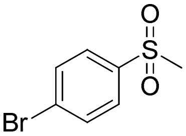
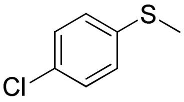
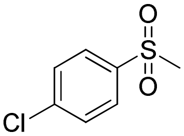
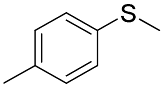
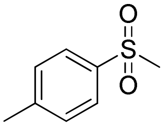
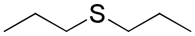
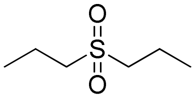
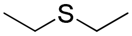
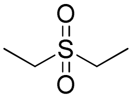
The optimum ratio of sulfide to H_2O_2 (1:2.5 equivalent) in the presence of MWCNTs-COOH (0.02 g) is found to be ideal for complete conversion of sulfides to the corresponding sulfones in a clean reaction. The yield of oxidation methyl phenyl sulfide to methyl phenyl sulfone as a function of time, catalyst quantity and substrate/H_2O_2 ratio is shown in Table 2.

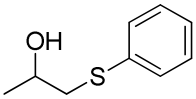
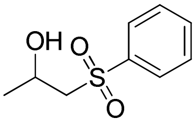
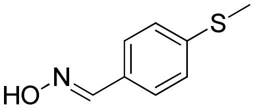
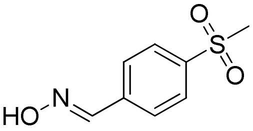
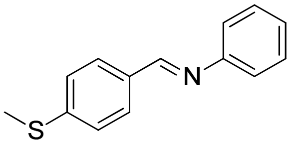
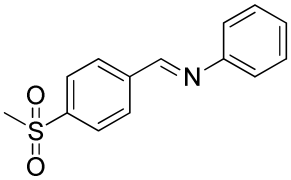
Table 2. Optimization of the reaction conditions

Entry	Cat. (g)	Tioanisol : H_2O_2	T (°C)	Time (h)	Yield (%)
1	0.01	1:1	25	0.5	0
2	0.01	1:1	60	0.5	<1
3	0.01	1:1	25	2	2
4	0.01	1:1.2	25	2	4
5	0.015	1:1.2	25	2	5
6	0.015	1:1.2	25	4	7
7	0.015	1:2	25	4	9
8	0.02	1:2	25	4	44
9	0.02	1:2	25	6	48
10	0.02	1:2.5	25	6	85
11	0.02	1:2.5	25	8	89
12	0.02	1:2.5	25	9	90
13	0.02	1:2.5	25	10	99
14	0.02	1:2.5	25	12	99

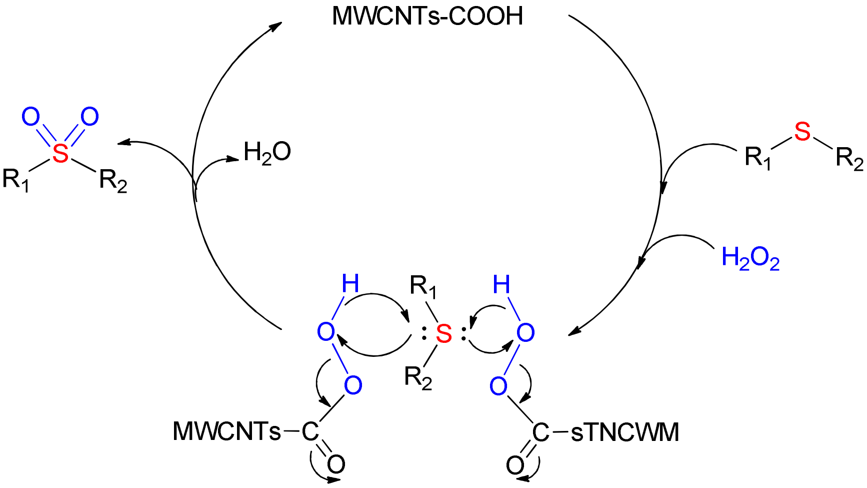
With the best reaction conditions in hand, we started testing the substrates. The generality of this approach is demonstrated by a facil and effortless oxidant of various sulfides as shown in Tables 3. This is a clean, straightforward synthetic method, in which sulfones are readily precipitated as the pure product, in high yields. This product analysis study demonstrates that sulfone is the only product formed under the present reaction conditions. It is notable that the sulfides were chemoselectively oxidized in the presence of oxidation-prone functional groups, such as OH, C=NH and C=NOH.

Table 3. Oxidation of sulfides to sulfones.

Entry	Substrate	Product	Yield (%)	Mp or Bp (ºC) found (reported)
1			94	143-144 (144-145)[33]
2			95	149-151 (149-153)[34]
3			99	86-87 (89-90)[35]
4			99	44-45 (46-46.5)[35]
5			96	127-128 (128-129)[35]
6			90	141-143 (142)[36]
7			95	43-44(43-44)[34]
8			91	95-96 (95-97)[34]
9			98	86-88 (88)[36]
10			99	29-30 (29-30)[33]
11			92	71-73 (73-75)[33]

12			89	44-46 (44-46)[35]
13			93	122-124 (122-125)[18]
14			85	91-93 (92-94)[37]

Observation of oxidation sulfides to the corresponding sulfones indicates that the reaction proceeds by way of an oxygen transfer mechanism. If the reaction involved electron transfer instead of oxygen transfer, substantial amounts of aldehyde would have been formed.[38,39] The possible mechanism for the oxidation of sulfide to the corresponding sulfone using H_2O_2 in the presence of MWCNTs-COOH is outlined in Scheme 2.



Scheme 2. Proposed mechanism for the oxidation of sulfide to the corresponding sulfone with aqueous hydrogen peroxide in the presence of MWCNTs-COOH.

Recyclability of a catalyst is an attractive feature. In order to investigate the recyclability of the catalyst, we selected methyl phenyl sulfide as a model substrate. The results of the recycling experiments indicated that the yields of the corresponding sulfone was still high after eight uses (Fig. 4), illuminating the fact that the catalytic activity of the catalyst did not change significantly, as compared with the fresh catalyst.

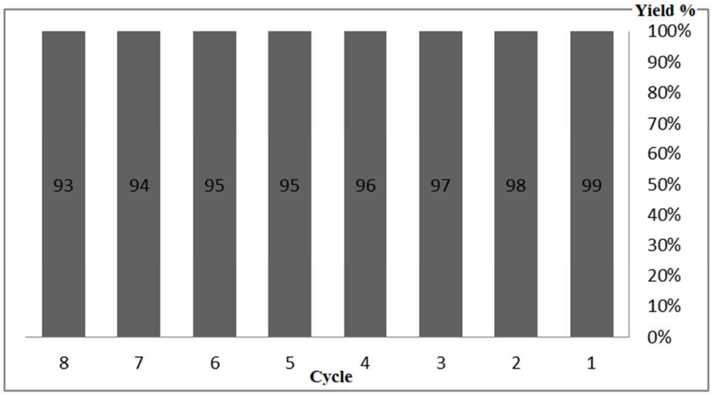


Fig. 4. Recyclability of the catalyst.

In summary, we have shown that the MWCNTs-COOH nanocatalyst, as an clean catalytic system efficiently catalyze the selectively synthesis of sulfone by the oxidation of sulfide by aqueous hydrogen peroxide at room temperature under solvent-free condition. Because of our enviromental friendly approach and ease of separation and recovery of MWCNTs-COOH, replacement of liquid acids and expensive toxic transition metal compounds with MWCNTs-COOH are disirable in the oxidation of sulfides to the corresponding sulfone in chemical industry.

Experimental

Chemicals were obtained from Merck, Fluka and Sigma Aldrich chemical companies. Nuclear magnetic resonance spectra were recorded on a Brucker Advanced DPX-250 MHz spectrometer using tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer.

Procedure for the synthesis of MWCNTs-COOH

The pristine MWCNTs (1g, 83.3 mmol of carbon) were first chemically functionalized with a mixture of concentrated sulfuric acid and nitric acid (3:1, 60 mL and 20 mL, respectively) under reflux at 80 ºC for 60 min. Then resulting mixture was diluted with distilled water and filtered repeatedly for 5-6 times until the pH of the filtrate was neutral. The sample was then dried at 60 ºC overnight under vacuum. The pristine MWCNTs treated in mixed acid were denoted as MWCNTs-COOH.

Typical experimental procedure for the preparation of sulfones

In a 25 ml round bottom flask, 30% (w/w) H_2O_2 (2.5 mmol) and the MWCNTs-COOH catalyst (20 mg) were successively added to sulfide (1 mmol) and the mixture was stirred magnetically at room temperature for 10 hours. The progress of the reaction was monitored by TLC. After completion of the reaction, to the reaction mixture was added 10 mL ethanol and stirred for 2 minutes. The catalyst was separated by the filtration, washed with the ethanol, and dried in vacuum before being recycled. The solvent was removed under reduced pressure to give the corresponding pure sulfones (Table 2). All reaction products were known and characterized by IR and ^{1}HNMR spectra and melting point as comparing with those obtained from authentic samples.

Acknowledgements

We gratefully acknowledge the financial support from the Payame Noor University (PNU).

Notes and references

1 M. Nielsen, C. B. Jacobsen, N. Holub, M. W. Paixão, K. A. Jørgensen, *Angew. Chem. Int. Ed. Engl.*, 2010, **49**, 2668.

2 See, for example: (a) O. O. Shyshkina, K. S. Popov, O. O. Gordivska, T. M. Tkachuk, N. V. Kovalenko, T. A. Volovnenko, Y. M. Volovenko, *Chem. Heterocycl. Compd.*, 2011, **47**, 923; (b) A. S. Newton, P. M. C. Gloria, L. M. Goncalves, D. J. V. A. dos Santos, R. Moreira, R. C. Guedes, M. M. M. Santos, *Eur. J. Med. Chem.*, 2010, **45**, 3858; (c) Y. Harrak, G. Casula, J. Basset, G. Rosell, S. Plescia, D. Raffa, M. G. Cusimano, R. Pouplana, M. D. Pujol, *J. Med. Chem.*, 2010, **53**, 6560.

3 B. Zajc, R. Kumar, *Synthesis,* 2010, 1822.

4 L. Field, J. E. Lawson, J. W. McFarland, *J. Am. Chem. Soc.*, 1956, **78**, 4389.

5 T. Doi, A. Orita, D. Matsuo, R. Saijo, J. Otera, *Synlett*, 2008, 55.

6 B. Maleki, S. Hemmati, A. Sedrpoushan, S. S. Ashrafi, H. Veisi, *RSC Adv.*, 2014, **4**, 40505.

7 K. Kamata, T. Hirano, N. Mizuno, *Chem. Commun.*, 2009, 3958.

8 S. Choi, J. D. Yang, M. Ji, H. Choi, M. Kee, K. H. Ahn, S. H. Byeon, W. Baik, S. Koo, *J. Org. Chem.*, 2001, **66**, 8192.

9 K. Bahrami, M. M. Khodaei, P. Fattahpour, *Catal. Sci. Tech.*, 2011, **1**, 389.

10 F. Hosseinpoor, H. Golchoubian, *Tetrahedron Lett.*, 2006, **47**, 5195.

11 N. Fukuda, T. Ikemoto, *J. Org. Chem.*, 2010, **75**, 4629.

12 L. Xu, J. Cheng, M. L. Trudell, *J. Org. Chem.*, 2003, **68**, 5388.

13 B. M. Trost, T. N. Salzmann, K. Hiroi, *J. Am. Chem. Soc.*, 1976, **98**, 4887.

14 R. Noyori, M. Aoki, K. Sato, *Chem. Commun.*, 2003, **9**, 1977.

15 K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, *Tetrahedron*, 2005, **61**, 8315.

16 B. Karimi, M. Ghoreishi-Nezhad, J. H. Clark, *Org. Lett.*, 2005, **7**, 625.

17 K. Bahrami, *Tetrahedron Lett.*, 2006, **47**, 2009.

18 K. Jeyakumar, D. K. Chand, *Tetrahedron Lett.*, 2006, **47**, 4573.

19 J. B. Feng, J. L. Gong, X. F. Wu, *RSC Adv.,* 2014, **4**, 29273.

20 K. Jeyakumar, R. D. Chakravarthy, D. K. Chand, *Catal. Commun.*, 2009, **10**, 1948.

21 C. A. Gamelas, T. Lourenço, A. P. da Costa, A. L. Simplício, B. Royo, C. C. Romão, *Tetrahedron Lett.*, 2008, **49**, 4708.

22 G. Kar, A. K. Saikia, U. Bora, S. K. Dehury, M. K. Chaudhuri, *Tetrahedron Lett.*, 2003, **44**, 4503.

23 A. Corma, M. Iglesias, F. Sánchez, *Catal. Lett.*, 1996, **39**, 153.

24 D. J. Robinson, L. Davies, N. McGuire, D. F. Lee, P. McMorn, D. J. Willock, G. W. Watson, P. C. B. Page, D. Bethell, G. J. Hutchings, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1523.

25 M. Rahimizadeh, G. Rajabzadeh, S. M. Khatami, H. Eshghi, A. Shiri, *J. Mol. Catal. A: Chem.*, 2010, **323**, 59.

26 B. Yu, A.-H. Liu, L.-N. He, B. Li, Z.-F. Diao, Y.-N. Li, *Green Chem.,* 2012, **14**, 957.

27 P. Serp, M. Corrias, P. Kalck, *Appl. Catal., A,* 2003, **253**, 337.

28 H. Tang, J. H. Chen, Z. P. Huang, D. Z. Wang, Z. F. Ren, L. H. Nie, Y. F. Kuang, S. Z. Yao, *Carbon,* 2004, **42**, 191.

29 P. Tribolet, L. Kiwi-Minsker, *Catal. Today,* 2005, **15**, 102.

30 A. Rezaeifard, M. Jafarpour, *Catal. Sci. Tech.*, 2014, **4**, 1960.

31 (a) H. Veisi, A. Aminimanesh, N. Khankhani and R. Ghorbani-Vaghei, *RSC Adv.*, 2014, **4**, 25057; (b) H. Veisi, A. Sedrpoushan, P. Mohammadi, A. R. Faraji and S. Sajjadifar, *RSC Adv.*, 2014, **4**, 25898; (c) H. Veisi, B. Maleki, F.H. Eshbala, H. Veisi, R. Masti, S. Sedigh Ashrafi and M. Baghayeri, *RSC Adv.*, 2014, **4**, 30683; (d) H. Veisi, *Synthesis,* 2009, 945; (e) H. Veisi *Synthesis*, 2010, 2631; (f) H. Veisi, S. Hemmati, H. Veisi, *J. Chin. Chem. Soc.*, 2009, **56**, 240; (g) H. Veisi*, Tetrahedron Lett.*, 2010, **51**, 2109; (h) A. Capan, H. Veisi, A. C. Goren, T. Ozturk, *Macromolecules*, 2012, **45**, 8228.

32\. A.M. Shanmugharaj, J. H. Bae, K.Y. Lee, W. H. Noh, S. H. Lee, S. H. Ryu, *Compos. Sci. Tech*. 2007, **67**, 1813.

33 A. Shaabani, P. Mirzaei, S. Naderi, D. G. Lee, *Tetrahedron,* 2004, **60**, 11415.

34 A. Shaabani, A. H. Rezayan, *Catal. Commun*., 2007, **8**, 1112.

35 K. Sato, M. Hyodo, M. Aoki, X. Q. Zheng, R. Noyori, *Tetrahedron*, 2001, **57**, 2469.

36 S. Rozen, Y. Bareket, *J. Org. Chem.*, 1997, **62**, 1457.

37 R. D. Chakravarthy, V. Ramkumar, D. K. Chand, *Green Chem.,* 2014, **16**, 2190.

38 E. Baciocchi, O. Lanzalunga, S. Malandrucco, *J. Am. Chem. Soc.*, 1996, **118**, 8973.

39 E. Baciocchi, O. Lanzalunga, B. Pirozzi, *Tetrehedron*, 1997, **53**, 12287.

Graphical Abstract

Selective hydrogen peroxide oxidation of sulfides to sulfones with caroxylated Multi-Walled Carbon Nano Tubes (MWCNTs-COOH) as heterogenous and recyclable nanocatalyst under organic solvent-free conditions

Hojat Veisi,* Fereshteh Hosseini Eshbala, Saba Hemmati, Mehdi Baghayeri