Cite this article as: Chin J Catal, 2010, 31: 1427–1432.



RESEARCH PAPER

Oxidation of Organic Compounds by Sulfonated Porous Carbon and Hydrogen Peroxide

Arash SHOKROLAHI*, Abbas ZALI, Mohammad Hossein KESHAVARZ

Chemistry Department, Malek-Ashtar University of Technology, Shahin-Shahr, P.O.Box 83145-115, Iran

Abstract: The oxidation of organic compounds by sulfonated porous carbon and H_2O_2 was studied at room temperature. Alkyl and aryl sulfides were oxidized to the corresponding sulfoxides or sulfones in excellent yields. Secondary alcohols were also converted to the corresponding esters/lactones and aldehydes to methyl esters in good yields. Moreover, aliphatic tertiary amines and substituted pyridines were oxidized to *N*-oxides.

Key words: sulfonated porous carbon; oxidation; hydrogen peroxide; sulfoxides; sulfones; ester; N-oxide

It is important to use industrial catalysts that are ecofriendly, green, and can be recycled easily from reaction mixtures. Therefore, green chemistry is defined as a set of principles that reduces or eliminates the use or generation of hazardous substances throughout the lifetime of chemical materials. Furthermore, solid acid catalysts have a prominent role in organic synthesis under heterogeneous conditions. For the applications considered here, an ideal solid material should have high stability and numerous strong protonic acid sites [1–4].

Hara and co-workers [5] reported the synthesis of a sulfonated (SO₃H-bearing) carbon catalyst with a mesoporous structure and a high specific surface area, which was prepared by impregnating the cellulosic precursor (wood powder) with ZnCl₂ before activation and sulfonation. The specific surface area of the porous carbon catalyst was found to increase with carbonization temperature to a maximum of 1 560 m^2/g at ca. 500 °C. The resulting black powder is insoluble in solvents such as water, methanol, ethanol, benzene, and hexane even at their boiling temperatures and it is referred to as a sulfonated porous carbon (SPC) catalyst. This catalyst has some advantages: (1) It is insoluble in common organic solvents, is weakly corrosive, and is environmentally friendly; (2) Reaction products are easily separated from the reaction mixture and the catalyst is recoverable without a decrease in activity; (3) SPC can be successfully used instead of sulfuric acid as a catalyst [5-8].

Oxidation is an important chemical process and is prevalent throughout chemistry. Studies in this area have focused on the use of transition-metal catalyzed processes [9–18]. However, a large number of oxidation reactions require the use of toxic metal reagents or catalysts. Therefore, from a green chemistry standpoint, green oxidation systems are required for chemical manufacturing. Because hydrogen peroxide is a strong oxidant and does not lead to toxic byproducts, it is considered to be an ideal green oxidant [19–26]. The purpose of this work is to study the oxidation of various organic compounds using SPC as a new medium and heterogeneous catalyst with H_2O_2 .

1 Experimental

Melting points were measured on an Electrothermal 9100 apparatus. All chemicals were commercial products. All melting points were obtained using a Stuart Scientific apparatus and are uncorrected. Thin layer chromatography (TLC) was used to monitor all reactions and all yields refer to isolated products. ¹H NMR spectra were recorded on a Bruker Avance AQS 300 MHz using tetramethylsilane (TMS) as an internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet IMPACT 400D instrument. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance instrument. The specific surface area and mean pore diameter were calcu-

*Corresponding author. Tel: +98-312-5225071; Fax: +98-312-5225068; E-mail: arshokrolahi@gmail.com

Foundation item: Supported by the Malek-Ashtar University of Technology.

Received date: 19 May 2010.

Copyright © 2010, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier BV. All rights reserved. DOI: 10.1016/S1872-2067(10)60127-1

lated using nitrogen adsorption isotherms at -196 °C with the standard Brunauer-Emmett-Teller (BET) equation and were obtained on a Nova 2200, Quantachrome Corporation. Elemental analysis was obtained using a Vario EL III instrument.

1.1 Preparation of SPC

Pine wood powder was used as the starting material in the preparation of the porous carbon material. In a typical procedure, wood powder (10 g) was impregnated with ZnCl₂ by immersion into a 50 ml aqueous solution of 1.0 mol/L HCl containing 20 g ZnCl₂ under mechanical agitation at 25 °C for 10 h. The supernatant liquid was then separated by filtration and the remaining solid was oven-dried at 80 °C for 24 h.

The ZnCl₂-impregnated wood powder was placed in a boat-like small size ceramic container and heated from room temperature to the maximum heat treatment temperature. The heating rate was 10 °C/min. The heating time at the maximum heat (450 °C) treatment temperature was 1 h. The sample was washed with aqueous HCl solution by heating in the wash solution at 100 °C for 1 h. The sample was then filtered and rinsed with warm distilled water to confirm that the wash solution was free of zinc ions. The resultant activated porous carbon material was finally dried at 80 °C in an oven for approximately 24 h. The activated porous carbon material (5 g) was heated for 10 h in 100 ml of oleum (18-24 wt% SO₃) at 80 °C under N₂ to introduce SO₃H. After heating and then cooling to room temperature, 400 ml distilled water was added to the mixture. A black precipitate formed and it was washed repeatedly with boiling distilled water until all the impurities such as sulfate ions were no longer detected in the wash water. The sample was finally dried overnight in an oven at 80 °C to afford the sulfonated acid catalyst [6-8].

1.2 Activity test

In a general procedure, a mixture of the SPC (0.5 g, 2.0 mmol H⁺) and substrate (1 mmol) was pulverized in a mortar for 1 min. The mixture was introduced into a 25 ml flat-bottomed flask and hydrogen peroxide (aq. 30%, 4 mmol) was added. The reaction mixture was then stirred magnetically at room temperature over the time given in Table 1. For aldehyde oxidation, excess methanol (4 mmol) and 1 g MgSO₄ as a water trapping agent were used. Reaction progress was monitored by TLC. After completion of the reaction, the mixture was washed with CHCl₃ (10 ml) and filtered to recover the catalyst. The solvent was evaporated under reduced pressure. Finally, the crude product obtained was purified by column chromatography on silica gel.

2 Results and discussion

The XRD pattern of the prepared SPC is shown in Fig. 1.

lu 20 30 40 50 60 70 2θ(°)

Fig. 1. XRD pattern of the prepared SPC.

The pattern had one broad and weak diffraction peak ($2\theta = 10^{\circ}-30^{\circ}$) attributed to amorphous carbon, which consists of small polycyclic aromatic carbon sheets.

The BET surface area, mean pore diameter, and pore size distribution were calculated from the adsorption isotherms of nitrogen at -196 °C. The surface area and the mean pore diameter were 925 m²/g and 2–8 nm, respectively. The FT-IR spectrum of the SPC (Fig. 2) shows a broad band at 3 300–3 500 cm⁻¹, which is assigned to OH groups (3 437 cm⁻¹). The vibration bands at 1 040 and 1 193 cm⁻¹ in the spectrum indicate that the resulting material possesses SO₃H groups. The density of the SO₃H groups was determined by elemental analysis. The total acid density (SO₃H + COOH) and (SO₃H + COOH + OH) were estimated by exchange with Na⁺ in aqueous NaCl and NaOH solutions, respectively.

The results reveal that the sample composition is $CH_{0.43}O_{0.29}S_{0.024}$ and that the amounts of SO₃H, COOH, and phenolic OH groups are 1.34, 0.28, and 2.51 mmol/g, respectively.

The SPC provides a valuable tool for the oxidation of sulfides, tertiary amines, and secondary alcohols. The reaction probably involves the in situ formation of peracid by reaction of the acid group of the SPC with hydrogen peroxide, followed by oxygen transfer to the organic substrate as shown in Scheme 1.



Fig. 2. FT-IR spectrum of the prepared SPC.



Scheme 1. Oxidation of various organic compounds with SPC and H_2O_2 .

We used the SPC as a heterogeneous catalyst in the presence of hydrogen peroxide, which acts as an oxidizing agent for the oxidation of both aliphatic and aromatic sulfides to the corresponding sulfoxides or sulfones. The optimum ratio of sulfide to H_2O_2 was found to be 1:1 in the presence of SPC (0.5 g) and this ratio was ideal for the complete conversion of sulfides to sulfoxides (with low amounts of sulfone). The reaction was incomplete for lesser amounts (Table 1, entries 1–8). At higher molar ratios of H_2O_2 to sulfide (4:1) and in the presence of SPC (0.5 g), the use of excess reagent affords the corresponding sulfone in a clean reaction (Table 1, entries 9–15).

As indicated in Table 1 (entries 16–20), secondary alcohols were converted into the corresponding esters/lactones in good yields. The reaction shows that carbonyl compounds can be effectively converted into corresponding esters in a Baeyer-Villiger-type reaction without the use of organic sol-

vents or highly concentrated hydrogen peroxide.

From Table 1 (entries 21–24), aldehydes were also studied using a method consisting of the dropwise addition of hydrogen peroxide to the stirred aldehyde mixture, SPC and methanol at room temperature in the presence of anhydrous MgSO₄. All aldehydes were selectively converted into the corresponding methyl esters in excellent yields. Furthermore, the corresponding acids were obtained as major products in the absence of a water trapping agent (MgSO₄).

The oxidation of several tertiary amines was carried out under similar reaction conditions and those results are shown in Table 1 (entries 25–31). The employed tertiary amines were oxidized to the corresponding *N*-oxides in high yields. However, aliphatic tertiary amines and pyridines containing electron-donating groups were found to be more reactive and required less reaction time.

Table 1	Oxidation of various organic compounds using SPC/H_2O_2 at room temperature	
---------	---	--

Entry	Substrate	Product	Yield ^a (%)	Time (min)	¹ H NMR spectral data (δ)	mp or bp (°C) found (reported)
1 ^b	CH3	S _{CH3}	90	25	2.78 (3H,s), 7.44–7.66 (5H,m)	28-29 (30-30.5)
2 ^b	H ₃ C	CH ₃	85	30	2.43 (3H,s), 2.72 (3H,s), 7.35 (2H,d), 7.54 (2H,d)	140 (138–140)
3 ^b	CI CH3	G CH3	85	45	2.79 (3H,s), 7.01 (2H,d), 7.40 (2H,d)	133–135 (136–137)
4 ^b	C) ^s C)	Cr op	87	30	7.43–7.65 (10H,m)	148–151 (153–155)
5 ^b	S-S-		90	35	3.96 (2H,s), 6.95–7.33 (10H,m)	42–43 (43–45)

Table 1 (Continued)								
Entry	Substrate	Product	Yield ^a	Time (min)	¹ H NMR spectral data (δ)	mp or bp (°C) found (reported)		
6 ^b	S O O	() S	91	180	7.02–7.24 (8H,m)	148–151 (153–155)		
7 ^b	~S		90	25	1.27 (6H,t), 2.75 (4H,q)	104 (103–106)		
8 ^b	~~~^S~~~~		92	25	0.84–0.91 (6H,t), 1.57 (8H,m), 2.48–2.63 (4H,m)	23–25 (24.5–25.5)		
9	S CH3	CH3	91	35	3.00 (3H,s) 7.44–7.64 (3H,m), 7.84–7.95 (2H,d)	86-88 (89-90)		
10	H ₃ C	H ₃ C	87	45	2.71 (3H,s), 3.01 (3H,s), 7.36 (2H,d), 7.83 (2H,d)	86-88 (88)		
11	CI-SCH3	CH ₃	90	60	3.11 (3H,s), 7.01 (2H,d), 7.53 (2H,d)	96–98 (95–97)		
12 ^c	C S C	Cr 0,0	90, 91, 88, 88	40	7.47–7.56 (6H,m), 7.92–7.96 (4H,m)	125–128 (128–129)		
13	S S		90	35	4.29 (2H,s), 7.08 (2H,d), 7.21–7.30 (3H,m), 7.43–7.48 (2H,m), 7.59–7.62 (3H m)	142–144 (144–145)		
14	∽s√	050	90	30	1.41 (6H,t), 3.02 (4H,m)	71–74 (73–75)		
15	<u>S</u>		89	30	0.93 (6H,t), 1.47 (4H,m), 1.79 (4H m), 2.91 (4H t)	29 (29–30)		
16	OH		92	420	1.57–1.83 (6H,m), 2.63 (2H,m), 4.23 (2H,m)	250–253 (253)		
17	OH		91	240	1.81 (4H,m), 2.34 (2H,m), 4.12 (2H,m)	203–207 (207–208)		
18	OH		73	720	6.81–7.24 (5H,m), 7.65–7.96 (5H,m)	65–69 (68–70)		
19	OH CH ₃	O CH3	75	660	2.42 (3H,s), 6.87–7.41 (5H,m)	193–197 (196)		
20	ОН		90	330	0.98 (6H,s), 1.08–1.41 (5H,m), 1.85 (3H,s), 1.89–2.05 (2H,m)	205–208 (209–210)		
21 ^d	O H	O CH3	85	300	3.91 (3H,s), 7.34–7.43 (3H,m), 7.89–8.22 (2H,m)	196–199 (198–199)		
22 ^d	H ₃ C	H ₃ C CH ₃	87	240	2.38 (3H,s), 3.88 (3H,s), 7.18–7.24 (2H,d), 7.89–7.95 (2H,d)	215–219 (220–223)		
23 ^d	Насо	H ₃ CO CH ₃	85	150	3.86 (3H,s), 4.12 (3H,s), 6.81–7.03 (2H,d), 7.80–8.11 (2H,d)	239–243 (244–245)		
24 ^d	CI OF	CI	87	180	3.91 (3H,s), 7.33–7.40 (1H,t), 7.49–7.90 (2H,m), 7.99 (1H,s)	227–229 (231)		

Table 1 (Continued)							
Entry	Substrate	Product	Yield ^a Time			mp or bp (°C)	
	Substrate	Ploduct	(%)	(min)	H NMR spectral data (0)	found (reported)	
25	N		90	240	7.39–7.44 (3H,m),	59-61 (61-62)	
					8.26-8.41 (2H,m)		
26	N	N-O	91	240	2.45 (3H,s), 7.10-7.20 (3H,m),	255-259 (259-261)	
					8.07-8.23 (1H,m)		
27	ČH ₃	ČH ₃					
	N	_N→O	89	210	2.33 (3H,s), 7.13–7.22 (2H,m),	43–49 (37–49)	
	H.C	нс			8.16–8.20 (2H,m)		
28			87	300	2.39 (3H s) 7.12–7.23 (2H d)	182-185 (182-185)	
	H ₃ C	H ₃ C			8.09–8.21 (2H,d)	102 100 (102 100)	
29			73	330	7.87–8.01 (2H,d),	178-180 (180-182)	
	NC N				8.43-8.45 (2H,d)	,	
30	C_2H_5	\sim C_2H_5 \sim C_2H_5	89	150	1.21 (6H,t), 3.28 (4H,q),	134-136 dec.	
	C ₂ H ₅				6.92 (3H,m), 7.32 (2H,m)		
		\sim C ₂ H ₅					
31	Q́ N−CH ₃	Q N	83	180	3.27 (5H,m), 3.43–3.54 (3H,m),	~150 dec.	
		\sim \sim_0			4.11–4.20 (3H,m)		

Reaction conditions: SPC 05 g (2.0 mmol H^+), substrate 1 mmol, H_2O_2 4 mmol. ^aIsolated yield. ^bExperiments were carried out in the presence of 1 mmol H_2O_2 . ^cThe same reagent was used for each of the four runs. ^d4 mmol methanol and 1 g MgSO₄ as a water trapping agent were added.

The recyclability of the SPC was also investigated using a model oxidation of diphenyl sulfide under similar reaction conditions. The SPC was separated by filtration after reaction completion. Subsequent experiments with fresh substrate and oxidant under similar reaction conditions were conducted over four run cycles. The activity of the SPC did not show any significant decrease after three runs. In subsequent recycle experiments, the reaction time needed to be increased gradually to obtain comparable yields of diphenyl sulfone.

3 Conclusions

In summary, we have shown that SPC, which can be easily prepared from commercially available starting materials, efficiently catalyzes the oxidation of sulfides to sulfoxides or sulfones, tertiary amines to *N*-oxides, secondary alcohols to esters/lactones, and aldehydes to methyl esters.

References

- Anastas P T, Warner J C. Green Chemistry: Theory and Practice. London: Oxford University Press, 1998
- 2 Clark J H. Green Chem, 1999, 1:1
- 3 Firouzabadi H, Jafari A A. J Iran Chem Soc, 2005, 2:85
- 4 Salehi P, Zolfigol M A, Shirini F, Baghbanzadeh M. Curr Org Chem, 2006, **10**: 2171
- 5 Kitano M, Arai K, Kodama A, Kousaka T, Nakajima K, Hayashi S, Hara M. *Catal Lett*, 2009, **131**: 242
- 6 Olivares-Marín M, Fernandez-González C, Macias-García A, Gomez-Serrano V. Appl Surf Sci, 2006, 252: 5967
- 7 Hudlicky M. Oxidations in Organic Chemistry, ACS Monograph Ser. 186. Washington: American Chemical Society, 1990

- 8 Trost B M, Fleming I. Comprehensive Organic Synthesis. Vol. 7. 1st Ed. Oxford: Pergamon Press, 1991
- 9 Buchner W, Schliebs R, Winter G, Buchel K H. Industrielle Anorganische Chemie, 2nd Ed. Weinheim: VCH, 1986
- 10 Venkataramanan N S, Kuppuraj G, Rajagopal S. Coord Chem Rev, 2005, 249: 1249
- Shul'pin G B, Suss-Fink G, Shul'pina L S. J Mol Catal A, 2001, 170: 17
- 12 Shaabani A, Lee D G. Tetrahedron Lett, 2001, 42: 5833
- 13 Carson E C, Lippard S J. Inorg Chem, 2006, 45: 837
- 14 Smith J R L, Murray J, Walton P H, Lowdon T R. Tetrahedron Lett, 2006, 47: 2005
- 15 Sheldon R A, Kochi J K. Metal-Catalyzed Oxidations of Organic Compounds. New York: Academic Press, 1981
- 16 Zhu Z L, Espenson J H. J Org Chem, 1995, 60: 1326
- 17 Warnhoff E W, Martin D G, Johnson W S. Org Synth, 1963, 4: 162
- 18 Shaabani A, Behnam M, Rezayan A H. Catal Commun, 2009, 10: 1074
- 19 Jones C W. Applications of Hydrogen Peroxide and Derivatives. Cambridge: Royal Society of Chemistry, 1999
- 20 Strukul G. Catalytic Oxidations with Hydrogen Peroxide as Oxidant. Dordrecht: Kluwer Academic,1992
- 21 Kroschwitz J I, Howe-Grant M. Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 13. 4th Ed. New York: John Wiley & Sons, 1995. 961
- 22 Elvers B, Hawkins S, Ravenscroft M, Schulz G. Ullmann's Encyclopedia of Industrial Chemistry. Vol. A13. 5th Ed. New York: VCH, 1989. 443
- 23 Noyori R, Aoki M, Satoc K. Chem Commun, 2003: 1977
- 24 Chu J W, Trout B L. J Am Chem Soc, 2004, 126: 900
- 25 Guo M L, Li H Z. Green Chem, 2007, 9: 421
- 26 Parmaliana A, Frusteri F, Arena F, Giordano N. *Catal Lett*, 1992,
 12: 353