Catalysis Letters Vol. 95, Nos. 1–2, May 2004 (© 2004)

$VO(acac)_2$ supported on titania: a heterogeneous protocol for the selective oxidation of sulfides using TBHP

M. Lakshmi Kantam[a,]*, B. Neelima[a], Ch. Venkat Reddy[a], M.K. Chaudhuri[b,]**, and S.K. Dehury[b]

[a]*Indian Institute of Chemical Technology, Hyderabad 500 007, India*
[b]*Department of Chemistry, Indian Institute of Technology, Guwahati–781039, India*

Received 2 December 2003; accepted 2 March 2004

The facile catalytic oxidation of sulfides to sulfoxides has been achieved with $VO(acac)_2$ supported on titania using *tert*-butyl hydroperoxide (TBHP) as an oxidant in dichloromethane in quantitative yields at room temperature. The catalyst is reusable and tested for five cycles without significant loss of activity and selectivity.

KEY WORDS: oxidation; VO $(acac)_2$; sulfides; sulfoxides; reusability; heterogeneous catalysis.

1. Introduction

The discovery of new catalysts leading to catalytic applications in synthetic organic chemistry is of much current interest in heterogeneous catalysis, in view of the following advantages, for example, easy workup, reusability, atom economy, and reduction of waste. The vast chemistry of sulfoxides and sulfones makes them very useful reagents in organic synthesis in general and useful synthetic intermediates for the construction of various chemically and biologically significant molecules in particular [1]. For this reason, the oxidation of sulfides to chiral/achiral sulfoxides or sulfones has been the subject of extensive studies and a number of synthetic procedures are now available [2–6]. To date, the most important method for preparing sulfoxides or sulfones involves the oxidation of sulfides. Various oxidising reagents are used for this purpose [3–6] and unfortunately most of these reagents are not satisfactory for medium to large-scale synthesis because of the low content of effective oxygen, the formation of environmentally unfavorable by-products and high cost.

Catalytic homogeneous reactions were preferred over reactions that use stoichiometric quantities, since the stoichiometric reactions are not only corrosive and hazardous at times, but they also generate copious amounts of heavy metal waste. The oxidation of sulfides has been performed under homogeneous conditions using aqueous hydrogen peroxide as an oxidant in the presence of metal catalysts [7,8].

An ideal system for such reactions is a solid catalyst capable of working under heterogeneous conditions. This would allow easy separation of the catalyst from the reaction mixture and adaptability in large-scale production to conform to the class of greener technologies. In recent years, selective oxidation of sulfides to sulfoxides or sulfones has been carried out with heterogeneous catalysts [9–11]. For instance, titanium silicates (TS-1 and TS-2) [9c] promote sulfide oxidation but the use of bulky sulfides is precluded by their limited access to the relatively small Ti active sites. In order to overcome this limitation, mesoporous materials have been used. Thus, Ti-MCM-41 allows the oxidation of bulky sulfides [10] but with the loss of selectivity. Subsequently, Fraile *et al.* [11] introduced $Ti(O^iPr)_4$ supported on silica as an efficient and selective catalyst for the oxidation of sulfides to sulfoxides but the drawback is the gradual leaching of titanium during the reaction. Recently, we reported the catalytic oxidation of sulfides by tungstate-exchanged Mg-Al-LDH catalyst ($LDH\text{-}WO_4$) in quantitative yields in aqueous media with higher selectivities towards sulfoxides at lower conversions [12].

Although many reagents have been employed for the oxidation of sulfides, there is still a need for ones that are efficient, selective and environmentally acceptable. One oxidant that meets the last criterion, in addition to being inexpensive and safe to handle even in large quantities [6], $(CH_3)_3COOH$ is commercially available, has high thermal stability, and is safer to handle than CH_3CO_3H or HOOH because of its much lower sensitivity to decomposition catalyzed by trace metallic impurities [6]. Moreover, its byproduct of oxidation, $(CH_3)_3COH$, is easily removed from reaction mixtures by distillation or rotary evaporation, obviating the need for aqueous workup as required for the traditionally used peroxyacid oxidants. This is particularly useful since the products of many oxidations are water soluble.], is *tert*-butyl hydroperoxide (TBHP)[$(CH_3)_3$ COOH]. However, used alone it is a poor oxidizing

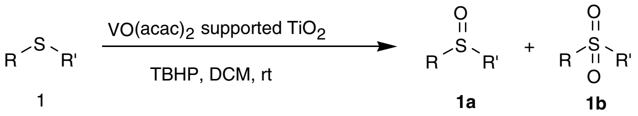
---

*To whom correspondence should be addressed.
E-mail: mlaxmi@iict.res.in
**To whom correspondence should be addressed.
E-mail: mkc@iitg.ernet.in

1011-372X/04/0500–0019/0 © 2004 Plenum Publishing Corporation

agent, thus it requires a metal or solid support to activate.

With an ever-increasing level of global competition, there is much incentive to find new and strategically important processes using a robust and recyclable catalyst. We herein report a heterogeneous catalytic system comprising of vanadium species supported on titania for the oxidation of sulfides using TBHP as an oxidant in dichloromethane in quantitative yields at room temperature (equation 1). We have a very clean and easy method for the preparation of highly pure VO(acac)$_2$ [13] which facilitated the catalyst preparation.



(1)

2. Experimental

2.1. Preparation of VO(acac)$_2$

To an aqueous suspension of vanadium pentoxide (5 g, 27.49 mmol) in 20 mL of water taken in a 500 mL beaker, 30% hydrogen peroxide (37.37 mL, 329.88 mmol) was added dropwise in an ice-cold condition and stirred till a clear dark solution was formed. To the dark brown colored solution, distilled acetylacetone (19.84 mL, 192.5 mmol) was added dropwise very carefully with continuous stirring. Vigorous effervescence took place after 15 min. Stirring for a period of 30 min led to a precipitation of a brown colored microcrystalline compound. The reaction mixture was heated at 70 °C for 15 min under stirring. The precipitate turned olive green with shiny crystalline appearance with the solution also turning green. The solution was concentrated by heating on a steam bath for 30 min and then placed in an ice-water bath for 15 min. The compound was filtered through Whatman No. 42 filter paper, washed with acetone and dried *in vacuo* over fused CaCl$_2$. Yield: 11.7 g (80%).

2.2. Preparation of VO(acac)$_2$ supported on titania (VO(acac)$_2$–TiO$_2$)

To a solution of VO(acac)$_2$ (265 mg) in anhydrous THF (50 mL), TiO$_2$ (1.0 g) was added and stirred at 293 K for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed several times with anhydrous THF, and finally dried *in vacuo*. Measurement of the mass increase of the resultant VO(acac)$_2$–TiO$_2$ indicates that 170 mg of VO(acac)$_2$ is supported, and the vanadium content is 0.64 mmol/g.

2.3. Typical procedure for the oxidation of methyl phenyl sulfide

To the stirred mixture of methyl phenyl sulfide (121 mg, 1 mmol) and VO(acac)$_2$–TiO$_2$ (50 mg, 0.032 mmol) in dichloromethane (10 mL), was added anhydrous TBHP (0.44 mL, 2.56 M in iso-octane) in two or three portions at room temperature. After completion of the reaction (followed by TLC), the catalyst was filtered off and washed with ethyl acetate (2 × 10 mL), dried over anhydrous Na$_2$SO$_4$ and evaporated *in vacuo* to afford the crude product. Analytically, pure compound was obtained after column chromatography (silica gel, hexane–ethyl acetate) (128 mg, 93% yield). The products were characterized by comparing the ^{1}H NMR spectra with those reported in the literature [12].

3. Results and discussion

The VO(acac)$_2$ supported on titania and its analogs were evaluated for the oxidation of methyl phenyl sulfide using anhydrous TBHP, and results are presented in table 1. The use of anatase or rutile form of titania in the oxidation of methyl phenyl sulfide does not influence the selectivity or yield of the products. VO(acac)$_2$ supported on titania afforded methyl phenyl sulfoxide >97% whereas VO(acac)$_2$ gave a mixture of sulfoxide and sulfone (table 1, entry 3). Thus, VO (acac)$_2$ supported on titania is proved to be the best

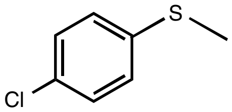
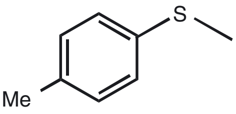
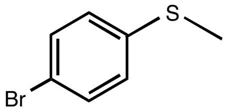
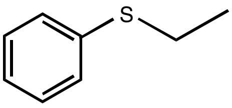
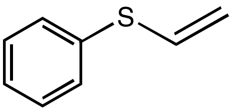
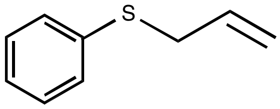
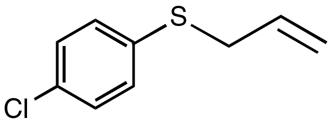
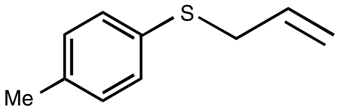
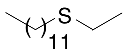
Table 1
The catalytic oxidation of methyl phenyl sulfide by TBHP using various catalysts[a]

Ex. no	Catalyst	Time (h)	Conversion (%)[b]	Selectivity[b]	
				Sulfoxide	Sulfone
1	TiO$_2$	24	99	56	44
2	VO(acac)$_2$–TiO$_2$	1.5	99	97	03
3	VO(acac)$_2$	1	99	70	30
4	None	2	No reaction	–	–
		24	70	98	2

[a] All reactions were carried out with 1 mmol of substrate, 50 mg of catalyst in 10 mL dichloromethane, 0.44 mL of anhydrous TBHP (2.56 M) at room temperature.

[b] Conversion and selectivity are based on ^{1}H NMR spectroscopic integration.

Table 2
The oxidation of sulfides by VO(acac)$_2$–TiO$_2$ using TBHP[a]

Entry	Sulfide **1–10**	Time (h)	Conversion (%)[b]	Sulfoxide **1a–10a**	Sulfone **1b–10b**
1		1.5	99(93)[c] 90[d]	97 95	03 05
2		2	99	87	13
3		5	99	93	7
4		5	99	92	8
5		6.5	99	46	54
6		4.5	99	100	–
7		6	99	100	–
8		5	99	98	02
9		5	99	78	22
10		2.5	99	100	–

[a] Reaction conditions are as exemplified in table 1, in footnote a.
[b] Conversion and selectivity are based on ^{1}H NMR spectroscopic integration.
[c] Isolated yield.
[d] Conversion after 5th cycle.

catalyst in terms of activity and selectivity. The non-catalyzed oxidation of methyl phenyl sulfide using TBHP afforded a conversion of 70% (selectivity 98%) and with H_2O_2 yield 60% sulfoxide respectively after 24 h [7], as opposed to the present reaction which is far more facile.

In an effort to understand the scope of the reaction, a series of sulfides having varied R groups containing aromatic and aliphatic attached to the sulfur atom were subjected to the oxidation using the VO(acac)$_2$ supported on titania and TBHP as an oxidant and the results are presented in table 2. It is significant to note that the allylic and vinylic sulfides afford the corresponding sulfoxides without the cleavage of carbon–carbon bonds (table 2, entries 6–9). It is important to note that the catalyst is reused for four times without significant loss of activity and selectivity as represented in figure 1.

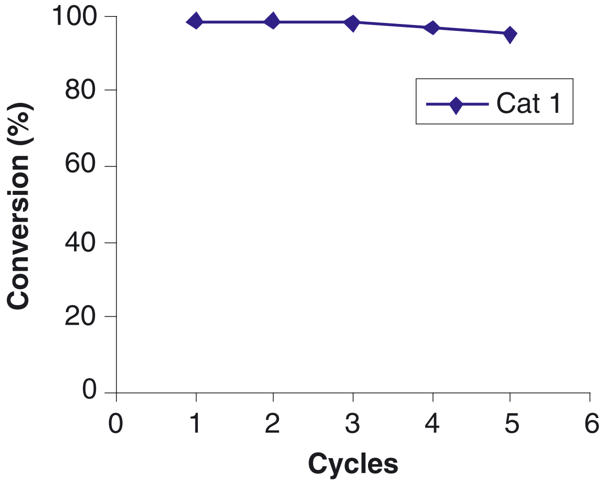


Figure 1. Conversion obtained with multiple cycles of $VO(acac)_2$–TiO_2 in the oxidation of methyl phenyl sulfide using TBHP. Reaction conditions: 1 mmol of methyl phenyl sulfide, 50 mg of catalyst in 10 mL dichloromethane, 0.44 mL of anhydrous TBHP (2.56 M) at room temperature, conversion is based on ^1H NMR spectroscopic integration (selectivity is omitted for clarity, the first and final run selectivities can be seen in table 2, entry 1).

Being guided by our previous experience on the peroxo-chemistry of titanium [14] and vanadium [15], it is believed that the catalyst interacts with TBHP to form a peroxometal intermediate of the type thereby activating the bound peroxide. The oxidation is then likely to proceed *via* metal–oxygen transfer mechanism in the present reaction. The ease of transfer of electrophilic oxygen from the peroxometal species to the nucleophilic sulfide facilitates the formation of sulfoxide with the eventual regeneration of the catalyst.

In summary, the present study represents the first example wherein the $VO(acac)_2$ supported on titania is used in catalytic amounts for the oxidation of sulfides to sulfoxides without significant loss of activity over a number of cycles. The high throughput of the product obtained lowers the inventories of the process to offer a potentially competitive and economically viable process.

Acknowledgments

B.N. and Ch.VR thank the Council of Scientific and Industrial Research (CSIR), India, for providing a research grant. S.K.D. is an IITG research fellow.

References

[1] (a) S. Patai and Z. Rappoport, *Synthesis of Sulfones, Sulfoxides and Cyclic Sulfides*, (J. Wiley, Chichester, 1994). (b) M. Mikolajczyk, Tetrahedron 42 (1986) 5459.
[2] (a) J.M. Brunel and H.B. Kagan, Synlett (1996) 404. (b) C. Bolm and F. Bienwald, Angew. Chem. Int. Ed. Engl. 34 (1995) 2640.
[3] (a) T. Durst, J. Am. Chem. Soc. 91 (1969) 1034. (b) P.J. Kropp, G.W. Breton, J.D. Fields, J.C. Tung and B.R. Loomis, J. Am. Chem. Soc. 122 (2000) 4280.
[4] K. Gopa, A.K. Saikia, U. Bora, S.K. Dehury and M.K. Chaudhuri, Tetrahedron Lett. 44 (2003) 4503.
[5] V.G. Shukla, P.D. Salgaonkar and K.G. Akamanchi, J. Org. Chem. 68 (2003) 5422.
[6] K.B. Sharpless and T.R. Verhoeven, Aldrichimica Acta 12 (1979) 63.
[7] M. Mateucci, G. Bhalay and M. Bradley, Org. Lett. 5 (2003) 235.
[8] K. Sato, M. Hyodo, M. Aoki, X-Qi. Zheng and R. Noyori, Tetrahedron 57 (2001) 2469.
[9] (a) M.H. Ali and W.C. Stevens, Synthesis (1997) 764. (b) V. Hulea, P. Moreau and F. Di Renzo, J. Mol. Catal. A 111 (1996) 325. (c) R.S. Reddy, J.S. Reddy, R. Kumar and P. Kumar, J. Chem. Soc., Chem. Commun. (1992) 84.
[10] A. Corma, M. Iglesias and F. Sanchez, Catal. Lett. 39 (1996) 153.
[11] M. Fraile, J.I. Garcia, B. Lazaro and J. Mayoral, Chem. Commun. (1998) 1807.
[12] B.M. Choudary, B. Bharathi, Ch. Venkat Reddy and M. Lakshmi Kantam, J. Chem. Soc. Perkin Trans 1 (2002) 2069.
[13] M.K. Chaudhuri, S.K. Dehury, S.S. Dhar, U. Bora, B.M. Choudary and M. Lakshmi Kantam, US Patent application. No. 10/335,103, December 31, 2002.
[14] M.K. Chaudhuri and B. Das, Inorg. Chem. 25 (1986) 168.
[15] H.N. Ravisankar, M.K Chaudhuri and T. Ramasarma, Inorg. Chem. 33 (1994) 3788.