Ti-beta-catalysed selective oxidation of sulfides to sulfoxides using urea–hydrogen peroxide adduct

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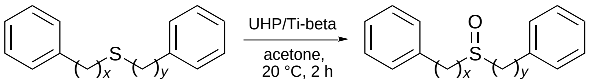
Ti-Beta zeolite catalyses the selective oxidation of organic sulfides to sulfoxides with urea–hydrogen peroxide adduct (UHP) as oxidant.

Crystalline microporous titanium silicate 1 (TS-1)[1] has found applications in the catalytic oxidation of a variety of organic compounds[2] with aqueous hydrogen peroxide as an oxygen source. TS-1, the titanium analogue of the ZSM-5 zeolite, is reported to catalyse the oxidation of hydrocarbons,[1,3] arenes,[1,4] alkenes,[2a–d] amines[5] and sulfides.[6a] Apart from their unique catalytic properties, these thermally stable solid materials can be recycled many times without any loss of activity, thus emphasizing their environmentally benign character. However, one serious limitation of catalysis by zeolites is the steric hindrance that stops bulkier molecules from reaching the active sites, as has been highlighted in a recent report that states that thioanisole and ethyl phenyl sulfide can access the catalytic sites for oxidation to the corresponding sulfoxides and sulfones whereas diphenyl sulfide fails under the same conditions.†,‡ Herein we report a thorough study of the oxidation of sulfides that determines the limitations of various oxidative catalysts (TS-1, VS-1 and Ti–beta; Table 1) in terms of their comparative reactivity and selectivity. Benzyl phenyl sulfide, bearing a benzylic methylene group, is used as a substrate in these reactions as it is easy to monitor the relative formation of sulfoxide/sulfone by ^{1}H NMR.

In the case of TS-1 and VS-1 (pore size 5.5 Å), no product could be detected, presumably on account of the inability of the substrate to enter the channel. At higher temperature, on the other hand, a poor yield of a mixture of products could be obtained. However, complete conversion to sulfoxides and sulfones occurs with a large pore (6.5 Å) zeolite, Ti-beta[7] (Table 1, entry 7), at room temperature using hydrogen peroxide.§,¶ Finally, selectivity is achieved‖ by replacing the potentially explosive hydrogen peroxide with the safer crystalline urea adduct of hydrogen peroxide (UHP), which compares favourably with existing protocols;[8] UHP adduct is known for the controlled release of the oxidant and is a well recognized source of oxygen.[2a,9]

Under these conditions, a facile and highly selective oxidation of bulkier organic sulfides [diphenyl sulfide, benzyl phenyl sulfide and dibenzyl sulfide, eqn. (1) and Table 2, entries 9–11] to the corresponding sulfoxides occurs with UHP in excellent yields.



(1)

$x = y = 0$; $x = 0$, $y = 1$; $x = y = 1$
conversion, mass balance and yield = >90%

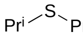
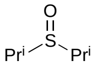
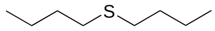
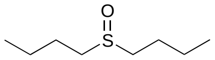
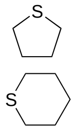
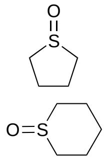
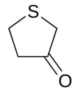
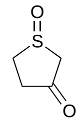
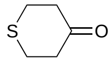
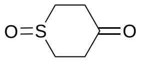
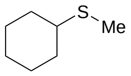
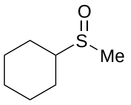
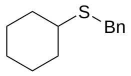
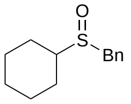
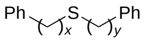
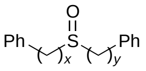
The scope of this protocol was further explored with a variety of sulfides (acyclic, cyclic and aromatic; Table 2) which were selectively oxidized to the corresponding sulfoxides in high yields with more than 95% mass balance. Acyclic and cyclic sulfides (Table 2, entries 1–4) were completely converted to the corresponding sulfoxides in 2 h at room temperature with 1.2 equiv. of UHP and 10 wt% of Ti-beta, whereas cyclic sulfides bearing a carbonyl functionality in their ring (Table 2, entries 5 and 6) required 3–4 h for complete conversion. All aromatic sulfides [as shown in eqn. (1)] produced clean sulfoxides with 100% selectively in 2 h.** Mechanistically, it is believed[2a] that the titanyl (Ti=O) function,[3a] the active site of the titanium silicates, binds with hydrogen peroxide to form a hydroxyhydroperoxo complex. This complex mimics *meta*-chloroperbenzoic acid and provides the required reactive oxygen (O*) species which oxidizes[2,3] sulfides to sulfoxides, generating water as a byproduct. Although it is not known whether the urea adduct (UHP) or free H_2O_2 enters the channels, it is known that the UHP complex is in equilibrium with free H_2O_2 and that the complex releases H_2O_2 at a rate which is, to some extent, solvent dependent.[9] In view of our own data and the background literature,[2a,3a] the use of the urea complex has two main advantages, namely the controlled release of H_2O_2 and the anhydrous nature of the oxidant. The sulfides and sulfoxides may enter or leave the zeolite channels at differing rates, but the oxidation undoubtedly occurs inside the zeolite catalyst.[2a,3a]

Table 1 Oxidation of benzyl phenyl sulfide with 30% aqueous hydrogen peroxide catalysed by Ti- and V-silicates[a]

Entry	Catalyst	Pore size/Å	*T*/°C	*t*/h	Conversion (%)[b]	Yield (%)[c]	Mass balance (%)
1	—	—	60	12	—	—	87
2	TS-1	5.5	20	12	trace	trace	83
3	TS-1	5.5	60	12	24	> 95	87
4	VS-1	5.5	20	12	trace	trace	90
5	VS-1	5.5	60	12	22	92	80
6	VS-1	5.5	60	24	27	77	71
7	Ti-beta	6.5	20	02	95	95	95

[a] Reactions were carried out in $(CD_3)_2CO$ with sulfide (1 equiv.), oxidant (1.2 equiv.) and 10 wt% of catalyst. Variation in the amount of catalyst did not increase the conversion and at one stage (> 50 wt%) it reduced the mass balance instead. [b] Conversions are based on ^{1}H NMR spectroscopic analysis of the characteristic methylene signal in the crude reaction mixture (error ±5% of the stated values). [c] Yields refer to isolated products and are based on substrate consumption.

Table 2 Selective oxidation of sulfides to sulfoxides with UHP catalysed by Ti-beta[a]

Entry	Sulfide	Sulfoxide	Yield (%)[b]
1			89
2			94[c]
3			95
4			95
5			82
6			85
7			92
8			94
9		$x = y = 0$	92
10		$x = 0, y = 1$	95
11		$x = y = 1$	94

[a] The reactions were carried out in acetone at room temperature with sulfide (1 equiv.), UHP (1.2 equiv.) and 10 wt% of catalyst Ti-beta; all the sulfides reached complete conversion in 2 h except tetrahydrothiophen-3-one (entry 5) and tetrahydrothiopyran-4-one (entry 6), which required 3–4 h. [b] Yields refer to the pure isolated product. [c] Traces of sulfone were observed by ^1H NMR spectroscopy.

Since a catalytic amount of the zeolite is used in this process and the reaction takes place at room temperature, we conclude that there are no restrictions placed on the sulfoxide as it leaves the channels. Apparently, the more reactive sulfide is oxidized more rapidly than the sulfoxide and the conversion of sulfoxide to sulfone is disfavoured due to the unavailability of a large excess of oxidant and possible steric crowding.

In conclusion, we have shown the versatility of the zeolite Ti-beta as a catalyst for selective oxidation of a variety of sulfides. The substrates which are not oxidized by TS-1 on account of their inaccessability are easily oxidized with this Ti-beta catalyst because of its larger pore size. The advantages of our environmentally benign approach over the conventional methods are the relative ease of separation of the catalyst and its recyclable nature.

We thank Dr M. Sasidharan, NCL, Pune, India for the supply of zeolite catalyst and the Texas Advanced Research Program (ARP) in Chemistry (Grant # 003606-023) and the Retina Research Foundation, Houston for generous support.

Footnotes

† Thioanisole, under the reported conditions, produced the corresponding sulfoxide and sulfone in 3.55 : 1 ratio. However, diphenyl sulfide does not have access to the catalytic sites, the channel size of the zeolite TS-1 being only 5.5 Å [ref. 6(*a*)].

‡ While writing this manuscript, an article has appeared in which bulky substrates such as diphenyl sulfide and dibenzyl sulfide were oxidized to the corresponding sulfoxides with 30% H_2O_2 catalysed by CrS-2 [ref. 6(*b*)].

§ A peroxide test showed complete consumption of hydrogen peroxide.

¶ Various equivalents of hydrogen peroxide were used for the oxidation of benzyl phenyl sulfide. Experiments were carried out in deuteriated acetone and the ratios determined by ^1H NMR analysis of characteristic signals in the crude reaction mixture (error ±5% of the stated values). Variation in the amount of catalyst used in the reaction did not produce any encouraging results in terms of selectivity.

		Yield (%)	
Equiv. H_2O_2	Conversion (%)	Sulfoxide	Sulfone
1.00	80	87	13
1.25	90	91	09
1.50	100	80	20

‖ Typical experimental procedure: Benzyl phenyl sulfide (100 mg, 0.64 mmol) in acetone (5 ml) was added to a well stirred mixture of UHP (72 mg, 0.77 mmol) and catalyst (10 mg, 10 wt% of sulfide) in the same solvent (10 ml) at 20 °C. This heterogenous mixture was then stirred for 2 h at the same temperature to complete the conversion of the sulfide to the corresponding sulfoxide. The reaction was monitored by TLC. The reaction mixture was then diluted with 10 ml of acetone and the catalyst filtered off and washed with acetone (2 × 5 ml). The combined solution was concentrated under reduced pressure to afford benzyl phenyl sulfoxide in 95% (105 mg, mp 118 °C).

** Other substrates investigated for their chemoselectivity include vinyl, allyl and prop-2-ynyl sulfides where alkenic moieties are preserved in the sulfoxide products. We have also performed the reactions with 1,4-thioxane, 5*H*-thiophen-2-one and thiomorpholine bearing a variety of substituents. The details of this work including stereoselectivity aspects will be published elsewhere.

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Received, 15th November 1996; Com. 6/07832J