

Sulfoxidation of Thioethers using Titanium Silicate Molecular Sieve Catalysts†

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Titanium silicate molecular sieves having MEL (TS-2) or MFI (TS-1) topology efficiently catalyse the oxidation of various thioethers to the corresponding sulfoxides and sulfones using dilute hydrogen peroxide (26 wt%) as an oxidising agent.

The advent of crystalline microporous titanium silicate molecular sieves, TS-1¹ (MFI) and TS-2² (MEL) has given an impetus to the catalytic oxidation of various organic compounds. Although, TS-1 or TS-2 facilitates the catalytic oxyfunctionalisation of carbon moieties^{2,3} in various organic molecules, nothing is known about the potential of these catalysts in the oxidation of other substrate moieties like sulfur in thioethers. Hydroperoxides⁴ as well as peracids⁵ are known to oxidise organic sulfides to sulfoxides and sulfones. Now we report a new catalytic method for sulfoxidation using crystalline titanium silicate molecular sieve catalysts and dilute H₂O₂.

When a reaction mixture of thioether (10 mmol) and H₂O₂ (12 mmol) in acetone as solvent was stirred in the presence of TS-2 catalyst at reflux temperature (except in the case of Me₂S, where the reaction was carried out at room temperature, 298 K), the corresponding sulfoxide was formed in high yield, along with some sulfone (Table 1). Me₂S was completely converted mainly to sulfoxide within 30 min, followed by Et₂S (90 min.), PhSMe (150 min) and PhSEt (180 min) suggesting that the reactivity of sulfide followed the order: Me₂S ≫ Et₂S > PhSMe > PhSEt. When TS-1 was used in place of TS-2 as catalyst, similar results were obtained except that more time was required for the completion of the reaction. Under similar conditions PhSPh was found to be unreactive, indicating that the active Ti^{IV} species, responsible for this reaction are located inside the pores, where bulky

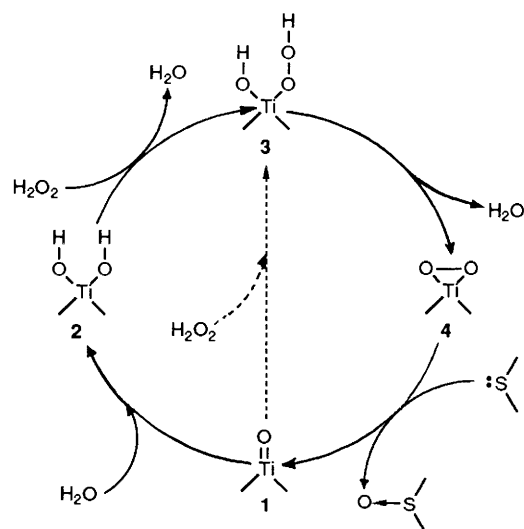
compounds like PhSPh have no access. The yield for sulfone, a secondary product, followed the reverse order probably because of the competition between reactant (sulfide) and primary product (sulfoxide) for oxidation. More reactive sulfides (*e.g.* Me₂S) compete with sulfoxide more efficiently for oxidation resulting in a very low yield of sulfone (Table 1). When sulfoxides were reacted under similar conditions in the presence of titanium silicate, the corresponding sulfones were obtained in quantitative yield. However, only 10–15% yields were obtained in the absence of the catalyst. The heterogeneous catalytic method described here is profitable as it provides high yields of the products and does not involve the use of a stoichiometric amount of hydroperoxide or peracid for sulfoxidation. In addition, the work up procedure is very simple, which involves merely the filtration of the catalyst.

Table 1 Oxidation of sulfides with H₂O₂ over TS-2 molecular sieve catalyst

	Me ₂ S ^a	Et ₂ S	PhSMe	PhSEt
Conversion, (wt%)	100	100	98	70
Product Distribution (wt%)				
Sulfoxide	97	85	78	75
Sulfone	3	15	22	15

^a Reaction was carried out at room temperature, in all other cases the reaction was performed at reflux temperature.

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Scheme 1

The catalyst can be reused many times without loss of activity and selectivity. Here, it may be pertinent to mention that in the oxidation of thiophenol and ethane thiol (PhSH and EtSH) with H_2O_2 using TS-2 catalyst dimeric products (PhSSPh and EtSSEt) were obtained in almost quantitative yields.

A time dependent study of sulfoxidation of PhSMe with H_2O_2 in the absence and in the presence of varying concentration of TS-2 catalyst indicated that even a small amount of catalyst (10 wt%) can significantly catalyse and accelerate the sulfoxidation. However, in the absence of catalyst the limited sulfoxidation occurred very slowly to a maximum extent of 25 wt% on the basis of sulfide even when the reaction was continued for 24 h. Pure silicalite-2, TiO_2 (both amorphous and crystalline), amorphous Ti-silicate and a physical mixture of silicalite-2 and TiO_2 were almost inactive in this reaction suggesting that Ti ions associated with zeolitic framework are responsible for the observed catalytic activity. As the concen-

tration of the catalyst was increased, the sulfoxidation became faster. However, 10 wt% (on the basis of sulfide) catalyst was sufficient to oxidise completely the sulfide providing a high yield of sulfoxide. In the absence of an adequate amount of catalyst, the decomposition of H_2O_2 into water and oxygen predominates. The titanium silicate molecular sieve ensures that H_2O_2 is utilized for the sulfoxidation reaction rather than for the non-selective decomposition.

The ability of titanium silicate molecular sieves to bind H_2O_2 is attributed³ to the formation of peroxo-species 4 as shown in Scheme 1. The Ti-silicate framework is believed³ to have species 1 or 2, which on reacting with H_2O_2 led first to species 3, similar to Caro's acid, and then to species 4, providing the reactive O^* species required for oxidation.

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References

- 1 M. Taramasso, G. Perego and B. Notari, US Pat., 4 410 501, 1983.
- 2 J. S. Reddy, R. Kumar and P. Ratnasamy, *Appl. Catal.*, 1990, **58**, L1; J. S. Reddy and R. Kumar, *J. Catal.*, 1991, **130**, 440; J. S. Reddy, S. Sivasanker and P. Ratnasamy, *J. Mol. Catal.*, 1991, **69**(3), 383.
- 3 B. Notari, *Stud. Surf. Sci. Catal.*, 1989, **60**, 413; A. Thangaraj, R. Kumar and P. Ratnasamy, *Appl. Catal.*, 1990, **57**, L1; T. Tatsumi, M. Nakamura, S. Negishi and H. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1990, 476; D. C. Huybrechts, L. D. Bruyckar and P. A. Jacobs, *Nature*, 1990, **345**, 240; M. R. Boccuti, K. M. Rao, A. Zecchina, G. Leofanti and G. Petrini, *Stud. Surf. Sci. Catal.*, 1989, **48**, 133.
- 4 T. Tezuka, M. Iwaki and Y. Haga, *J. Chem. Soc., Chem. Commun.*, 1984, 325; T. C. Bruice, J. B. Noar, S. S. Ball and U. Venkataram, *J. Am. Chem. Soc.*, 1983, **105**, 2452; A. L. Baumstark and P. C. Vasquez, *J. Org. Chem.*, 1983, **48**, 65.
- 5 O. Bortolini, S. Campestrini, F. Di Furia and G. Modena, *J. Org. Chem.*, 1987, **52**, 5093; R. A. Sheldon and J. K. Kochi, *Metal catalyzed oxidation of compounds*, Academic Press, New York, 1981.