

# Thioether oxidation by hydrogen peroxide using titanium-containing zeolites as catalysts

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Received 19 January 1996; accepted 22 May 1996

## Abstract

Titanium substituted ZSM-5 (TS-1) and BEA (Ti-beta) are investigated as catalysts for the selective oxidation of thioethers with diluted H<sub>2</sub>O<sub>2</sub>, in a protic solvent, at 303 K. The performances of TS-1 and Ti-beta samples are analyzed in relation with structure of thioethers, nature of solvent and shape selectivity effect of catalysts. A mechanism for organic sulfides oxidation on Ti-containing zeolites is proposed.

*Keywords:* Titanosilicates; Oxidation; Sulfides; Sulfoxides; Hydrogen peroxide

## 1. Introduction

The oxidation of organic compounds with H<sub>2</sub>O<sub>2</sub> on Ti-containing zeolites has received much attention in recent years [1–3]. In this context, a high activity and selectivity of the catalytic system H<sub>2</sub>O<sub>2</sub>–TS-1 for mild oxidation of olefins [4], amines [5], alcohols [6], paraffins [7], hydroxylation of aromatics [8] and phenol [9] have been demonstrated. However, the use of TS-1 is restricted to reactions of relatively small molecules due to diffusion limitations which result from active sites being situated in a

channel system of about 0.55 nm average diameter [7,10].

The catalytic applications have been expanded to the oxidation of bulkier substrates by synthesizing large-pore Ti-containing molecular sieves, i.e. Ti-beta [11], Ti-ZSM-12 [12], TAPSO-5 [13] or mesoporous titanium silicates Ti-MCM-41 [14] and Ti-HMS [15]. Thus, Ti-beta zeolite is much more active than TS-1 for the oxidation of cyclic and long linear alkenes or branched alkanes [16]. This catalyst is also active in the oxidation of propylamine [17] and aniline [18].

As compared to other reactions, only a limited number of reports deals with the sulfoxidation of thioethers in the presence of titanium silicates and H<sub>2</sub>O<sub>2</sub> [19–22].

The oxidation of sulfides by various oxidizing reagents including peracids, hydrogen per-

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oxide and organic hydroperoxides, is the standard method for the preparation of corresponding sulfoxides [23]. An electrophilic catalyst is necessary to activate the oxidizing agent. Hydrogen peroxide has taken new importance in recent years because of its environmental implications, water being the only chemical byproduct of oxidation reaction.

In the present paper we report the selective oxidation of organic sulfides with  $H_2O_2$  to sulfoxides using Ti-beta and TS-1 as catalysts. The activity of the Ti-containing zeolites has been investigated in relation with their nature and sulfide structure.

## 2. Experimental

### 2.1. Materials

Ethyl sulfide (98%), n-Propyl sulfide (97%), Allyl sulfide (97%), Allyl methyl sulfide (98%), tert-Butyl methyl sulfide (97%), n-Butyl sulfide (96%), sec-Butyl sulfide (98%), Methyl phenyl

sulfide (99%) and Phenyl sulfide (98%) from Aldrich, were used as supplied. Hydrogen peroxide (aqueous solution 31 wt.%) was obtained from Prolabo. Methanol, analytical grade (SDS) and tert-Butanol, HPLC grade (Sigma-Aldrich) were used as solvents.

### 2.2. Catalysts

Two Ti-containing zeolites, TS-1 and Ti-beta, with structure MFI and BEA, respectively, have been tested in oxidation reaction of thioethers with  $H_2O_2$ . The molar composition of the catalysts and texture data are reported in Table 1.

Both catalysts show the characteristic IR band at  $970\text{ cm}^{-1}$ , and well-defined single-phase X-ray diffraction patterns. The DR-UV vis spectra of the two samples are shown in Fig. 1.

The presence of absorption band at  $48000\text{ cm}^{-1}$  indicates that Ti (IV) is incorporated in the framework of molecular sieves [24]. No band corresponding to segregated  $TiO_2$  particles [24,25] was found to be present in our UV-vis spectra.

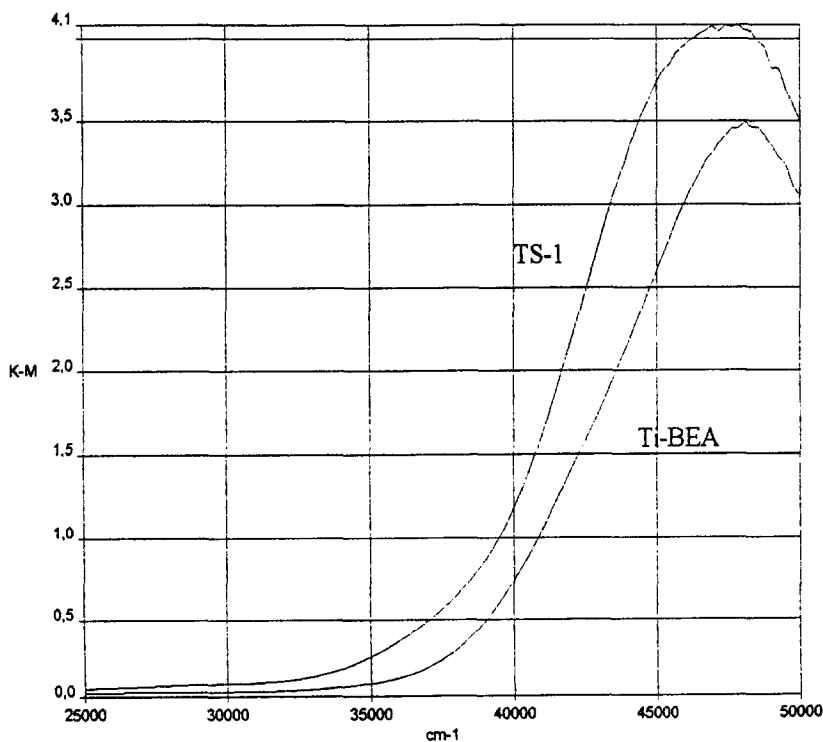


Fig. 1. Diffuse reflectance spectra in the UV-visible region of TS-1 and Ti-beta samples.

Table 1  
Characterization of catalysts; molar composition and micropore volume after calcination at 550°C in air flow

	Ti/Si	Al/Si	Na/Si	V <sub>mp</sub> (ml/g)
TS-1	0.011	0.000	0.001	0.14
Ti-BEA	0.008	0.000	0.000	0.21

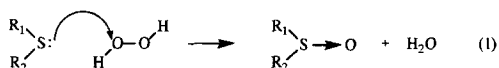
Crystal size as determined by scanning electron microscopy (Cambridge Stereoscan 260) was 0.1  $\mu\text{m}$  for TS-1 isometric crystals and 0.4  $\mu\text{m}$  for zeolite beta spheroidal grains.

### 2.3. Catalytical Experiments

The catalytic sulfoxidation of thioethers with hydrogen peroxide was carried out in a glass flask equipped with a magnetic stirrer, a thermometer and a condenser. In a typical experiment, TS-1 (40 mg) or Ti-beta (50 mg) was stirred with sulfide (2 mmol), a solvent (10 ml),  $\text{H}_2\text{O}_2$  (2 mmol) at a constant temperature. Samples were periodically collected and analyzed by GC in a capillary column (Methyl Silicone Gum, 25 m  $\times$  0.2 mm  $\times$  0.33  $\mu\text{m}$  Film thickness). The identification of the products was established by GC-MS and by comparison with authentic compounds. The hydrogen peroxide was measured by standard iodometric titration.

## 3. Results and discussion

It is known that organic sulfides are oxidized by hydrogen peroxide in an heterolytic process involving the nucleophilic attack of the sulfur atom on the oxygen according to Eq. (1) [26–29].



Due to the high nucleophilicity of the sulfur atom, thioethers are much more reactive than hydrocarbon compounds (alkenes, alkanes or

aromatic) in the oxidation reaction by  $\text{H}_2\text{O}_2$ . Thus, dialkylsulfides can be oxidized with an excess of hydrogen peroxide in an alcoholic solvent and at room temperature, even in the absence of any catalyst [30]. In homogeneous medium, the reactivity of thioethers is in agreement with the nucleophilicity of the sulfur atom, so that dialkylsulfides are more easily oxidized than diarylsulfides by electrophilic oxidants [23,29].

In the present work, the catalytic activities of the two samples of TS-1 and Ti-beta described above were studied in the oxidation of various thioethers (dialkyl and diarylsulfides respectively) using dilute  $\text{H}_2\text{O}_2$  as oxidant, at 303 K. The concentration of both organic substrate and hydrogen peroxide was 0.19 M in methanol and t-butanol respectively as solvents. These mild conditions, i.e. a low temperature and a dilute reactional medium, have been used in order to avoid the decomposition of hydrogen peroxide and to obtain a nearly quantitative efficiency of this oxidant in the sulfoxidation reaction. Such conditions, which allow to obtain an almost quantitative selectivity on hydrogen peroxide, have been recently reported in the oxidation of propene [2], hexene [31] and aniline [32] over TS-1 and Ti-beta. Moreover, it has been shown that the decomposition of  $\text{H}_2\text{O}_2$  over TS-1 becomes effective only at a temperature higher than 50°C [33].

Fig. 2 shows the thioether conversion versus time for the oxidation of respectively ethyl sulfide ( $\text{Et}_2\text{S}$ ), n-butyl sulfide ( $\text{n-Bu}_2\text{S}$ ) and phenyl sulfide ( $\text{Ph}_2\text{S}$ ), in methanol as solvent under conditions described above, conditions for which the  $\text{H}_2\text{O}_2$  efficiency is quantitative.

The results obtained confirm first that dialkylsulfides can be oxidized even in mild conditions and without catalyst, but that, under such conditions, phenyl sulfide is found to be unreactive.

Concerning the oxidation over Ti-containing zeolites, the consideration of the results shown in Fig. 2 leads to the following remarks and comments:

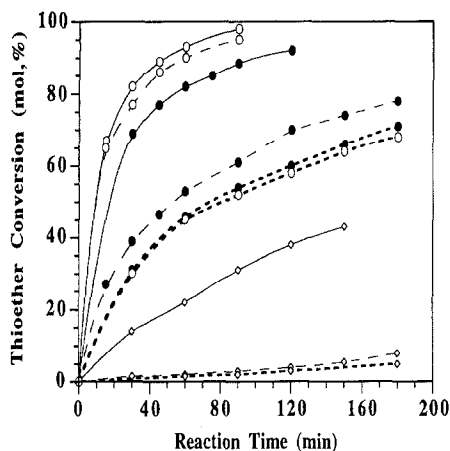


Fig. 2. Kinetics of oxidation of thioethers with  $H_2O_2$  in MeOH, at 303 K. (○)  $Et_2S$ ; (●)  $n-Bu_2S$ ; (◇)  $Ph_2S$  (—) Ti-beta; (---) TS-1; (· · ·) without catalyst.

- TS-1 and Ti-beta show the same high activity towards the oxidation of small size substrates such as ethyl sulfide, which can be the proof that the efficiency of the active sites is the same for the two catalysts;
- on both catalysts, butyl sulfide is less reactive than ethyl sulfide, in contrast with the reaction without catalyst. Such a result means that the accessibility of the sulfides to the Ti active sites located inside the zeolite framework is controlled by the size of the molecules;
- Ti-beta is more active than TS-1 in the sulfoxidation of hindered molecules such as butyl sulfide and phenyl sulfide, which can be interpreted as the result of a high shape-selectivity towards the reactants of the TS-1, due to its pore diameter of 0.55 nm.

Similar results have been reported in the case of oxidation of cyclic or branched alkanes and alkenes [16,34]. The results obtained in the oxidation of ethyl sulfide and butyl sulfide, in *t*-BuOH as solvent, are shown in Fig. 3.

Considering both Figs. 2 and 3, the following remarks can be made:

- in *t*-BuOH, the non-catalytic reaction occurs, but it is slower than in MeOH for both  $Et_2S$  and  $n-Bu_2S$ ;
- in *t*-BuOH, Ti-beta is much more active than TS-1 for the oxidation of ethyl sulfide,

whereas, in MeOH as mentioned above, the activity of the two zeolites is nearly the same. It appears that the access of the sterically hindered molecule of *t*-butanol to the pores of the TS-1 is slowed, leading to a possible shape-selectivity effect towards the solvent;

- the activity of Ti-beta for the oxidation of  $Et_2S$  is nearly the same whatever the solvent: MeOH = *t*BuOH, which indicates that for Ti-beta, in the contrast of TS-1, there is no limitation to the diffusion of the *t*-BuOH molecule;
- nevertheless, an effect of the nature of solvent is observed for the oxidation of  $n-Bu_2S$ , not only for TS-1 (for which such an effect is very important) but also for Ti-beta: MeOH > *t*-BuOH. These latter results can be the reflect of a cumulative effect of the diffusion of both substrates and solvent into the pores of zeolites.

The catalytic activity of the TS-1 zeolite versus the size of solvent molecules has been previously reported for the epoxidation of olefins; for example, in the case of 1-pentene epoxidation, the following order has been shown:  $CH_3OH > C_2H_5OH > t-C_4H_9OH$  [35]. Moreover, whereas the epoxidation of 1-hexene with hydrogen peroxide does not occur over TS-1 when *a*-methyl benzyl alcohol is used as

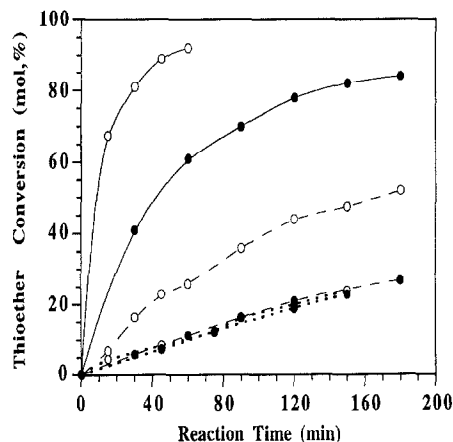


Fig. 3. Kinetics of oxidation of thioethers with  $H_2O_2$  in *t*-BuOH, at 303 K. The symbols as in Fig. 2.

Table 2  
Oxidation of thioethers with H<sub>2</sub>O<sub>2</sub> on Ti-beta and TS-1 catalysts<sup>a</sup>

Example	R <sub>1</sub> -S-R <sub>2</sub>		Catalyst	Solvent	V <sub>0</sub> × 10 <sup>3</sup> (M min <sup>-1</sup> )	Conversion R <sub>1</sub> -S-R <sub>2</sub> (%)	S <sub>80</sub> (%) <sup>b</sup>	t <sub>1/2</sub> (min)
	R1	R2						
1	Ethyl	Ethyl	Ti-beta	t-BuOH	8.67	99.0	99.5	11
2	n-Propyl	n-Propyl			7.34	97.0	98.0	13
3	Methyl	Allyl			5.40	87.0	95.1	24
4	Allyl	Allyl			4.55	79.0	84.6	36
5	n-Butyl	n-Butyl			3.94	78.0	95.8	38
6	Methyl	Phenyl			3.84	77.2	92.8	40
7	Methyl	t-Butyl			3.27	76.0	95.0	46
8	Phenyl	Phenyl			0.33	18.5		410
9	sec-Butyl	sec-Butyl			0.20	14.1		
10	Ethyl	Ethyl	TS-1	t-Bu OH	1.11	42.5	92.0 <sup>c</sup>	180
11	Methyl	Allyl			0.80	37.2		210
12	Allyl	Allyl			0.77	35.5		215
13	n-Butyl	n-Butyl			0.26	20.5		
14	Ethyl	Ethyl	Ti-beta	MeOH	10.5	98.2 <sup>d</sup>	99.7	10
15	n-Butyl	n-Butyl			5.61	89.0	97.9	24
16	Phenyl	Phenyl			1.07	37.6		193
17	Ethyl	Ethyl	TS-1	Me OH	10.05	97.1	96.6	11
18	n-Butyl	n-Butyl			3.08	61.5	94.9 <sup>c</sup>	60
19	Methyl	t-Butyl			1.31	45.8		131
20	Phenyl	Phenyl			0.06	5.1		

<sup>a</sup> 120 min, 30°C, 2 mmol R<sub>1</sub>SR<sub>2</sub>, 2 mmol H<sub>2</sub>O<sub>2</sub>, 10 ml solvent, 40 mg TS-1, 50 mg Ti-beta.

<sup>b</sup> S<sub>80</sub> = [R<sub>1</sub>SOR<sub>2</sub>]/([R<sub>1</sub>SOR<sub>2</sub>] + [R<sub>1</sub>SO<sub>2</sub>R<sub>2</sub>]) × 100, for a conversion of R<sub>1</sub>SR<sub>2</sub>, α = 80%.

<sup>c</sup> S<sub>50</sub>, for α = 50%.

<sup>d</sup> Reaction time: 60 min.

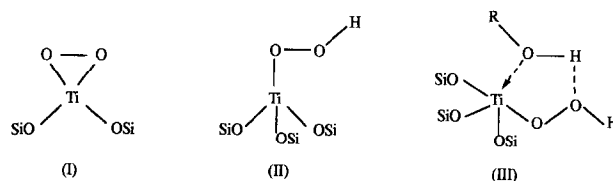
solvent, such a reaction is possible in this solvent over Ti-beta [36].

The results, listed in Table 2, concerning the sulfoxidation reaction of some other thioethers over the two catalysts and in both methanol and t-butanol as solvents, confirm the above remarks.

It can be seen, for example, that, under similar conditions, the reactivity of the thioether (initial rate, conversion) is directly linked to its molecular size for both catalysts. In general, the catalytic activity of Ti-beta is higher than that of TS-1, particularly in t-BuOH as solvent (Table

1, E 1, 3, 4, 5 and 10, 11, 12, 13). On the other hand, the more hindered sulfides (sec-Bu<sub>2</sub>S, Ph<sub>2</sub>S) show a poor reactivity, even over Ti-beta (E 8, 9).

A shape-selectivity effect towards reactants and solvent has been put forward above to explain the lower catalytic activity of TS-1 in the sulfoxidation reaction, compared with Ti-beta. Nevertheless, we must also take into account the possibility of spatial limitations of the transition state. It is now established that the active catalytic species in the oxidation reactions with hydrogen peroxide over Ti-containing



Scheme 1. Proposed active species in oxidation catalyzed by Ti-containing molecular sieves.

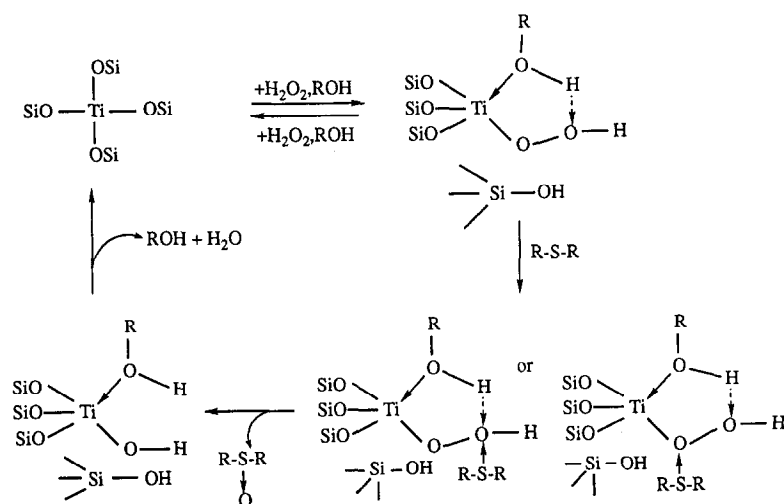
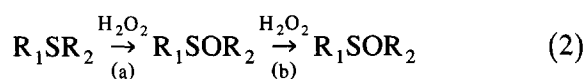
molecular sieves like TS-1 is a complex containing a peroxo (I) or a hydroperoxo ligand (II), [9,35,37,38] (Scheme 1).

In the presence of a protic solvent, the proposed mechanisms involve the coordination of an alcohol molecule to the active titanium site of the hydroperoxo species [35], as shown by structure III on Scheme 1. Coordination of the alcoholic solvent becomes more and more difficult with increasing bulkiness, which could explain the rate decrease observed ( $\text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{t-BuOH}$ ) in the alkene epoxidation [35], and the same ( $\text{CH}_3\text{OH} > \text{tBuOH}$ ) obtained in our sulfoxidation results (Figs. 2 and 3). The nucleophilic attack of the sulfur atom on an oxygen atom of such a complex leads to the sulfoxide formation according to the mechanism shown in Scheme 2, by analogy with the mechanism proposed in literature [33,35] for the alkene oxidation.

Such a mechanism allows to take into account that the reactivity of thioethers can be linked to their molecular size, due to the relative easiness of their accessibility to the Ti active sites of the catalytic species located in the zeolite framework. It must be pointed out that the use of a Ti-containing mesoporous silica, such as Ti-MCM 41, in the oxidation of *n*-butylsulfide under the same conditions (t-BuOH as sol-

vent) led to a lower conversion of the sulfide than with both TS-1 and Ti-beta, in agreement with previous results obtained in the oxidation of hexene [31]. Moreover, despite the higher crystal size of the Ti-beta sample which could lead to diffusion limitations, the catalytic activity of this zeolite is higher than that of TS-1 in almost all the cases. Such results allow to consider that, in this sulfoxidation reaction, the higher diffusivity in zeolite beta due to larger pore size offsets any diffusional limitations due to the crystal size.

If we consider now the selectivity of the sulfoxidation reaction, it can be seen, from Table 2, that selectivity in sulfoxide is higher than 90% (at a 80% conversion) in most of the cases for both catalysts; the only other product obtained is the corresponding sulfone. For a given substrate, the selectivity is directly linked to the reactivity: fast and high conversions lead to high selectivities in sulfoxides (Table 1, E 1, 2, 5, 14, 15). Such a result can be explained by the relative rates of the formation of the sulfoxide (step a) and of the corresponding sulfone (step b) in the oxidation reaction of thioethers (reaction 2).



Scheme 2. Proposed mechanism for the sulfoxidation reaction of thioethers with  $\text{H}_2\text{O}_2$  catalyzed by Ti-containing zeolites.

It is known that, for dialkylsulfides, sulfoxide formation proceeds much faster than sulfone formation [23]. In our case, for the oxidation of  $\text{Et}_2\text{S}$ ,  $\text{Pr}_2\text{S}$  and  $\text{Bu}_2\text{S}$ , the fast consumption of  $\text{H}_2\text{O}_2$ , initially in a stoichiometric amount in relation to the starting sulfide, thus limits the second step, which explains the high selectivity in sulfoxide. For the less reactive allyl and phenyl sulfides, the selectivity in sulfoxide is lower, because the difference in the rates of the two steps (a) and (b) of the oxidation reaction is less important, due to the conjugation of the lone electron pairs on the sulfur atom with the unsaturated system [23].

It is interesting to point out, that for ethyl sulfide under the same conditions of reactivity, the selectivity in sulfoxide is quantitative, whatever the catalyst and the solvent. It appears that, for small size molecules, the nature of the solvent does not affect the selectivity.

#### 4. Conclusion

Both TS-1 and Ti-beta are active in the sulfoxidation of thioethers with hydrogen peroxide under mild conditions. It has been shown first that the reactivity of thioethers is in agreement with both the nucleophilic character of the sulfur atom (alkylsulfides are more easily oxidized than arylsulfides) and their molecular size. Ti-beta is more active than TS-1 in the sulfoxidation of larger molecules, and gives a higher activity when t-butanol is used as solvent instead of methanol; such results can be the consequence of a cumulative effect of the diffusion of both substrates and solvent into the pores of the zeolites.

A mechanism, involving the nucleophilic attack of the sulfur atom on an oxygen atom of a hydroperoxo-Ti complex coordinated by a molecule of the solvent, allows to give an account of both reactivity sequence of thioethers and influence of the solvent. These results show that the oxidation of thioethers by hydrogen peroxide using Ti-beta zeolites as catalysts may be

an interesting mild and easy method for the selective preparation of sulfoxides.

#### Acknowledgements

Financial support from Elf-Aquitaine is acknowledged. Many thanks are due to D. Plee from the Groupement de Recherches de Lacq for providing a sample of TS-1 zeolite.

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