

# Selective oxidation reactions over metallosilicate molecular sieves: a comparison of titanium and vanadium silicates with MEL structure

A.V. Ramaswamy \*, S. Sivasanker, P. Ratnasamy

*National Chemical Laboratory, Pune 411 008, India*

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## Abstract

Selective oxidation of alkanes, aromatic compounds such as benzene and phenol, alcohols and thioethers has been carried out over titanium and vanadium analogues of ZSM-11 (MEL structure, termed as TS-2 and VS-2, respectively) with aqueous hydrogen peroxide. The results show interesting similarities and contrasts between TS-2 and VS-2. VS-2 produces more secondary oxidation products. It is also more effective in oxidizing alcohol and thioethers than TS-2. The differences are attributed to the differences in the mechanism of oxidation of the different substrates over TS-2 and VS-2. While a predominantly heterolytic oxidation is postulated in the case of TS-2, the principal path is probably homolytic in the case of VS-2.

*Key words:* Metallosilicate molecular sieves; Titanium silicates; Vanadium silicates; Selective oxidation reactions; Oxidation with hydrogen peroxide

## 1. Introduction

Substitution of transition metal ions with redox character in the framework of molecular sieves can, in principle, give rise to catalysts with shape-selective oxidation properties [1–4]. The  $Ti^{4+}$  analogues of ZSM-5 (TS-1) and ZSM-11 (TS-2) catalyze various oxidation reactions involving hydrogen peroxide [1,5]. Recently, V-MFI molecular sieves (VS-1) possessing redox characteristics (reversible  $V^{4+}$  to  $V^{5+}$  transitions) have been prepared [3,6]. We have reported the synthesis of vanadium silicates with MEL topology (VS-2), which are active in many oxidation reactions in the presence of aqueous  $H_2O_2$ , but differ significantly in some respects from titanium silicates

[4,7,8]. In this paper, a comparison is being made of the oxidation efficiency of well characterized Ti and V silicates in a number of selective oxidation reactions with different organic substrates.

## 2. Experimental

Detailed information on the synthesis and characterization of TS-2 and VS-2 molecular sieves have been reported in our earlier publications [2,4]. The samples were highly crystalline [ $>95\%$  by X-ray diffraction (XRD)] and had a similar crystal size of *ca.* 2  $\mu m$ . The  $TiO_2$ - and  $V_2O_5$ -supported silicalite-2 samples were prepared by impregnation of silicalite-2 with appropriate concentrations of Ti (OBu)<sub>4</sub> and VOSO<sub>4</sub> solutions

\* Corresponding author.

to give an Si/M ratio of 80 and calcination at 623 K, respectively. The oxidation of alkanes was carried out in a stirred autoclave (Parr Instruments, USA) of 300 ml capacity at 373 K under autogeneous pressure. Typically, 100 mg of the catalyst, 2.53 g of aqueous H<sub>2</sub>O<sub>2</sub> [26 wt.-% solution; alkane/H<sub>2</sub>O<sub>2</sub> (mol) = 3] and 5 g of alkane were mixed with 25 ml of the solvent, and the reaction was allowed to proceed for 8 h. The reaction occurred in the liquid phase under these conditions. The hydroxylation of aromatic hydrocarbons, phenol and thioethers was carried out in a 100-ml batch reactor at 333–342 K for 8 h. Other details of the reaction, product separation and analysis are given elsewhere [2,4,7–10].

### 3. Results and discussion

#### 3.1. Oxyfunctionalization of alkanes

Both TS-2 and VS-2 [the Ti and V analogues of ZSM-11 (MEL), respectively] catalyze the oxyfunctionalization of alkanes with H<sub>2</sub>O<sub>2</sub>. The results of our studies using *n*-hexane as the substrate are presented in Table 1. A comparison of the activities of TS-2 and VS-2 on the one hand and other crystalline samples with MEL structure (*viz.*, silicalite-2, ZSM-11, Ti- or V-impregnated in silicalite-2) on the other hand shows that the most active catalysts are TS-2 and VS-2. They are also found to be the most selective catalysts for the

formation of monofunctional compounds. The major products of the reaction are 2- and 3-hexanols and corresponding hexanones, the latter being the secondary oxidation products. Interestingly, the oxyfunctionalization of the primary carbon atom leading to the formation of primary alcohols and aldehydes is observed only with V silicate. It is observed that the activation of the carbon atom at the second position is preferred to others, and the activation follows the order 2C > 3C > 1C on VS-2 and 2C > 3C, with no activation of the 1C on TS-2. A higher aldehydes plus ketones-to-alcohol ratio in the product distribution for VS-2 than for TS-2 (2.77 and 1.27, respectively; Table 1) indicates a deeper oxidation capability of V silicate than of Ti silicate.

#### 3.2. Hydroxylation of aromatic hydrocarbons

The hydroxylation of aromatic hydrocarbons to phenols and phenol derivatives by dilute H<sub>2</sub>O<sub>2</sub> at 333–373 K takes place readily on TS-2 and VS-2 (Table 2). The hydroxylation of benzene leads to the formation of phenol and *p*-benzoquinone (PBQ), the latter resulting from the further hydroxylation and subsequent oxidation of the initially formed phenol. The product distribution is comparable, and selectivities to the monofunctional product are *ca.* 90% on both catalysts. With toluene as the substrate, the hydroxylation rates are higher, the conversion levels (up to 8 h) being higher than those observed in benzene hydroxylation.

Table 1  
Oxidation of *n*-hexane over titanium and vanadium silicates and related molecular sieves<sup>a</sup>

Catalyst <sup>b</sup>	Conversion (mol-%)	Product distribution <sup>c</sup> (mol-%)						
		1-ol	2-ol	3-ol	1-al	2-one	3-one	Others <sup>d</sup>
TS-2	15.9	—	19.1	17.1	—	23.7	23.0	16.6
VS-2	14.6	3.7	9.2	8.2	7.2	26.3	25.0	21.4
Silicalite-2	3.6	—	9.5	9.5	—	4.7	7.1	69.2
TiO <sub>2</sub> /silicalite-2	2.8	—	3.8	4.7	—	14.4	13.9	63.2
V <sub>2</sub> O <sub>5</sub> /silicalite-2	3.5	—	8.0	12.0	—	4.0	4.0	72.0

<sup>a</sup>Reaction conditions: catalyst = 0.1 g; *n*-hexane = 5 g; *n*-hexane/H<sub>2</sub>O<sub>2</sub> (mol) = 3; solvent (acetonitrile) = 20 g; temperature = 373 K; reaction duration = 8 h; reaction carried out with stirring in a Parr autoclave under autogeneous pressure.

<sup>b</sup>TS-2, Si/Ti = 77; VS-2, Si/V = 79; silicalite-2, Si/Al = >2000; Ti- and V-impregnated silicalite-2, Si/M = 80.

<sup>c</sup>1-ol, 2-ol and 3-ol = 1-, 2- and 3-hexanols; 1-al = hexaldehyde; 2-one and 3-one = 2- and 3-hexanones.

<sup>d</sup>Mostly polyfunctional oxygenates and lactones.

Table 2  
Hydroxylation of benzene and toluene with aqueous H<sub>2</sub>O<sub>2</sub> over TS-2 and VS-2 molecular sieves<sup>a</sup>

	Benzene		Toluene	
	TS-2	VS-2	TS-2	VS-2
Conversion (mol-%)	17.1	7.2	13.2	11.7
H <sub>2</sub> O <sub>2</sub> selectivity <sup>b</sup> (mol-%)	42.2	18.2	37.8	49.5
Phenol	88.0	90.0	—	—
<i>p</i> -Benzoquinone	9.0	7.0	—	—
<i>o</i> -Cresol	—	—	36.0	20.0
<i>p</i> -Cresol	—	—	59.0	17.0
Benzyl alcohol	—	—	—	8.0
Benzaldehyde	—	—	—	52.0
Others <sup>c</sup>	3.0	3.0	5.0	3.0

<sup>a</sup>Reaction conditions: catalyst = 0.1 g; substrate = 1 g; substrate H<sub>2</sub>O<sub>2</sub> (mol) = 3; temperature = 333 K; reaction duration = 8 h; 100-ml glass reactor with stirring.

<sup>b</sup>H<sub>2</sub>O<sub>2</sub> utilised for the formation of catechol, *p*-benzoquinone or cresols, benzylalcohol and benzaldehyde.

<sup>c</sup>Mainly polyhydroxy compounds.

tion. Electron-releasing groups such as -CH<sub>3</sub>, -OH or -OMe attached to the benzene ring promote this hydroxylation, while substrates containing electron-withdrawing groups do not react so easily [10]. This indicates that this reaction is a typical electrophilic substitution reaction. The product distribution in toluene hydroxylation shows vital differences between TS-2 and VS-2, even though the conversions are somewhat similar (Table 2). Whereas only ring hydroxylation takes place yielding *o*- and *p*-cresols almost exclusively on TS-2, the methyl substituent also undergoes oxidation on VS-2 leading to the formation of benzyl alcohol and benzaldehyde, in addition to the cresols. In fact, the extent of the side-chain oxidation is greater than the aromatic hydroxylation. Further, the large concentration of benzaldehyde (52 wt.-%) in the product shows that the secondary oxidation of benzyl alcohol to benzaldehyde is fast.

Another aspect of the oxidation of alkyl aromatics on both TS-2 and VS-2 is that the reaction of bulky substrates like *tert*-butylbenzene does not take place due to the steric restrictions imposed by the narrow channels within the molecular sieves. Among the alkyl aromatics, the relative rates of conversions over VS-2 were toluene (3.6) > *p*-

xylene (2.4) > *m*-xylene (1) = *o*-xylene (1) = 1,3,5-trimethylbenzene (1). This trend parallels the diffusivities of these molecules in the MEL molecular sieves [11]. Assuming a diffusion-controlled first-order reaction, the rates derived from the diffusion coefficients at 373 K for these molecules compare very well with the observed oxidation rates and indeed show the presence of the active sites *inside* the channel system [8]. Apart from the reactant shape selectivity described above, the product distribution in the hydroxylation of toluene on TS-2 (where only ring hydroxylation takes place) demonstrates product shape selectivity. The observed *o*-cresol/*p*-cresol ratio of 0.61 (Table 2) is lower than that expected from purely electronic considerations and in the absence of diffusional restrictions for these products (2.0).

### 3.3. Hydroxylation of phenol

TS-2 and VS-2 are also found to be active in this reaction [7,10]. The phenol conversion, H<sub>2</sub>O<sub>2</sub> selectivity and product distribution as a function of time on VS-2 and TS-2 are presented in Fig. 1A and B, respectively. At the end of an 8-h run, phenol conversions were 25.8 and 26.7 mol-%, with H<sub>2</sub>O<sub>2</sub> selectivities of 58.7 and 62.3% for VS-2 and TS-2, respectively. Fig. 1 shows that the initial activity of VS-2 is much lower than that of TS-2. The difference in the product distributions at the end of the run on the two catalysts is seen from the catechol-to-hydroquinone ratios, which are 1.3 and 1.1 for VS-2, and TS-2, respectively.

The results on the use of different solvents in the hydroxylation of phenol on TS-2 and VS-2 are presented in Table 3. As seen from this table, the solvent affects both the conversion and the H<sub>2</sub>O<sub>2</sub> efficiency. The conversions are high in acetone and methanol in the case of TS-2. On the V silicate, the phenol conversion increases in general with increasing polarity of the solvent with a corresponding increase in the efficiency of H<sub>2</sub>O<sub>2</sub> utilization. Under identical conditions, maximum phenol conversion is observed in water. The influence of the solvent on the product distribution is complex. Though *p*-benzoquinone is obtained (4–5%) in all three solvents (acetone, acetonitrile and water) over VS-2, surprisingly no hydroquinone is formed

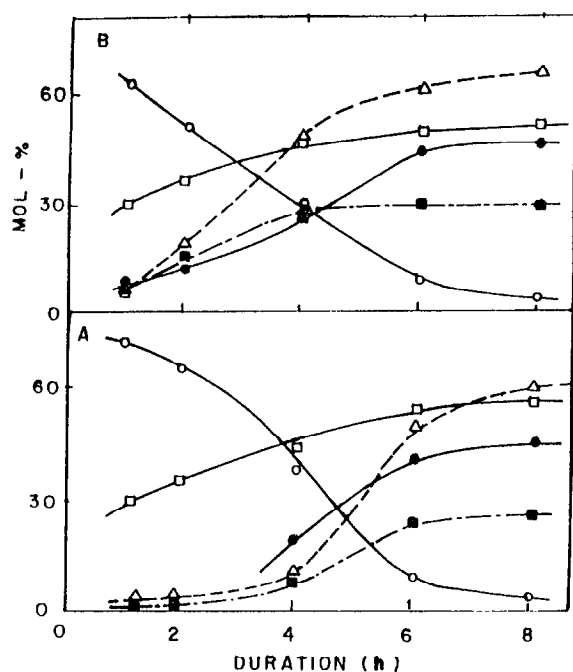


Fig. 1. Hydroxylation of phenol over VS-2 (A) and TS-2 (B). (■) Phenol conversion; (△)  $H_2O_2$  selectivity; (□) catechol; (●) hydroquinone; (○) *p*-benzoquinone. Conditions: solvent = water; temperature = 353 K; phenol/ $H_2O_2$  (mol) = 3; catalyst = 0.1 g; phenol = 1 g; reaction carried out under stirring in 100-ml glass reactor.

when acetone is used as the solvent. On TS-2, on the other hand, an almost equimolar mixture of catechol and hydroquinone is obtained in acetone (Table 3).

#### 3.4. Sulfoxidation of thioethers

The results of the sulfoxidation of methyl phenyl sulfide ( $Me-S-Ph$ ) over TS-2 and VS-2 are presented in Table 4. Under similar conditions, VS-2 exhibits a significantly higher activity than TS-2. For example, only 30 min were needed for the complete conversion of methyl phenyl sulfide on VS-2, whereas on TS-2 the reaction took 120 min for completion. However, on silicalite-2 and ZSM-11, the conversion levelled off at around 50 mol-%, even after continuing the reaction. The reactivity of the sulfides, in general, follows the order  $Me-S-Me > Et-S-Et > Ph-S-Me > Ph-S-Et$ .

Table 3

Influence of solvents on the hydroxylation of phenol over TS-2<sup>a</sup> and VS-2<sup>b</sup> molecular sieves

Catalyst/ solvent	Conversion (mol-%)	$H_2O_2$ selectivity (mol-%)	Product distribution <sup>c</sup> (mol-%)		
			Catechol	HQ	PBQ
<i>TS-2</i>					
Acetone	20.8	70.0	49.3	49.8	0.9
Methanol	28.4	66.2	39.7	60.3	0.0
Acetonitrile	15.4	41.0	51.4	46.7	1.9
2-Butanone	17.1	46.9	61.7	32.5	5.8
<i>VS-2</i>					
Acetone	7.0	12.7	95.1	0.0	4.9
Acetonitrile	13.9	29.7	55.4	39.8	4.8
Water	24.3	55.7	44.1	52.0	3.9

<sup>a</sup>Conditions: catalyst = 0.1 g; phenol = 1 g; phenol/ $H_2O_2$  (mol) = 3; temperature = 342 K; duration = 24 h; catalyst = TS-2 (Si/Ti = 29); 100-ml glass reactor with stirring.

<sup>b</sup>Conditions: catalyst = 0.1 g; phenol = 1 g; phenol/ $H_2O_2$  (mol) = 3; temperature = 333 K; duration = 8 h; catalyst = VS-2 (Si/V = 79); 100-ml glass reactor with stirring.

<sup>c</sup>Excluding tars; HQ = hydroquinone; PBQ = *p*-benzoquinone.

Over TS-2, though the order remained the same, the rates were considerably lower. Interestingly, the product distribution is not too different on the two catalysts.

#### 3.5. Oxidation of ethanol

The results of the liquid-phase oxidation of ethanol are reported in Table 5. VS-2 is more active than TS-2 in this reaction. While TS-2 produces acetaldehyde selectively, VS-2 yields a significant amount of acetic acid, that reacts under these conditions with the substrate ethanol to produce ethylacetate.

#### 3.6. Comparison of TS-2 and VS-2

Earlier workers [12] have reported that differences in crystallite size can influence the activity and selectivity of the molecular sieves, especially in reactions involving large substrates such as phenol, and, hence, comparisons between catalysts with different crystal sizes are not meaningful. In the present case, the studies have been carried out

Table 4  
Sulfoxidation of methyl phenyl sulfide over TS-2 and VS-2<sup>a</sup>

Catalyst	Reaction time (min)	Conversion (mol-%)	Product distribution (mol-%)	
			Ph-S(O)-CH <sub>3</sub>	Ph-(O)-S(O)-CH <sub>3</sub>
TS-2	30	22	74	26
TS-2	120	100	78	22
VS-2	30	100	84	16
Silicalite-2	120	47	84	16

<sup>a</sup>Reaction conditions: catalyst=0.1 g; sulfide=1 g; sulfide/H<sub>2</sub>O<sub>2</sub> (mol)=1; solvent (acetonitrile)=10 g; temperature=333±1 K; VS-2, Si/V molar ratio=79; TS-2, Si/Ti molar ratio=77; 100-ml glass reactor with stirring.

Table 5  
Oxidation of ethanol over TS-2 and VS-2<sup>a</sup>

	TS-2	VS-2
Conversion, mol-%	1.6	9.9
Product distribution (wt.-%)		
Acetaldehyde	100.0	40.5
Acetic acid	Nil	33.0
Ethyl acetate	Nil	26.4
Others <sup>b</sup>	Nil	0.1

<sup>a</sup>Reaction conditions: temperature=358 K; ethanol/H<sub>2</sub>O<sub>2</sub> (mol)=0.3; catalyst=5 wt.-%; duration=5 h.

<sup>b</sup>Mainly heavier products.

with VS-2 and TS-2 of similar crystal size ( $\approx 2 \mu\text{m}$ ) and size distribution. Examining the performance of the two metallosilicates in the different oxidation reactions, the following observations can be made.

(1) Both TS-2 and VS-2 have fairly similar activities in the oxidation of most substrates studied except ethanol and the thioethers, the oxidation of which is faster over VS-2; the reaction of benzene is faster over TS-2 than over VS-2.

(2) In the case of alkanes, oxidation of the carbon at the 1-position is found only over VS-2.

(3) Oxidation of the CH<sub>3</sub>- group in toluene occurs more readily than the hydroxylation of the aromatic ring in the case of VS-2. Only ring hydroxylation takes place on TS-2.

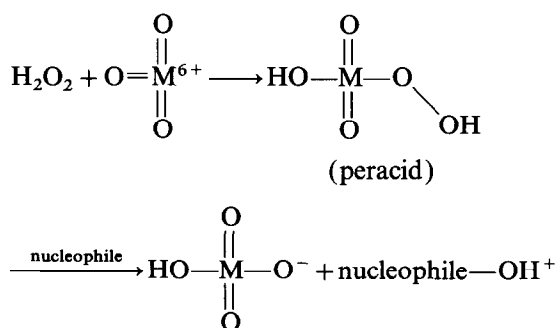
(4) There is always more formation of the secondary products in the case of VS-2 than with TS-2 denoting deeper oxidation.

(5) In general, the utilization of H<sub>2</sub>O<sub>2</sub> (selectivity with respect to H<sub>2</sub>O<sub>2</sub>) is poorer in the case of

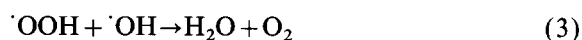
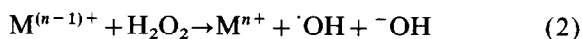
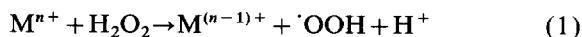
VS-2 than with TS-2, suggesting a greater decomposition of H<sub>2</sub>O<sub>2</sub> (to H<sub>2</sub>O and O<sub>2</sub>) by the former.

### 3.7. Mechanism of the reactions

Most of the above observations, especially the differences between TS-2 and VS-2, can be explained by analogy with the catalytic behaviour of Ti<sup>4+</sup> and V<sup>5+</sup> complexes in solutions. The differences observed can be traced to the type of mechanism (homolytic or heterolytic) predominant over the two catalysts in the oxidation of different substrates. Metal-catalyzed oxidations have been classified into two types, designated by Sheldon and Kochi [13] as heterolytic and homolytic. The catalysis of H<sub>2</sub>O<sub>2</sub> oxidations by acidic metal oxides such as OsO<sub>4</sub>, WO<sub>3</sub>, MoO<sub>3</sub>, CrO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> (via the formation of inorganic peracids) has been suggested to take place through the heterolytic mechanism. The intermediate peracids closely resemble organic peracids and undergo reactions with nucleophiles at the O-O bond through -OH<sup>+</sup> species:



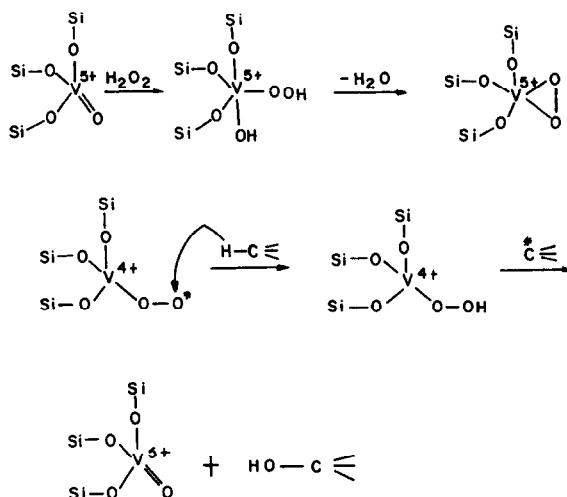
No free radicals are involved in the reaction. In homolytic reactions involving  $\text{H}_2\text{O}_2$  oxidations,  $\cdot\text{OH}$  free radicals are generated and these react with substrate free radicals. The homolytic catalytic reaction also necessitates the cycling of the metal species between at least two oxidation states. Therefore, ions that catalyze via the homolytic path are those that can undergo easy reduction–oxidation processes in the presence of  $\text{H}_2\text{O}_2$  as shown below:



As  $\text{H}_2\text{O}_2$  is a weak reducing agent and a strong oxidizer, reaction 1 is generally the slow step, and hence the homolytic mechanism is more likely when the metal ion undergoes easy reduction. The reducibility of a metal ion is governed by its redox potential of the  $[\text{M}^{n+}/\text{M}^{(n-1)+}]$  couple under the conditions of the reaction: the larger the redox potential, the larger its reducibility. The more easily reducible ions are also more potent in decomposing  $\text{H}_2\text{O}_2$ . The redox potentials of the  $[\text{V}^{5+}/\text{V}^{4+}]$  and  $[\text{Ti}^{4+}/\text{Ti}^{3+}]$  couples (in aqueous solutions) are 1.0 and 0.06 eV [14]. These values, however, will be different in different solvents and in the presence of ligands.  $\text{V}^{5+}$  with a larger redox potential is more likely to operate through a free radical mechanism than  $\text{Ti}^{4+}$ . Hence,  $\text{V}^{5+}$  is expected to cause greater homolytic decomposition of  $\text{H}_2\text{O}_2$  resulting in a lower  $\text{H}_2\text{O}_2$  utilization (poorer  $\text{H}_2\text{O}_2$  selectivity) in the reactions than  $\text{Ti}^{4+}$ .

#### Oxyfunctionalization of alkanes: VS-2

Even though the as-synthesized VS-2 has vanadium mostly in the 4+ state, the calcined samples have been shown to possess  $\text{V}^{5+}$  ions [4]. The following mechanism of the oxidation of alkanes involving reversible reduction–oxidation of the V ions appears likely:



A similar mechanism for the oxidation of alkanes by  $\text{V}^{5+}$  peroxo complexes in homogeneous solutions has been suggested by Mimoun *et al.* [15]. The critical (slow) step in the mechanism is the C–H bond breaking, which is dependent on its bond strength. For most secondary C–H bonds, it is *ca.* 94 kcal/mol. The –O–H bond formation energy for many peroxo species of the type  $\text{ROO}-\text{H}$  is around 90 kcal/mol. Though the exact value of the –O–H bond formation energy in the case of  $\text{V}^{4+}-\text{O}-\text{O}-\text{H}$  is not known, it is likely to be larger due to the electron-withdrawing nature of  $\text{V}^{4+}$ . Thus, the overall step involving the breaking of the C–H bond and the formation of the  $\text{V}^{4+}-\text{O}-\text{O}-\text{H}$  species appears energetically favourable.

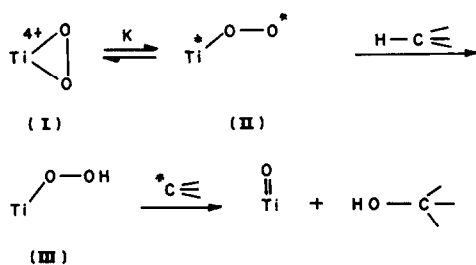
This mechanism also explains the ease of oxidation of the  $\text{CH}_3-$  group in toluene and the larger yields of benzyl alcohol and benzaldehyde than of the cresols (Table 2). The C–H bond energy in the  $\text{CH}_3-$  group in toluene is only 85 kcal/mol due to the stabilization of the benzylic radical by the aromatic nucleus.

The oxidation of the terminal carbon in alkanes is generally more difficult because of the larger C–H bond energy (99 kcal/mol) at the terminal carbon. The formation of small amounts of primary oxidation products in the case of VS-2 is probably due to the large O–H bond formation energy in the  $\text{V}^{4+}-\text{O}-\text{O}-\text{H}$  species leading to favourable energetics. However, Mimoun *et al.* [15], who studied *n*-alkane oxidation with V

complexes, have not observed the formation of  $C_1$  oxidation products. This could be due to the V ions being complexed with highly electron-donating ligands which tend to weaken the Lewis acidity (electron-withdrawing nature) of the V ions. Further, in the case of VS-2, the silica matrix to which the V ions are attached may also accentuate the electron-withdrawing property of the V ions.

#### Oxyfunctionalization of alkanes: TS-2

Huybrechts *et al.* [16] have recently proposed the following mechanism involving  $Ti^{4+}$  ions:



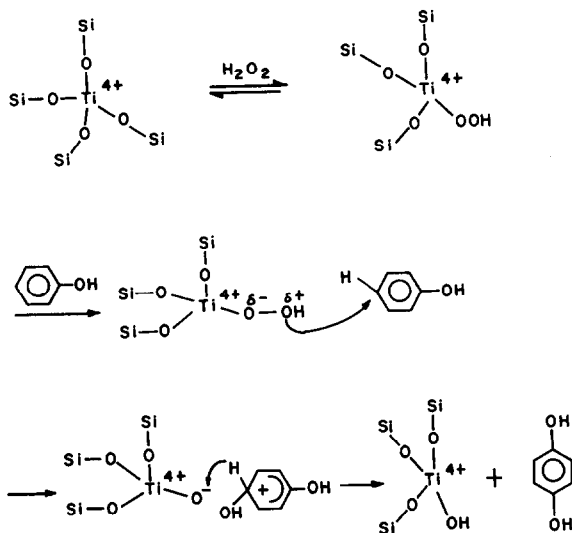
The above mechanism is similar to the one proposed earlier by Mimoun *et al.* [15] in the case of V complexes. However, the shortcomings of this mechanism (in the case of  $Ti^{4+}$ ) are that the cyclic peroxo compound of  $Ti^{4+}$  (I) has been reported to be very stable [17] and that the formation of the species of type II is not favoured as this involves the reduction of  $Ti^{4+}$  which is not probable in aqueous medium [14]. However, if the O-H bond formation energy in species of type III is large and is comparable to the -C-H bond energy in the hydrocarbons, the mechanism may still be feasible.

#### Hydroxylation of aromatics

The hydroxylation of phenol over TS-2 and VS-2 produces only the *p*- and *o*-dihydroxybenzenes. Similarly, no *meta* isomer is found in the hydroxylation of toluene. These observations suggest that the hydroxylation of the aromatic nucleus proceeds by an electrophilic mechanism. The hydroxylation of phenol by Fenton's reagent involving free radicals ( $\cdot OH$ ) usually produces more catechol than hydroquinone, the *o/p* ratio of the dihydroxybenzenes in the product being greater

than 2. In our studies over both TS-2 and VS-2, the *o/p* ratio is generally less than 1 in most solvents, even though one would expect larger yields of the *ortho* product due to the greater probability of hydroxylation at the *ortho* position (two *ortho* positions and one *para* position). This could be due to steric or shape selectivity considerations inside the pores of TS-2 and VS-2.

In the case of TS-2, where the heterolytic fission is more likely (due to the lower redox potential of  $Ti^{4+}$ ), the following mechanism may be suggested:

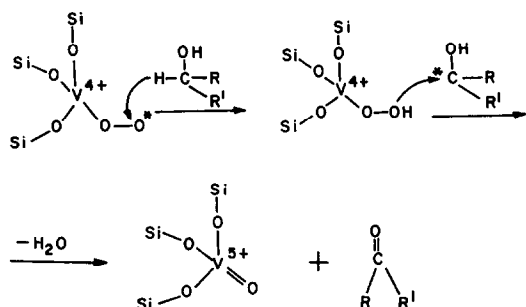


In the above mechanism, it is assumed that the Ti-peroxo complex is attached to the lattice by at least three linkages following the model of Clerici and Ingallina [18] and not by two linkages as postulated by others [16]. It is likely that a similar mechanism is also operative in the case of VS-2. However, a significant contribution from the homolytic mechanism involving free radicals ( $\cdot OH$ ) cannot also be ruled out. The similarity in the *o/p* ratios on both TS-2 and VS-2 is probably due to similar micropore structures in the two samples. Further, the greater sensitivity of VS-2 (compared with TS-2) to solvents in the hydroxylation of phenol suggests that the mechanism of hydroxylation or the strength of the interaction of the solvents with the active centers in the two cases could be different, the  $V^{5+}$  ions interacting more strongly with the solvent molecules than the  $Ti^{4+}$  ions.

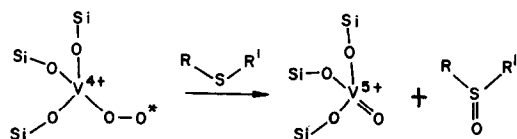
### Oxidation of alcohols and thioethers

The oxidation of alcohols and thioethers is very fast over VS-2. The following homolytic mechanism is suggested for these oxidation reactions.

For alcohols:



For thioethers:



As the bond energy of the C–H bond in the  $\alpha$ -position ( $-\text{CH}-\text{OH}$ ) is smaller than the C–H bond energy in alkanes, the reaction is faster in the case of alcohols. Similarly, the C–H bond energy in the  $-\text{CHO}$  group is also quite weak and easy to break. This explains the formation of more secondary oxidation products like the ketones, aldehydes and acids in the case of VS-2. In the case of TS-2, however, as the  $\text{Ti}-\text{O}-\text{O}^*$  species is less likely to be formed (as explained earlier), the oxidation of alcohols and aldehydes is much slower.

### 4. Conclusions

Both TS-2 and VS-2 are active in the selective oxidation of alkanes, cycloalkanes, aromatic compounds and organic sulfides under mild conditions in the presence of aqueous  $\text{H}_2\text{O}_2$ . The studies demonstrate that the active sites (Ti or V) are inside the channel system giving rise to both reactant and product shape selectivities. The differences

in the catalytic performance of TS-2 and VS-2 are: (1) VS-2 oxyfunctionalizes the primary carbon atoms also (in alkanes and alkyl aromatics) while TS-2 does not; (2) in general, better utilization of  $\text{H}_2\text{O}_2$  is observed over TS-2 than over VS-2; and (3) the oxidations are deeper on VS-2 than on TS-2. These observations could be explained on the basis of differences in the mechanism of oxidation of the substrates over TS-2 and VS-2. A heterolytic mechanism of oxidation is postulated over TS-2, while the principal path is probably homolytic in the case of VS-2.

### References

- [1] B. Notari, *Stud. Surf. Sci. Catal.*, 37 (1987) 413; 60 (1991) 343.
- [2] J.S. Reddy, R. Kumar and P. Ratnasamy, *Appl. Catal.*, 58 (1990) L1.
- [3] M.S. Rigutto and H. Van Bekkum, *Appl. Catal.*, 68 (1991) L1.
- [4] P.R. Hari Prasad Rao, A.V. Ramaswamy and P. Ratnasamy, *J. Catal.*, 137 (1992) 225.
- [5] J.S. Reddy and S. Sivasanker, *Indian. J. Technol.*, 30 (1992) 64.
- [6] G. Centi, S. Perathoner, F. Trifiro, A. Aboukais, C.F. Aissi and M. Guelton, *J. Phys. Chem.*, 96 (1992) 2617.
- [7] P.R. Hari Prasad Rao and A.V. Ramaswamy, *Appl. Catal. A, General*, 93 (1993) 123.
- [8] P.R. Hari Prasad Rao, A.A. Belhekar, S.G. Hegde, A.V. Ramaswamy and P. Ratnasamy, *J. Catal.*, 141 (1993) 595.
- [9] P.R. Hari Prasad Rao, A.V. Ramaswamy and P. Ratnasamy, *J. Catal.*, 141 (1993) 604.
- [10] J.S. Reddy, S. Sivasanker and P. Ratnasamy, *J. Mol. Catal.*, 71 (1992) 373.
- [11] D.M. Ruthven, M. Eic and E. Richard, *Zeolites*, 11 (1991) 647.
- [12] A.J.H.P. van der Pol, A.J. Verduyn and J.H.C. van Hoof, *Appl. Catal. A, General*, 92 (1992) 113.
- [13] R.A. Sheldon and J.K. Kochi, *Adv. Catal.*, 25 (1976) 272.
- [14] R.A. Sheldon, in R. Ugo (Ed) *Aspects of Homogeneous Catalysis: a Series of Advances*, Vol. IV, Reidel, Boston, MA, 1981, p. 17.
- [15] H. Mimoun, L. Saussine, E. Daire, M. Portel, J. Fischer and R. Weiss, *J. Am. Chem. Soc.*, 105 (1983) 3101.
- [16] D.R.C. Huybrechts, P.L. Busseens and P.A. Jacobs, *J. Mol. Catal.*, 71 (1992) 129.
- [17] M.G. Clerici, *Appl. Catal.*, 68 (1991) 249.
- [18] M.G. Clerici and P. Ingallina, *J. Catal.*, 140 (1993) 71.