Selective oxidation reactions over titanium and vanadium metallosilicate molecular sieves

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Selective oxidation reactions like the oxyfunctionalization of alkanes, hydroxylation of aromatics and sulfoxidation of thioethers have been carried out with dilute hydrogen peroxide over titanium and vanadium metallosilicate molecular sieves with MEL topology, viz., TS-2 and VS-2. Though both the catalysts possess similar activities, substantial differences in the product distribution are observed. The oxyfunctionalization of the primary carbon atoms of the alkanes and the oxidation of the methyl substituents of the aromatic hydrocarbons distinguish VS-2 from TS-2. Both the catalysts are found to be equally active in the hydroxylation of phenol, though they possess different activities in different solvents. In general, the oxidations are "deeper" over VS-2 than on TS-2.

Keywords: Ti silicates; V silicates; metallosilicates; TS-2; VS-2; selective oxidation reactions; oxyfunctionalization of hydrocarbons; hydroxylation of phenol; oxidation of sulfides

1. Introduction

The isomorphous substitution of Si^{4+} and Al^{3+} by other ions has been reported in many zeolite (aluminosilicate) systems and has been the subject of discussion in the preceding paper in this issue [1]. The incorporation of Ti^{4+} in the MFI and MEL lattices yields molecular sieves with interesting selective oxidation properties [2–6]. More recently, well characterized vanadium containing molecular sieves of the MFI and MEL types have also been reported [7–9]. These materials also possess interesting selective oxidation properties [10,11].

In this communication, a systematic comparison is being made of the oxidation efficiency of well characterized Ti and V silicates with MEL topology in a number of selective oxidation reactions with different organic substrates. The purpose is to highlight the similarities and differences in the activity and selectivity to different products and offer, wherever possible, an explanation to the observations made in the light of our present understanding of the location and environment of Ti and V in the pentasil structure.

2. Experimental

Detailed information on the synthesis and characterization of TS-2 and VS-2 molecular sieves have been reported in our earlier publications [5,9]. The samples were highly crystalline ($>95\%$ by XRD) and similar crystal size (~ 2 μm). The oxidation of alkanes was carried out in a stirred autoclave (Parr Instrument, USA) of 300 ml capacity at 373 K under autogeneous pressure. Typically, 100 mg of the catalyst, 2.53 g of aqueous H_2O_2 (26 wt% solution; alkane/H_2O_2 (mol) = 3) and 5 g of alkane were mixed with 25 ml of the solvent and the reaction was carried out for 8 h. Under these conditions, the reaction occurs in the liquid phase. The hydroxylation of aromatic hydrocarbons, phenol and thioethers was carried out in a 100 ml batch reactor at 333 K for 8 h. Other details of the reaction, product separation and analysis are given elsewhere [5,10–12].

3. Results and discussion

3.1. OXYFUNCTIONALIZATION OF ALKANES

The results of our studies on the oxidation of *n*-hexane 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, shows that the most active catalysts are TS-2 and VS-2, which are also the most selective for the formation of mono-functional compounds. The major products of the reaction are 2- and 3-hexanols and correspond-

Table 1

Oxidation of *n*-hexane over titanium and vanadium silicates and related molecular sieves [a]

Catalyst [b]	Conv. (mol%)	H_2O_2 sel. (mol%) [c]	Product distribution (mol%) [d]							Product sel. (mol%) [f]
			1-ol	2-ol	3-ol	1-al	2-one	3-one	others [e]	
TS-2	15.9	58.6	–	19.1	17.1	–	23.7	23.0	16.6	83.4
VS-2	14.6	57.1	3.7	9.2	8.2	7.2	26.3	25.0	21.4	79.5
silicalite-2	3.6	4.4	–	9.5	9.5	–	4.7	7.1	69.2	30.8
Ti-impregnated silicalite-2	2.8	5.2	–	3.8	4.7	–	14.4	13.9	63.2	36.8
V-impregnated silicalite-2	3.5	3.6	–	8.0	120	–	4.0	4.0	72.0	28.0

[a] Reaction conditions: catalyst = 0.1 g; *n*-hexane = 5 g; *n*-hexane/H_2O_2 (mol) = 3; solvent (acetonitrile) = 20 g; temp. = 373 K; reaction duration = 8 h. Reaction carried out with stirring in ss autoclave (Parr, 300 ml capacity) under autogeneous pressure.

[b] TS-2, Si/Ti = 77; VS-2, Si/V = 79; silicalite-2, Si/Al$\geqslant$2000; Ti- and V-impregnated silicalite-2, Si/M = 80. Preparation procedures are outlined in ref. [20] (TS-2), [33] (VS-2) and [47,48] silicalite-2.

[c] H_2O_2 utilized for mono-functional product formation.

[d] 1-ol, 2-ol and 3-ol = 1-, 2- and 3-hexanols; 1-al = hexaldehyde; 2-one and 3-one = 2- and 3-hexanones.

[e] Mostly oxygenates with more than one functional group and lactones.

[f] (Alcohol, aldehyde and ketone/alkane reacted) × 100 (mol/mol).

ing hexanones, the latter being the secondary oxidation products. The oxyfunctionalization of the primary carbon atom leading to the formation of primary alcohols and aldehydes is observed only with the vanadium silicate. An examination of the product distribution shows 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. Investigation of the oxidation kinetics has revealed that the ratio of carbonyl compounds to alcohol increased with time (fig. 1), suggesting that the aldehydes and ketones are secondary products from the corresponding primary and secondary alcohols [11]. A higher ratio of aldehydes plus ketones to alcohol in the product distribution in the case of VS-2 compared to TS-2 (2.77 and 1.27, respectively) (table 1) indicates a deeper oxidation capability of the vanadium silicates compared to titanium silicates in the secondary oxidation reactions.

In addition to nC_6, the oxidation of nC_7, nC_8 and cyclohexane has been studied on both TS-2 and VS-2 samples with Si/Ti = 55 and Si/V = 79 at 373 K. The results are summarized in table 2. The oxidative conversions and H_2O_2 selectivities decrease in the order, $nC_6 > nC_7 > nC_8 >$ cyclohexane. This order is consistent with the observed large decrease in the diffusivity of these alkanes in zeolites with increasing chain length and molecular size [13]. The product selectivity, however, is high in the case of cyclohexane oxidation, with cyclohexanol and cyclohexanone being the major products. Among other alkanes also, the formation of the primary alcohol and corresponding aldehydes was detected on VS-2 but not on TS-2. The greater efficiency for the secondary oxidation reaction on VS-2 is seen in the oxidation of cyclohexane also, wherein the cyclohexanone/-ol ratio is found to be 1.8 and 0.57, on VS-2 and TS-2, respectively (table 2).

In the liquid phase oxidation using H_2O_2 or other peroxides as oxidants, peroxo compounds are the likely intermediates [14]. The Ti–O–Si groups in titanium silicates and V–O–Si groups in vanadium silicates are known to exhibit and IR absorp-

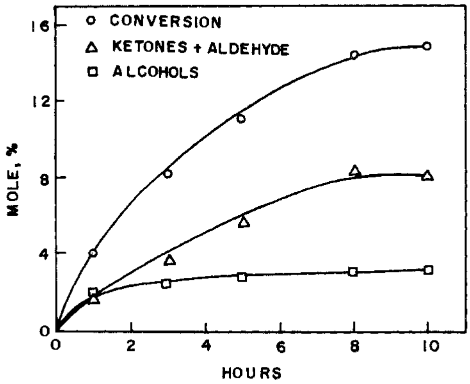


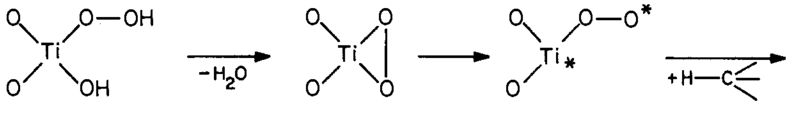
Fig. 1. Kinetics of oxidation of *n*-hexane over VS-2 (Si/V = 79) in aqueous H_2O_2 at 373 K [17]. Conditions as in table 1.

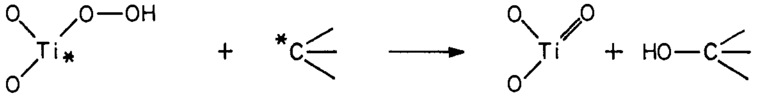
Table 2
Oxidation of *n*-alkanes and cyclohexane over TS-2 and VS-2 [a]

Substrate	TS-2			VS-2		
	conv. (mol%)	prod. sel. (mol%)	H_2O_2 sel. (mol%)	conv. (mol%)	prod. sel. (mol %)	H_2O_2 sel. (mol%)
n-hexane	15.9	83.4	58.6	14.6	79.5	57.1
n-heptane	15.6	79.5	57.1	14.3	75.8	50.1
n-octane	13.9	79.3	51.5	12.8	75.6	43.4
cyclohexane	10.9	93.4	35.4	8.4	94.0	32.5

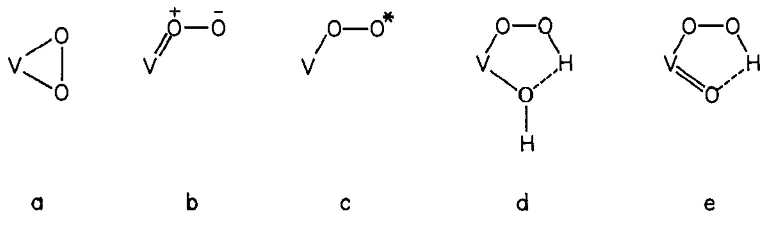
[a] Reaction conditions and definitions as in table 1.

tion band around 960 cm^{-1} which is absent in the Ti- or V-free silicalites or the V- or Ti-impregnated silicalites [5,9]. On addition of H_2O_2 to TS-2, the 960 cm^{-1} band disappears and a new Ti–OOH species with absorption in the visible region at 425 nm appears [15]. The 960 cm^{-1} band is, however, attributed by some authors to be due to Ti=O species [2]. In any case, the formation of the hydroxy–peroxy titanium complex, which is stable at the reaction temperature appears to be well established. A free-radical mechanism, similar to the one proposed by Huybrechts et al. [15,16] can be extended to the oxidation of alkanes over TS-2 also, as shown below:

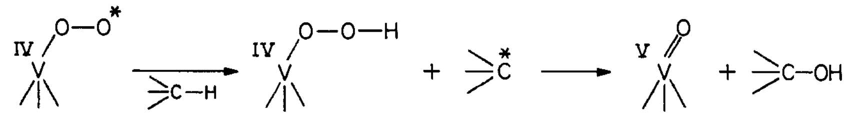




V(V) peroxo complexes in non-protic solvents are also known to be effective oxidants of olefins (to epoxides), aromatics (to phenols) and alkanes (to alcohols and ketones) [14]. Their activity was attributed to a peroxo radical V^{4+}–O–O* species. The peroxo complexes are derived from the reaction of V=O groups with H_2O_2 and may be represented as



Since the influence of the type of solvent used in the oxidation reaction on the activity is different over VS-2 and TS-2 (table 3), the reaction intermediates involved in the two systems are also probably different. In the case of VS-2, activity increases with increasing polarity of the solvent, while the reverse is true for TS-2. Further, as H_2O is always present in the reaction medium, the formation of intramolecularly hydrogen-bonded species such as d and e may be inhibited. Oxyperoxide and hydroxy-peroxides of the type d and e transform to reactive radicals of the type c, V–O–O* [14]. In our studies, we have observed the formation of a radical species (an ESR signal with $g = 1.987$) when VS-2 was added to a mixture of *n*-octane and H_2O_2 [17]. This signal was not observed in the absence of VS-2. The intensity of this signal increased upto 30 min and then decreased. The formation of the radical and its subsequent decay by reaction with the alkane molecule may be envisaged to proceed as given below:



One conclusion of the solvent studies could be that the metal peroxo–substrate complex (intermediate) is significantly more polar in the case of VS-2 than TS-2.

3.2. HYDROXYLATION OF AROMATIC HYDROCARBONS

The hydroxylation of aromatic hydrocarbons to phenols and phenol derivatives by dilute H_2O_2 at 333–373 K takes place readily on TS-2 and VS-2. The results are presented in table 4. The hydroxylation of benzene leads to the formation of phenol and para-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 mono-functional product are about 90% on both the catalysts. With toluene as the substrate, the hydroxylation rates are faster, the conversion levels (upto 8 h) being higher than observed in ben-

Table 3
Influence of solvents on *n*-hexane oxidation over TS-2 and VS-2 [a]

Solvent		VS-2 [b]		TS-2 [b]	
name	dielectric constant (298 K)	conv. (mol%)	prod. sel. (mol%)	conv. (mol%)	prod. sel. (mol%)
acetonitrile	37.5	14.6	79.5	12.3	88.3
acetone	20.7	5.4	68.6	18.9	89.4
acetonitrile + acetone	–	8.4	67.2	–	–

[a] Reaction conditions and definitions as in table 1.
[b] Si/V = 79 for VS-2 and Si/Ti = 33 for TS-2.

Table 4
Hydroxylation of benzene and toluene with aqueous H_2O_2 over TS-2 and VS-2 molecular sieves[a]

Substrate /sample	Conv. (mol%)	H_2O_2 sel. (mol%)[b]	Product distribution (mol%)						
			phenol	PBQ[c]	*o*-cresol	*p*-cresol	benzyl alcohol	benzal-dehyde	others[d]
benzene									
TS-2	17.1	42.2	88	9	–	–	–	–	3
VS-2	7.2	18.2	90	7	–	–	–	–	3
toluene									
TS-2	13.2	37.8	–	–	36	59	–	–	5
VS-2	11.7	49.5	–	–	20	17	8	52	3

[a] Reaction conditions: catalyst = 0.1 g; substrate = 1 g; substrate/H_2O_2 (mol) = 3; temp. = 333 K; reaction duration = 8 h. Reactions carried out in a 100 ml glass reactor with stirring.

[b] H_2O_2 utilized for the formation of catechol, para-benzoquinone or cresols, benzylalcohol and benzaldehyde.

[c] PBQ = para-benzoquinone.

[d] Mainly polyhydroxy compounds.

zene hydroxylation. 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 benzylalcohol and benzaldehyde, in addition to the cresols. In fact, the rate of side chain oxidation is faster than the rate of aromatic hydroxylation. Further, the large concentration of benzaldehyde (52 wt%) in the product shows the secondary oxidation of benzylalcohol to benzaldehyde is faster.

Another aspect to the oxidation of alkyl aromatics on both the TS-2 and VS-2 is that the reaction of bulky substrates like tert-butyl benzene does not take place due to the steric restrictions imposed by the narrow channels within the molecular sieves. Among other 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 [18], suggesting the presence of active centers inside the channel system [12]. 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*/*p*-cresol ratio of 0.61 (table 4) is far lower than that expected from purely electronic considerations in the absence of diffusional restrictions for these products.

3.3. HYDROXYLATION OF PHENOL

Several reports have appeared on the influence of various reaction parameters such as Ti content, feed ratio and solvents on the conversion and product distribution over TS-1 and TS-2 in the hydroxylation of phenol [19–22]. A comparison of the activities of titanium silicates, TS-1 and TS-2, and the vanadium silicate, VS-2 in the hydroxylation of phenol under similar conditions is now made. The phenol conversion, H_2O_2 selectivity and product distribution as a function of time on VS-2, TS-2 and TS-1 are presented in figs. 2A, 2B and 2C, respectively. The reactions were carried out using water as solvent at 353 K and at a phenol to H_2O_2 mole ratio of 3.0. 100 mg of each of the three catalysts having almost similar Si/M ratio and particle sizes was used in this batch reaction.

Fig. 2 shows that the initial activity of VS-2 is much lower compared to those of TS-1 and TS-2. The rates follow the order, TS-1 > TS-2 > VS-2. The difference in the product distributions at the end of the run on the three catalysts is seen from the catechol to hydroquinone ratios, which are 1.3, 1.1 and 0.9 for VS-2, TS-2 and TS-1, respectively.

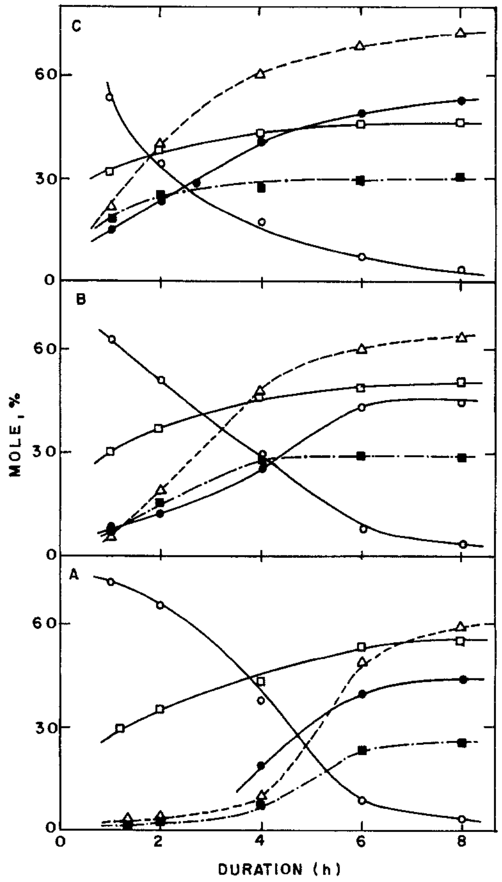


Fig. 2. Hydroxylation of phenol over VS-2 (A), TS-2 (B) and TS-1 (C) catalysts [10]: (■) phenol conversion; (△): H_2O_2 selectivity; (○): para-benzoquinone; (□): catechol; (●): hydroquinone. Conditions: solvent = water; temp. = 353 K; phenol/H_2O_2 (mol) = 3; catalyst (wt.) = 0.1 g; phenol (wt.) = 5 g; reaction done under stirring in 100 ml glass reactor.

Among other reaction parameters, the influence of different solvents on the conversion and product distribution is, perhaps, the most striking feature that distinguishes titanium silicates from the vanadium silicate. The results on the use of different solvents in the hydroxylation of phenol on TS-2 and VS-2 are given in table 5. As seen from table 5, the solvent affects both the conversion and H_2O_2 efficiency. In the case of TS-2, the conversions are high in acetone and methanol irrespective of differences in the polarity of the solvent. On the vanadium silicate, the phenol conversion increases in general with increase in the polarity of the solvent with a corresponding increase in the efficiency of H_2O_2 utilization. Under identical conditions, maximum phenol conversion is observed in water. Interestingly, no hydroxylation products were obtained in methanol which is more polar (dielectric constant = 33) than acetone (dielectric constant = 20.7). Even an increase in temperature upto 353 K or a higher concentration of the catalyst in the reaction mixture did not lead to the formation of any dihydroxylated product from phenol. This observation is in contrast to that observed on TS-2 (or TS-1). In the case of the latter, a H_2O_2 selectivity around 80% has been reported by Tuel et al. in methanol [20]. Further studies are necessary to clarify the negative influence of methanol as a solvent in this reaction over VS-2.

The influence of the solvent on the product distribution is more complex. Though para-benzoquinone is obtained (4–5%) in all the three solvents (acetone, acetonitrile and water) over VS-2, surprisingly, no hydroquinone is formed 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 5). In sum-

Table 5
Influence of solvents on the hydroxylation of phenol over TS-2 [a] and VS-2 [b]

Catalyst /solvent	Conv. (mol%)	H_2O_2 sel. (mol%)	Product distribution (mol%) [c]		
			Catechol	HQ	PBQ
TS-2					
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
VS-2					
acetone	7.0	12.7	95.1	0.0	4.9
methanol	0.0	0.0	0.0	0.0	0.0
acetonitrile	13.9	29.7	55.4	39.8	4.8
water	24.3	55.7	44.1	52.0	3.9

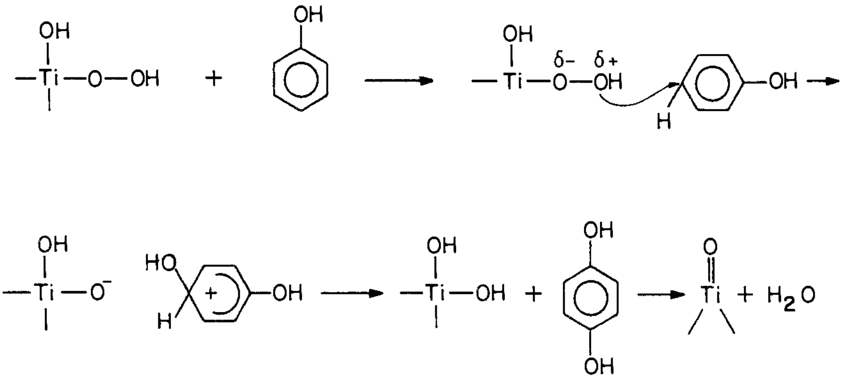
[a] Reaction conditions: catalyst = 0.1 g; phenol = 1 g; phenol/H_2O_2 (mol) = 3; temp. = 342 K; reaction duration = 24 h; catalyst = TS-2 (Si/Ti = 29).

[b] Reaction conditions: catalyst = 0.1 g; phenol = 1 g; phenol/H_2O_2 (mol) = 3; temp. = 333 K; reaction duration = 8 h; catalyst = VS-2 (Si/V = 79).

[c] Products excluding tars; HQ = hydroquinone; PBQ = parabenzoquinone.

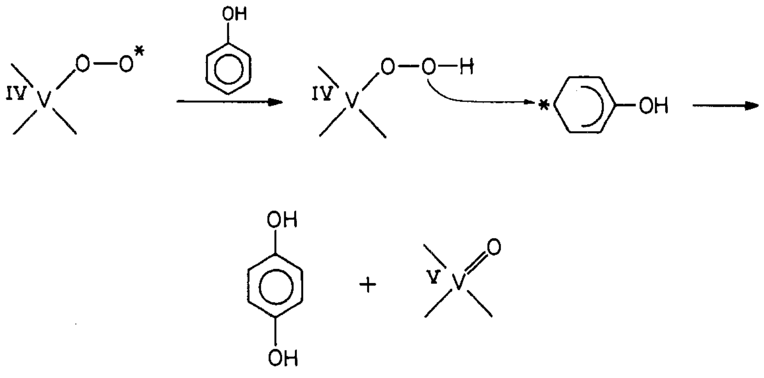
mary, though the vanadium silicate is active in this hydroxylation reaction, the influence of solvent on the conversion and product selectivity is significantly different from that observed on titanium silicates.

Considering the positive influence of substituents such as $-CH_3$, $-OMe$, or $-OH$ on the rate and the formation of exclusively *o*- and *p*-isomers on these catalysts, the reaction is suggested to be a case of electrophilic substitution, probably involving $(OH)^+$ species or free radicals [22]. The reaction may be envisaged to take place by the ionic mechanism on TS-2 as follows:



A slightly different non-radical mechanism has been proposed by Huybrechts et al. for the hydroxylation of phenol over TS-1 [16].

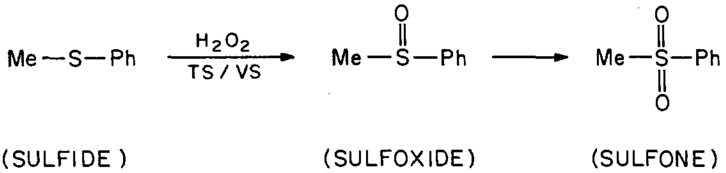
Based on the earlier reports on homogeneous hydroxylation reaction with vanadium peroxo complexes [14], a radical mechanism as shown below is being suggested for vanadium silicates:



The abstraction of H from the aromatic substrate by the V^{IV}–O–O* radical is followed by the addition of *OH to the aromatic ring as a result of oxidation of V^{IV} to V^{V} state. The solvent might influence the stability of any of the intermediates formed in the reaction sequence and hence the conversion. However, it is likely that both ionic and radical type mechanisms are operative during hydroxylation on both the catalysts depending on the reaction conditions.

3.4. SULFOXIDATION OF THIOETHERS

The details of the sulfoxidation of methyl phenyl sulfide (Me–S–Ph) over TS-2 and VS-2 are given in table 6. The two steps of oxidation proceed as follows:



Under similar conditions, VS-2 exhibits significantly higher activity than TS-2. For example, only 30 min were needed for the complete conversion of methyl phenyl sulfide over 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 for longer duration. The reactivity of the sulfides, in general, follows the order Me–S–Me > Et–S–Et > Ph–S–Me > Ph–S–Et. Over TS-2, though the order remained the same, the rates were considerably slower. Interestingly, the product distribution is not too different on the two catalysts.

4. Conclusions

Both TS-2 and VS-2 are active in the selective oxidation of substrates like alkanes, cycloalkanes, aromatic compounds and organic sulfides under mild conditions in the presence of aqueous H_2O_2. These studies demonstrate that the active sites (Ti or V) are inside the channel system giving rise to both reactant and product shape selectivities.

The major difference between TS-2 and VS-2 is that the latter molecular sieve oxyfunctionalizes the primary carbon atoms also (in alkanes and alkyl substituted aromatic hydrocarbons) while TS-2 does not. In addition, the activity of VS-2 is

Table 6
Sulfoxidation of methyl phenyl sulfide over TS-2 and VS-2 [a]

Catalyst	Reaction time (min)	Conv. (mol%)	Product distribution (mol%)	
			sulfoxide	sulfone
TS-2	30	22	74	26
TS-2	120	100	78	22
VS-2	30	100	84	16
silicalite-2	120	47	84	16

[a] Reaction conditions: catalyst = 0.1 g; sulfide = 1 g; sulfide/H_2O_2 (mol) = 1; solvent (acetonitrile) = 10 g; temp. = 333 ± 1 K; (VS-2, Si/V molar ratio = 79; TS-2, Si/Ti molar ratio = 77).

influenced to a greater extent than TS-2 by the nature of the solvent used in the reaction. Metal peroxy intermediates are involved in the above reactions over both TS-2 and VS-2. It is suggested that the reactions proceed by a radical mechanism over VS-2, while both radical and ionic mechanisms appear to be possible over TS-2.

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