

# Oxidation of ethylbenzene over Ti-, V- and Sn-containing silicalites with MFI structure

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## Abstract

The oxidation of ethylbenzene has been carried out over TS-1, VS-1 and Sn-silicalite-1 (MFI structure) using  $H_2O_2$  as oxidant at 333–353 K. The major products were 1-phenylethanol and acetophenone arising from the oxidation of the side chain. Aromatic ring hydroxylation leads to the formation of *ortho*- and *para*-hydroxy ethylbenzene as a minor side reaction. The differences in the product selectivities could be explained on the basis of the reaction intermediates. Among the three metallo-silicates, Sn-silicalite-1 is found to be the most active with an  $H_2O_2$  efficiency of about 60 mol.%. The influence of various reaction parameters on the conversion and selectivity of ethylbenzene over Sn-silicalite-1 is reported.

**Keywords:** Metallo-silicates; TS-1; VS-1; Sn-silicalite; Molecular sieves; Ethylbenzene oxidation; Oxidation with  $H_2O_2$

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## 1. Introduction

Shape selective oxidation of many organic substrates using  $H_2O_2$  as oxidant over  $Ti^{4+}$  analogues of ZSM-5 (TS-1) and ZSM-11 (TS-2) has been well documented [1–3]. Among other metallo-silicates, vanadium containing MFI (VS-1) and MEL silicalites (VS-2) show redox properties (reversible  $V^{4+}$  to  $V^{5+}$  transitions) which are responsible for their catalytic activity in many oxidation reactions [4,5]. The product selectivities, however, have been found to be different in reactions catalyzed by titanium and vanadium silicate molecular sieves [6]. We have recently reported the synthesis of Sn-containing silicalites of

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MFI, MEL and MTW types, which have been characterized to have  $\text{Sn}^{4+}$  in both tetrahedral and octahedral coordinations [7–9]. These Sn-silicates have also been found to catalyze oxidation/hydroxylation reactions with aqueous  $\text{H}_2\text{O}_2$ .

Effective utilization of ethylbenzene, available in the xylene stream of the petrochemical industry to more value added products is an interesting proposition. Well known are the isomerization of ethylbenzene to xylenes and dehydrogenation to styrene monomer. Oxidation of ethylbenzene has not drawn much attention due to the complexity of the products that could be formed, particularly in the vapor phase catalytic oxidation using molecular oxygen. In this study, we have used Ti-, V- and Sn-silicate molecular sieves as catalysts in the oxidation of ethylbenzene with aqueous  $\text{H}_2\text{O}_2$  as oxidant in the liquid phase. The main interest is to understand the course of the reaction, which has more than one possibility, viz., the aromatic ring hydroxylation and the activation of the primary or the secondary carbon atom of the ethyl substituent. From a study of the activities of the three metallo-silicates and product distributions, the differences between the systems could be rationalized. Since Sn-silicate shows a higher  $\text{H}_2\text{O}_2$  efficiency under identical conditions compared to the other two, a more detailed study of different reaction parameters with Sn-silicates is presented.

## 2. Experimental

### 2.1. Synthesis

The Ti-, V- or Sn-containing molecular sieves with MFI structure with different Si/M molar ratios were synthesized hydrothermally using tetraethyl *ortho*-silicate (Aldrich, 99%) as the Si source, titanium butoxide as a source of titanium, vanadyl sulphate trihydrate as a source of vanadium and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (Loba Chemie, 99%) as the tin source. Tetrapropyl ammonium hydroxide (20% aqueous solution prepared at our laboratory starting from tripropylamine and having less than 20 ppm of  $\text{Na}^+$  and  $\text{K}^+$  ion impurities) was used as the organic template. The details of the synthesis of TS-1 and VS-1 are given in Refs. [10,4]. Other details of the synthesis and characterization of Sn-silicate molecular sieves with MFI structure (Sn-Sil-1) are given in Ref. [7]. The samples were calcined at 773 K for 16 h.

### 2.2. Catalytic oxidation reactions

The oxidation of ethylbenzene was carried out batchwise using a (100 ml capacity) glass vessel fitted with a mechanical stirrer, a condenser and a feed pump (Sage instruments, USA) at temperatures between 333 and 353 K. Either acetonitrile, *tert*-butanol, acetone or water was used as the solvent. All the

samples were of fairly uniform (0.2–0.3  $\mu\text{m}$ ) size. Aqueous  $\text{H}_2\text{O}_2$  (26 wt.%) was added in one lot after attaining the steady-state temperature for the reaction. The total duration of each run was about 24 h. The products were taken out at every 2 h intervals, diluted with the solvent and analyzed on a capillary GC (HP 5880) using a 50 m long silicon gum column. The products were identified by GC-MS (Shimadzu) wherever required.

### 3. Results and discussion

The samples used in this catalytic reaction are microporous, crystalline materials and do not contain any alkali metals ( $\text{Na}^+$  and  $\text{K}^+$  impurities < 5 ppm). To remove the extra framework species of titanium and vanadium, the TS-1 and VS-1, were treated with dilute  $\text{H}_2\text{SO}_4$  and ammonium acetate, respectively. The detailed characterization of Sn-Sil-1 samples indicates [7] that only a part (20%) of the  $\text{Sn}^{4+}$  ions are probably in the lattice positions (giving rise to an expansion of the unit cell, XRD). The well dispersed  $\text{Sn}^{4+}$  ions are active in many oxidation reactions [7–9]. It may be mentioned that silicalite-1, Ti-, V- or Sn-impregnated silicalite-1 or pure oxides of Ti, V or Sn showed negligible activity in many of these oxidation reactions under similar conditions. The turnover number (TON) is defined as the number of moles of ethylbenzene converted per mol of metal ion. The  $\text{H}_2\text{O}_2$  selectivity is defined as the mol.% of  $\text{H}_2\text{O}_2$  consumed in the formation of all products excluding polyhydroxy heavier products.

#### 3.1. Activity of the catalysts

A comparison of the activities of TS-1 (Si/Ti = 33), VS-1 (Si/V = 40) and Sn-Sil-1 (Si/Sn = 40) in the oxidation of ethylbenzene is given in Table 1. Oxidation of ethylbenzene to the different products can take place in two ways. One is the aromatic ring hydroxylation under which the hydroxylation at the *para*-position is preferred to some extent to the *ortho*-position. The other is the side chain (ethyl group) oxidation at primary and secondary carbon atoms. The primary and secondary carbinols formed from the side chain oxidation undergo further oxidation to the respective aldehyde and ketone. The side chain oxidation at the secondary carbon predominates over the primary carbon atom. In the case of TS-1, the oxidation does not occur at the primary carbon atom. This difference between TS-1 on the one hand and VS-1 and Sn-Sil-1, on the other, probably arises from the reaction intermediates. Such hydroxylation reactions are reported to follow an ionic mechanism on TS-1 and TS-2 [11,12]. We have shown earlier that with VS-1, VS-2 and Sn-Sil-1 samples peroxy radicals may be the intermediates [13,14]. Nevertheless, between the two path ways, the product distribution indicates that the side chain product selectivity is around 4

Table 1  
Activity of different catalysts in the oxidation of ethylbenzene <sup>a</sup>

	TS-1	VS-1	Sn-Sil-1
Si/M (molar ratio)	33	40	40
Number of moles of M <sup>b</sup> × 10 <sup>5</sup>	9.7	8.0	7.8
TON <sup>c</sup>	8.4	4.9	15.4
H <sub>2</sub> O <sub>2</sub> selectivity <sup>d</sup> (mol.%)	36.2	20.1	60.9
<i>Product distribution (mol.%)</i>			
1-Phenylethanol	33.0	20.8	14.2
Acetophenone	41.4	62.0	58.2
2-Phenylethanol	Nd <sup>e</sup>	3.0	1.2
2-Phenylethanal	Nd <sup>e</sup>	2.5	2.4
<i>o</i> -Hydroxy-EB <sup>f</sup>	10.6	4.3	11.2
<i>p</i> -Hydroxy-EB	12.4	5.2	10.8
Others	2.6	2.2	2.0

<sup>a</sup> Reaction conditions: ethylbenzene = 1 g; catalyst = 200 mg; ethylbenzene/H<sub>2</sub>O<sub>2</sub> (mol) = 3; acetonitrile/ethylbenzene (mol) = 20; temp. = 353 K; time = 24 h.

<sup>b</sup> For 200 mg of the catalyst (M = Ti, V or Sn).

<sup>c</sup> Number of moles of ethylbenzene consumed per mol of metal ion.

<sup>d</sup> mol.% of H<sub>2</sub>O<sub>2</sub> consumed in the formation all products excluding polyhydroxy heavier products grouped as others.

<sup>e</sup> Not detected.

<sup>f</sup> EB = ethylbenzene.

to 5 times that of aromatic ring oxidation products. Fig. 1 shows the course of the oxidation on the three metallo-silicates. The TON of ethylbenzene over TS-1 and VS-1 are 8.4 and 4.9, respectively whereas over Sn-Sil-1 it is 15.4. The product selectivity shows that in the side chain oxidation of ethylbenzene, TS-1 gives 1-phenylethanol (33%) and acetophenone (41.4%) whereas VS-1 and Sn-Sil-1 give 1-phenylethanol (20.8% and 14.2%, respectively) and acetophenone (62% and 58.2%, respectively). The latter (VS-1 and Sn-Sil-1) exhibit a greater ability to oxidize 1-phenylethanol to acetophenone in comparison to TS-1. The peroxo (radical) intermediate formed on VS-1 and Sn-Sil-1 is able to oxyfunctionalize the primary carbon atom of the ethyl substituent to some extent that leads to the formation of minor quantities of 2-phenylethanol (3.0% and 2.4%) and 2-phenylethanal (2.5% and 1.2%, respectively, Table 1). On TS-1, the electrophilic intermediate attacks the secondary carbon atom stabilizing the secondary carbenium ion preferentially leading to the formation of 1-phenylethanol and acetophenone only. It is also possible that the contribution of surface V and Sn species to the overall activity could be significant in the VS-1 and Sn-Sil-1 samples [13,14]. Among the three metallo-silicates, Sn-Sil-1 is distinguished from the other two in terms of a higher TON and a better H<sub>2</sub>O<sub>2</sub> efficiency in this reaction, under the conditions studied (60.9 mol.% H<sub>2</sub>O<sub>2</sub> efficiency on Sn-Sil-1, compared to 36.2% on TS-1 and 20.1% on VS-1, Table 1).

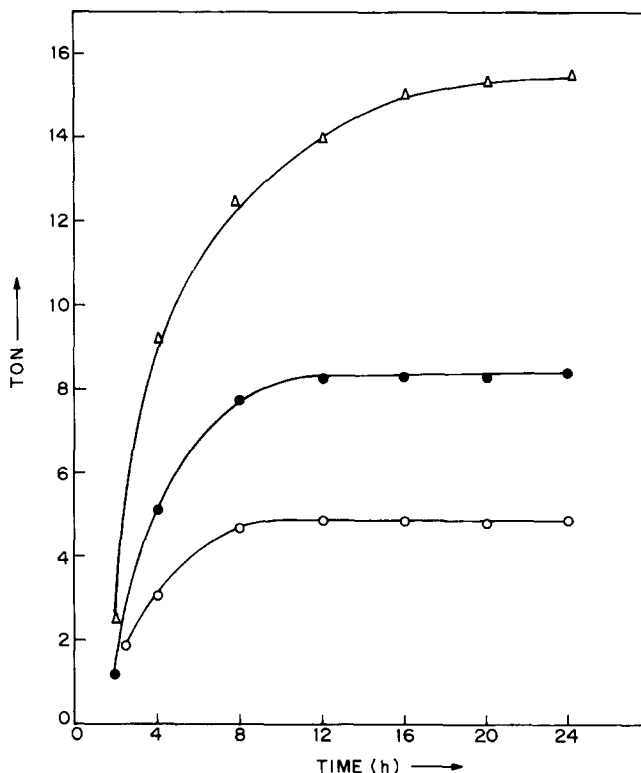


Fig. 1. TON of ethylbenzene at different intervals of time over different catalysts with aqueous  $H_2O_2$  at 353 K. TS-1 (●), VS-1 (○) and Sn-Sil-1 (△).

### 3.2. Oxidation of ethylbenzene over Sn-silicalite-1

Further detailed studies on the oxidation of ethylbenzene under different reaction conditions are restricted to Sn-Sil-1 with a Si/Sn ratio of 70. The product distribution and  $H_2O_2$  selectivity are given in Fig. 2. It is clear that the rate of oxidation of the secondary carbon atom of the ethyl group is high. In the beginning of the reaction (up to 2 h), only 1-phenylethanol (major) and its corresponding ketone (acetophenone) were detected. After 4 h, other reaction products were observed. The reaction is almost complete after about 12 h, when the  $H_2O_2$  efficiency reaches a maximum. After 24 h, no  $H_2O_2$  was detected in the reaction mixture. Since Sn-Sil-1 is mildly acidic (compared to TS-1), the self decomposition of  $H_2O_2$  could be limiting its efficiency for the oxidation reaction.

### 3.3. Influence of the Si/Sn molar ratio

The oxidation of ethylbenzene did not take place in the absence of a catalyst. Negligible conversion of ethylbenzene was observed in the presence of silicalite-

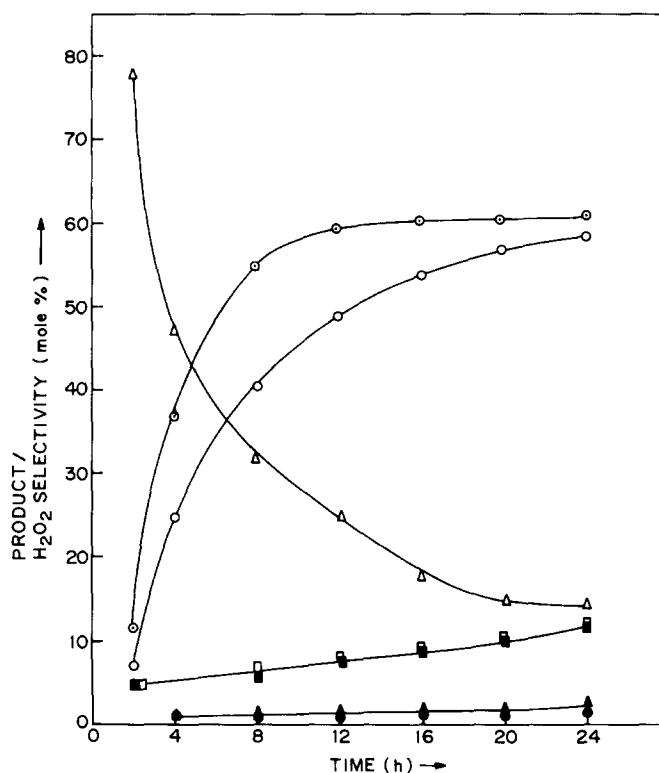


Fig. 2. The course of the oxidation of ethylbenzene over Sn-silicalite-1 (Si/Sn mol ratio = 70) with aqueous  $\text{H}_2\text{O}_2$  at 353 K.  $\text{H}_2\text{O}_2$  efficiency (mol.%) ( $\odot$ ); product distribution (%): 1-phenylethanol ( $\Delta$ ), acetophenone ( $\circ$ ), 2-phenylethanol ( $\bullet$ ), 2-phenylethanal ( $\blacktriangle$ ), *o*-hydroxy ethylbenzene ( $\square$ ), *p*-hydroxy ethylbenzene ( $\blacksquare$ ).

1, pure  $\text{SnO}_2$  or Sn-impregnated silicalite-1. The effect of Sn content of Sn-Sil-1 on the oxidation of ethylbenzene is illustrated in Table 2. It is clear from the data given in Table 2 that the  $\text{H}_2\text{O}_2$  selectivity increases with increasing Sn

Table 2  
Effect of Sn content of Sn-Sil-1 in the oxidation of ethylbenzene <sup>a</sup>

Si/Sn (molar ratio)	40	50	70	100	130
Number of moles of Sn $\times 10^5$	7.8	6.4	4.6	3.3	2.5
TON	15.4	18.4	24.6	24.4	25.5
$\text{H}_2\text{O}_2$ selectivity (mol.%)	60.9	59.4	56.4	39.6	32.0
<i>Product distribution (mol.%)</i>					
1-Phenylethanol	14.2	14.3	15.2	15.1	15.0
Acetophenone	58.2	58.7	57.5	57.4	57.6
2-Phenylethanol	1.2	0.8	0.7	0.8	0.7
2-Phenylethanal	2.4	2.0	1.8	2.0	1.9
<i>o</i> -Hydroxy-EB	11.2	10.5	10.3	10.2	10.3
<i>p</i> -Hydroxy-EB	10.8	11.5	12.0	12.2	12.1
Others	2.0	2.2	2.5	2.3	2.4

<sup>a</sup> Reaction conditions and other descriptions are as given in Table 1.

Table 3  
Effect of catalyst concentration in the oxidation of ethylbenzene<sup>a</sup>

Catalyst amount (g)	0.02	0.01	0.1	0.2
TON	12.3	18.9	23.8	24.6
H <sub>2</sub> O <sub>2</sub> selectivity (mol.%)	26.2	41.8	54.4	56.4
<i>Product distribution (mol.%)</i>				
1-Phenylethanol	24.0	19.5	15.4	15.2
Acetophenone	51.2	54.7	57.2	57.5
2-Phenylethanol	0.3	0.6	0.9	0.7
2-Phenylethanal	0.6	1.0	1.7	1.8
<i>o</i> -Hydroxy-EB	7.1	9.0	10.3	10.3
<i>p</i> -Hydroxy-EB	10.3	11.1	11.8	12.0
Others	6.5	4.1	2.7	2.5

<sup>a</sup> Catalyst: Sn-Sil-1 (Si/Sn = 70). Reaction conditions and other descriptions are as given in Table 1.

content of Sn-Sil-1 up to about  $7.8 \times 10^{-5}$  mol of Sn. It shows that the concentration of active Sn-peroxo species that contribute to the oxidation of ethylbenzene increases. Even at a low Sn concentration in the catalyst (Si/Sn = 130), the H<sub>2</sub>O<sub>2</sub> selectivity is found to be 32.0 mol.%. The TON is maximum or nearly the same for samples with Si/Sn (molar ratio) of > 70 but decreases with higher Sn content (Si/Sn < 50) as shown in Table 2. This indicates that Sn is uniformly dispersed at the surface and in the bulk of the catalyst for samples with Si/Sn of > 70 and that the surface of the sample is richer with Sn than the bulk for samples with Si/Sn of < 50. This is in accordance with our earlier XPS studies of Sn-Sil-1 samples of different Si/Sn ratios [7,8]. In all the cases, however, the product distribution shows that the oxidation of the secondary carbon is more predominant, with 1-phenylethanol and acetophenone together contributing to about 72% of the total products. The aromatic ring hydroxylation gives about 22% of *o*- and *p*-hydroxy ethylbenzene. Further investigations were carried out using a Sn-Sil-1 sample with a Si/Sn molar ratio of 70.

### 3.4. Effect of catalyst concentration

Table 3 shows that when the amount of the catalyst is between 0.10 and 0.20 g in the reaction mixture, there is little change in TON and H<sub>2</sub>O<sub>2</sub> selectivity. However, when the amount of the catalyst is reduced to 0.05 and 0.02 g, the TON and H<sub>2</sub>O<sub>2</sub> selectivity decrease considerably (TON = 24.6 and 12.3, H<sub>2</sub>O<sub>2</sub> selectivity = 56.4 and 26.2 for 0.20 and 0.02 g catalyst, respectively.) The selectivity to product of primary carbon atom oxidation (2-phenylethanol and 2-phenylethanal) decreases from 2.5 to 0.9, and the ratio of acetophenone to the corresponding alcohol (1-phenylethanol) decreases from 3.8 to 2.1, when the amount of catalyst is reduced from 0.2 to 0.02 g, respectively. We may also note that when the catalyst concentration is low, the amount of undesirable, polyhydroxy products designated together as “others” in Table 3 increases.

Table 4  
Effect of H<sub>2</sub>O<sub>2</sub> concentration<sup>a</sup>

EB/H <sub>2</sub> O <sub>2</sub> (molar ratio)	5.0	3.0	1.0
TON	17.0	24.6	51.9
H <sub>2</sub> O <sub>2</sub> selectivity (mol.%)	65.4	56.4	39.2
<i>Product distribution (mol.%)</i>			
1-Phenylethanol	16.7	15.2	14.0
Acetophenone	58.3	57.5	55.3
2-Phenylethanol	0.6	0.7	0.8
2-Phenylethanal	1.4	1.8	2.5
<i>o</i> -Hydroxy-EB	9.2	10.3	12.1
<i>p</i> -Hydroxy-EB	11.8	12.0	12.6
Others	2.0	2.5	2.7

<sup>a</sup> Reaction conditions: Si/Sn (molar ratio) = 70; (Table 1).

### 3.5. Effect of H<sub>2</sub>O<sub>2</sub> concentration

As illustrated in Table 4, a maximum H<sub>2</sub>O<sub>2</sub> selectivity of 65.4 mol.% is observed at ethylbenzene/H<sub>2</sub>O<sub>2</sub> molar ratio of 5. However, the lower concentration of H<sub>2</sub>O<sub>2</sub> results in a lower TON of ethylbenzene. The lower concentration of H<sub>2</sub>O<sub>2</sub> favors the oxidation of secondary carbon atom rather than primary in the side chain reaction. For example, at ethylbenzene/H<sub>2</sub>O<sub>2</sub> molar ratios of 5 and 1, the ratios of secondary to primary carbon atom oxidation products are 37.5 and 21.0%, respectively. At the same time, the product selectivity for aromatic hydroxylation increases marginally from 21.0 to 24.7%.

### 3.6. Influence of ethylbenzene concentration

The effect of the concentration of the solvent (acetonitrile) is shown in Table 5. An increase in the acetonitrile to ethylbenzene molar ratio from 10 to 30 leads

Table 5  
Effect of ethylbenzene concentration<sup>a</sup>

Acetonitrile/ethylbenzene (molar ratio)	10	20	30
TON	25.5	24.6	22.2
H <sub>2</sub> O <sub>2</sub> selectivity (mol.%)	58.4	56.4	50.6
<i>Product distribution (mol.%)</i>			
1-Phenylethanol	14.8	15.1	15.5
Acetophenone	57.7	57.4	57.2
2-Phenylethanol	0.6	0.7	1.0
2-Phenylethanal	1.8	1.8	1.5
<i>o</i> -Hydroxy-EB	10.5	10.3	10.7
<i>p</i> -Hydroxy-EB	12.2	12.0	11.6
Others	2.4	2.5	2.5

<sup>a</sup> Catalyst: Sn-Sil-1 (Si/Sn = 70); other conditions are as given in Table 1.



to a marginal decrease of the TON from 25.5 to 22.2 and the H<sub>2</sub>O<sub>2</sub> selectivity from 58.4 to 50.6%, respectively. Little effect of solvent dilution on the product distribution was observed.

### 3.7. Influence of various solvents

The effect of various solvents such as acetonitrile, *tert*-butanol, acetone and water used in the oxidation of ethylbenzene is illustrated in Table 6. In all the earlier experiments acetonitrile was used as solvent. The role of solvent on the reaction is very complex, especially on the product distribution. Acetone has a negative influence on the reaction, as seen from the very low TON and H<sub>2</sub>O<sub>2</sub> efficiency. Also, no product due to the oxidation of primary carbon atom was detected. In our earlier report [14] on the influence of different solvents on the hydroxylation of phenol, we have argued that acetone coordinates strongly with isolated Sn<sup>4+</sup> ions in the catalyst inhibiting the formation of active peroxy species. With water, a higher TON (27.7) and H<sub>2</sub>O<sub>2</sub> selectivity (62.1 mol.%) was observed under tri-phase conditions, with a solid (catalyst) phase and two immiscible liquids. Some remarkable improvement in TON under tri-phase conditions using TS-1 as catalyst in the hydroxylation of different organic substrates has recently been reported by Bhaumik and Kumar [15]. Between the two polar media, water and *tert*-butanol, the aromatic hydroxylation appears to be more favorable with water than with *tert*-butanol. At the moment, the reasons are not clear. More work has got to be carried out to understand the role of different polar and non-polar molecules at the reaction interface with Sn<sup>4+</sup> as the active species.

Table 6  
Effect of different solvents in ethylbenzene oxidation <sup>a</sup>

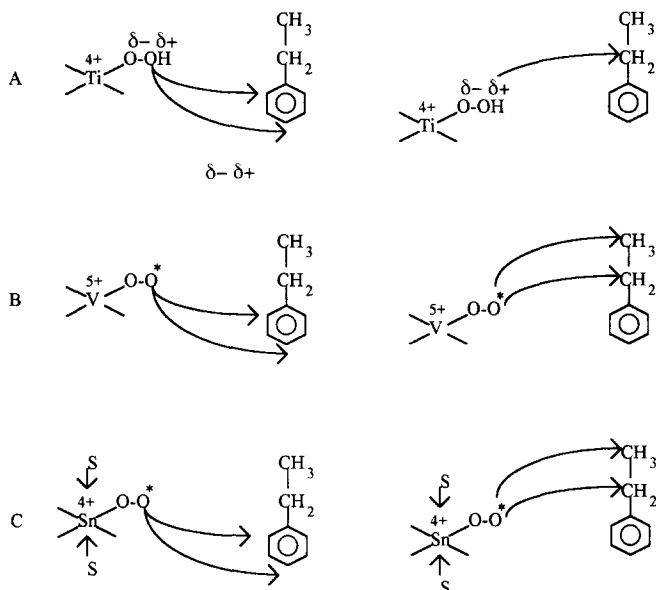
Solvent	Acetonitrile	<i>tert</i> -Butanol	Acetone	Water
TON	24.6	20.9	8.8	27.7
H <sub>2</sub> O <sub>2</sub> selectivity (mol.%)	56.4	48.4	19.8	62.1
<i>Product distribution (mol.%)</i>				
1-Phenylethanol	15.1	15.5	16.5	14.0
Acetophenone	57.4	58.6	57.0	53.8
2-Phenylethanol	0.7	1.6	Nd <sup>b</sup>	0.3
2-Phenylethanal	1.8	2.7	Nd	1.7
<i>o</i> -Hydroxy-EB	10.3	8.9	10.7	13.0
<i>p</i> -Hydroxy-EB	12.0	9.5	12.3	15.1
Others	2.5	3.2	3.5	2.1

<sup>a</sup> Catalyst: Sn-Si1-1 (Si/Sn = 70); the reactions were carried out at reflux temperatures in each solvent. Other conditions are as given in Table 1.

<sup>b</sup> Not detected.

### 3.8. Reaction scheme

Based on our earlier understanding the reactive peroxy intermediates of Ti, V and Sn ions formed in the presence of  $\text{H}_2\text{O}_2$  within the silicalite structure [16], the following key mechanistic steps in the oxidation of ethylbenzene can be envisaged.



In the above scheme, the hydroxylation follows mainly an ionic mechanism on TS-1 (A), where  $\text{Ti}^{4+}$  ions are isomorphously substituted in the silicalite-1 structure. With vanadium silicates (VS-1 and VS-2), we have earlier proposed a peroxy radical intermediate capable of the side chain oxidation in aromatic substrates and oxyfunctionalization of primary carbon atoms in alkane oxidation [17,18]. The formation of 2-phenylethanol and 2-phenylacetaldehyde (B) is in accordance with the earlier observation and the possible reaction pathway involving the  $\text{V}^{5+}$  and  $\text{V}^{4+}$  redox system [18]. With Sn-Sil-1, a peroxy radical ion may be the intermediate [14] (C). The formation of such an intermediate and its ability to attack the carbon of the substrate (either in aromatic hydroxylation or in side chain oxidation) is influenced to a great extent by the solvent molecules (S). These solvent molecules tend to coordinate strongly or weakly with  $\text{Sn}^{4+}$  depending on the donor/acceptor properties of the solvent, thereby changing the coordination around  $\text{Sn}^{4+}$  from a four- to six-fold one. The  $\text{Sn}^{4+}$  species with a larger ionic size (than  $\text{Si}^{4+}$ ) are probably more stable in the octahedral coordination and present as a part of the defect silanol groups. These

Sn-Sil-1 samples are also thermally stable, do not leach out Sn in the reaction medium and can be re-used a number of times without much loss in activity.

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