Hydroxylation of phenol over Sn–silicalite-1 molecular sieve: solvent effects

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Abstract

Tin–silicalite-1 (MFI) prepared by hydrothermal synthesis has been used as catalyst in the hydroxylation of phenol with aqueous H_2O_2. Isolated Sn^{4+} ions which are probably attached to the defect silanols are active in this reaction. At optimum conditions, a H_2O_2 efficiency of 70% and a ortho to para product ratio of 1.6 have been achieved. The solvent used has a strong influence on the activity. The UV–Vis spectral studies indicate that acetone and acetonitrile probably coordinate strongly with Sn^{4+} centers preventing the solvolysis of the Si–O–Sn units and the formation of peroxo intermediate. Methanol probably causes the cleavage of Si–O–Sn bond to form Si–OH and Sn–OMe species. Water was found to be an efficient solvent. The formation of EPR active radical ion in presence of H_2O_2 and H_2O and its attenuation in presence of acetone, acetonitrile and methanol support the above conclusion.

1. Introduction

Subsequent to the announcement of the synthesis of titanosilicate molecular sieve, TS-1 [1] and its application in the commercial production of dihydroxybenzenes from phenol using aqueous H_2O_2 by Enichem [2], several reports on the possible use of other metallosilicate molecular sieves in the hydroxylation of phenol have appeared to take advantage of the shape-selective oxidative property of these molecular sieves. These include TS-2 [3], vanadium silicates, VS-1 and VS-2 [4,5], Ge–silicalite [6], Zr- and Sn-containing zeosilicates [7] and Sn–silicalites [8,9]. With all these catalysts the H_2O_2 efficiency for the forma-

tion of dihydroxybenzenes was found to be lower and the product *ortho* to *para* ratio much higher than with TS-1. Except in the case of carefully synthesized TS-1, the isomorphous substitution of Si^{4+} by other metal cations within the oxygen framework of MFI or MEL has not been unequivocally established. It is possible that isolated and well-dispersed M^{4+} ions in the silicalite network which are capable of forming peroxo intermediates with H_2O_2 are active in the oxidation reactions and that the resulting *ortho/para* product ratios depend on their location, either on the external surface or within the channels of molecular sieves [9,10].

Substitution of tin for aluminium or silicon in molecular sieves has been attempted both by post synthesis procedures [11–14] and by hydrother-

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mal crystallization [7,15,16]. The resulting materials have interesting properties [15–17]. The synthesis of stannosilicates of novel structures having alkali metals and Al or Ga, where Sn ions are octahedrally coordinated has been claimed by Exxon [16]. The hydrothermal synthesis of Al-free, Sn- or Zr-containing MFI silicalites and their use in the hydroxylation of phenol and phenol ethers are described in a recent patent [7]. However, no details of the location and environment of Sn^{4+} ions in Sn–MFI are given. In our earlier reports on Sn-containing silicalite-1 [8] and Sn–MEL-silicalite[9], we have suggested that the Sn^{4+} ions are probably incorporated at or very close to the defect silanol sites and that they assume octahedral coordination. The hydroxylation of phenol to dihydroxy benzenes catalysed by these Sn–silicalites was demonstrated in these reports [8,9]. A complete description of the reaction in a batch reactor and the influence of various reaction parameters, particularly the influence of different solvents on the activity and product distribution are presented here. Based on our present understanding of the location and environment of Sn^{4+} ions in these samples, an attempt is made to explain the solvent effects from the UV–Vis DR spectral observations of the sample in presence of different solvent molecules.

2. Experimental

The tin-containing molecular sieves with MFI structure (Sn–Sil-1) with different Si/Sn ratios were synthesized hydrothermally using tetraethyl orthosilicate (TEOS) (Aldrich, 99%) as the Si source and $SnCl_4 \cdot 5H_2O$ (Loba Chemie, 99%) as the tin source. Tetrapropyl ammonium hydroxide (20% aqueous solution prepared at our laboratory starting from tripropylamine and having less than 5 ppm of Na^+ and K^+ impurities) was used as the organic base. The details of the synthesis and characterization of Sn–Sil-1 samples are given in Ref. [8]. The samples were calcined at 773 K for 16 h. The composition and the physico-chemical properties of the samples are given in Table 1. These samples were of fairly uniform (0.2–0.3 μm) size as seen by SEM. For comparison, a silicalite-1 (Sil-1) and a Sil-1 impregnated with Sn (through $SnCl_4$ solution followed by calcination) to give Si/Sn = 50 were prepared. An amorphous Sn–silica gel (Si/Sn = 70) was also prepared by mixing thoroughly under stirring a solution of $SnCl_4$ with TEOS, drying and calcining the resultant material at 773 K.

The hydroxylation of phenol was carried out batchwise in a (100 ml capacity) glass vessel fitted with a mechanical stirrer, a condenser and a

Table 1
Sample composition and physico-chemical characteristics

Sample	Si/Sn. mole ratio		Av. particle size [a] μm	Sorption capacity [b], wt%			Surface area $m^2 g^{-1}$	UV-Vis absorbance nm ($\pm$3)
	gel	product		H_2O	Cy-C_6	n-C_6		
Sn Sil-1	33	28	0.15	8.0	6.0	16.5	527	205, 285
Sn Sil-1	50	46	0.20	7.5	4.8	16.0	522	205
Sn Sil-1	70	65	0.25	7.2	4.6	15.2	516	205
Sn Sil-1	100	96	0.35	6.8	4.4	14.5	506	205
Sn Sil-1	133	84	0.40	6.5	4.2	13.5	500	205
Silicalite-1	–	–	2.0	4.8	4.0	12.5	384	–
Sn-impreg. Sil-1	–	50	2.0				375	285
Sn Sil-gel [c]	70	70	–	10.6	12.7	12.5	530	285
SnO_2	–	–	–	–	–	–	–	285

[a] From scanning electron micrograph.
[b] Gravimetric adsorption at $p/p_0 = 0.5$ and at 298 K.
[c] Amorphous sample for comparison (see Experimental).

feed pump (Sage instruments, USA) at 348 K using mainly water as solvent. Acetone, methanol or acetonitrile was used to study the influence of the solvent on the hydroxylation. Aqueous H_2O_2 (26%) was added (phenol to H_2O_2 mole ratio of 3) either in one lot or over a period of time after maintaining the temperature of the reaction. The reaction was carried out for 24 h. The products were taken out at the end of every 2 h interval, diluted with a solvent and analysed in a capillary GC (HP 5880) using a 50 m long silicon gum column. Invariably, the conversion of H_2O_2 was found to be almost 100% after 24 h. The activity data are presented in terms of turnover number and H_2O_2 yield (efficiency) for the formation of dihydroxybenzenes. The amount of tar formed was estimated independently by TG analysis of the products.

3. Results and discussion

3.1. The characteristics of the Sn–Sil-1 samples

The Sn–silicalite-1 samples used in this study are microporous, well-defined and crystalline materials. Detailed characterization of the samples by a variety of techniques has revealed [8] that (a) during hydrothermal synthesis the interaction between Si–OH and Sn–OH monomers leads to the formation of Si–O–Sn linkages in the calcined samples (FTIR spectra); (b) the oxidation state of tin is 4+ both on the surface and in the bulk (XPS and chemical analysis); (c) a part of Sn^{4+} ions are probably in the edge-sharing or corner-sharing positions of the silicalite-1 structure (XRD, unit cell expansion with Sn^{4+} content); and that (d) the Sn^{4+} ions which are probably close to the defect silanol groups are octahedrally coordinated (^{119}Sn MAS-NMR). It is possible that Sn^{4+} grafted at the defect sites may also affect the unit cell parameters. The UV–Vis diffuse reflectance spectra of completely dehydrated samples, however, show absorption at 205 ± 3 nm (Fig. 1) only. For comparison, the spectra of pure SnO_2, Sn-impregnated silicalite-1
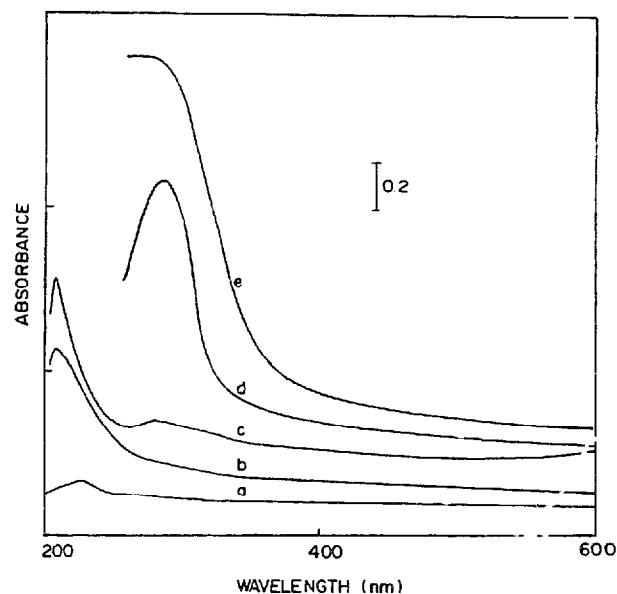

Fig. 1. Diffuse reflectance UV–Vis spectra of (a) silicalite-1; (b) Sn–Sil-1 (Si/Sn = 65); (c) Sn–Sil-1 (Si/Sn = 33); (d) Sn-impregnated silicalite-1 and (e) SnO_2.

are also included in Fig. 1. Both Sn-impregnated Sil-1 and SnO_2 show strong absorption at 283 ± 3 nm which may be assigned to hexacoordinated polymeric Sn–O–Sn type of species. This band in addition to the one at 205 nm has been observed in some of the Sn–Sil-1 samples having a Si/Sn mole ratio of less than 40 (Fig. 1, Table 1) or when the synthesis procedure (sequence of mixing of TEOS and $SnCl_4$ during the gel formation) is changed. For catalytic reactions, Sn–Sil-1 samples with Si/Sn > 45 have been used.

The DR spectral observations could be interpreted in terms of Sn^{4+} in Td configuration in the silicate structure. However, larger cations such as Ti^{4+} and Sn^{4+} (compared to Si^{4+}) have a tendency to expand its coordination to a five- or six-fold one, on interaction with one or more ligands [18]. Evidence for the transformation of four-fold coordinated Ti into six-fold coordinated species has recently been reported by means of UV–Vis reflectance study [19]. The CT in Sn–Sil-1 is clearly distinguishable from that in pure SnO_2 and from the UV absorption in Sn-impregnated Sil-1 sample. It is possible to make a qualitative distinction between zeolitic-tin, occluded SnO_2 and bulk SnO_2 based on the UV–Vis DR spectra. The following structures representing Sn in lattice (a)

and edge-sharing positions (b) in Sn–Sil-1 may be proposed:

a   b
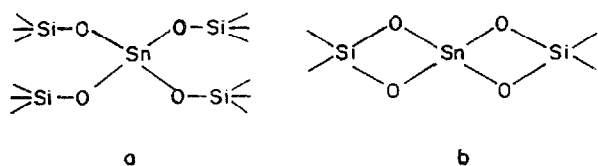
3.2. The hydroxylation of phenol

The course of the hydroxylation reaction over Sn–Sil-1 catalyst under three different modes of addition of aqueous H_2O_2 to the reaction mixture is shown in Fig. 2. The mode of addition did not influence much the phenol conversion, but a considerable difference was noticed in the product distribution. The rate of hydroxylation is much slower than observed with TS-1 [20]. Up to almost 2 h, the analysis of the product samples showed negligible conversion of phenol to catechol and hydroquinone. Such an induction period has been observed with acidic Ti–zeolites [21]. Our Sn–Sil-1 samples are mildly acidic (catalyse dehydration of cyclohexanol to cyclohexene). The lower activity of Sn–Sil-1 samples, in general, compared to that of TS-1 may be due to a combination of competitive adsorption of reactants and solvent molecules, self decomposition of H_2O_2 on the mildly acidic sites of Sn–Sil-1 and a slower rate of formation of the peroxo intermediates. Also, the stability of the peroxo species in the presence of a solvent probably plays an important role. Table 2 shows that addition of H_2O_2 in 1 h leads to a slightly better H_2O_2 selectivity, the ortho to para product ratio being about 1.6. The formation of the ortho isomer (catechol) is more when H_2O_2 was added in one lot and hence depends on the initial concentration of the peroxide. Since the surface composition (Si/Sn ratio) is similar to that in the bulk [8] and since the crystallite sizes of the Sn–Sil-1 samples are small, it is likely that the reaction takes place on the external surface of the crystals as well. Fig. 2 shows that in the beginning of the reaction, the product selectivity to p-benzoquinone (PBQ) is

high when the phenol conversion is very low (TON = 6.9) and goes down rapidly with time. In the beginning, the formation of catechol (CAT) and hydroquinone (HQ) is less but increases rapidly with further progress of the reaction and reaches a maximum after about 12 h. Millan et al. [22] have suggested that PBQ results from the fast oxidation of HQ in the reaction medium by the large excess of H_2O_2 in the beginning of the reaction. PBQ may act as an autocatalyst or an intermediate and cause the oxidation of H_2O_2 to O_2 forming HQ [22], which results in the low amount of formation of tar. On the basis of the above studies, all subsequent investigations were carried out up to 24 h with slow addition of H_2O_2 over a period of 1 h.

From the course of the hydroxylation reaction shown in Fig. 2, one might suspect that Sn^{4+} leached from the catalyst by H_2O_2 into the aqueous medium is catalytically active. However, at the end of the reaction we could estimate only traces (about 10 ppm) of Sn in the liquid phase. Also, it is noticed that after separation from the reaction mixture and subsequent calcination, the Sn–Sil-1 samples could be reused many times without significant loss in activity.

3.3. The influence of Sn concentration on hydroxylation

The hydroxylation of phenol did not take place in the absence of any catalyst. Under the conditions mentioned, Sil-1, Sn-impregnated Sil-1 and pure SnO_2 showed negligible activity in this reaction. The effect of Sn content of Sn–Sil-1 on the hydroxylation of phenol is illustrated from the data given in Table 3. It is clear that Sn^{4+} ions are the active species and that the conversion of phenol and H_2O_2 selectivity increase with increasing Sn content in the sample up to about 2.4 Sn per unit cell and then level off (Fig. 3 A). There is not much of a difference in the product distribution with the increase in the Sn content. The ortho/para product ratio remains almost similar at around 1.6 at the end of the reaction on all the Sn–Sil-1 samples (Table 3). These results show
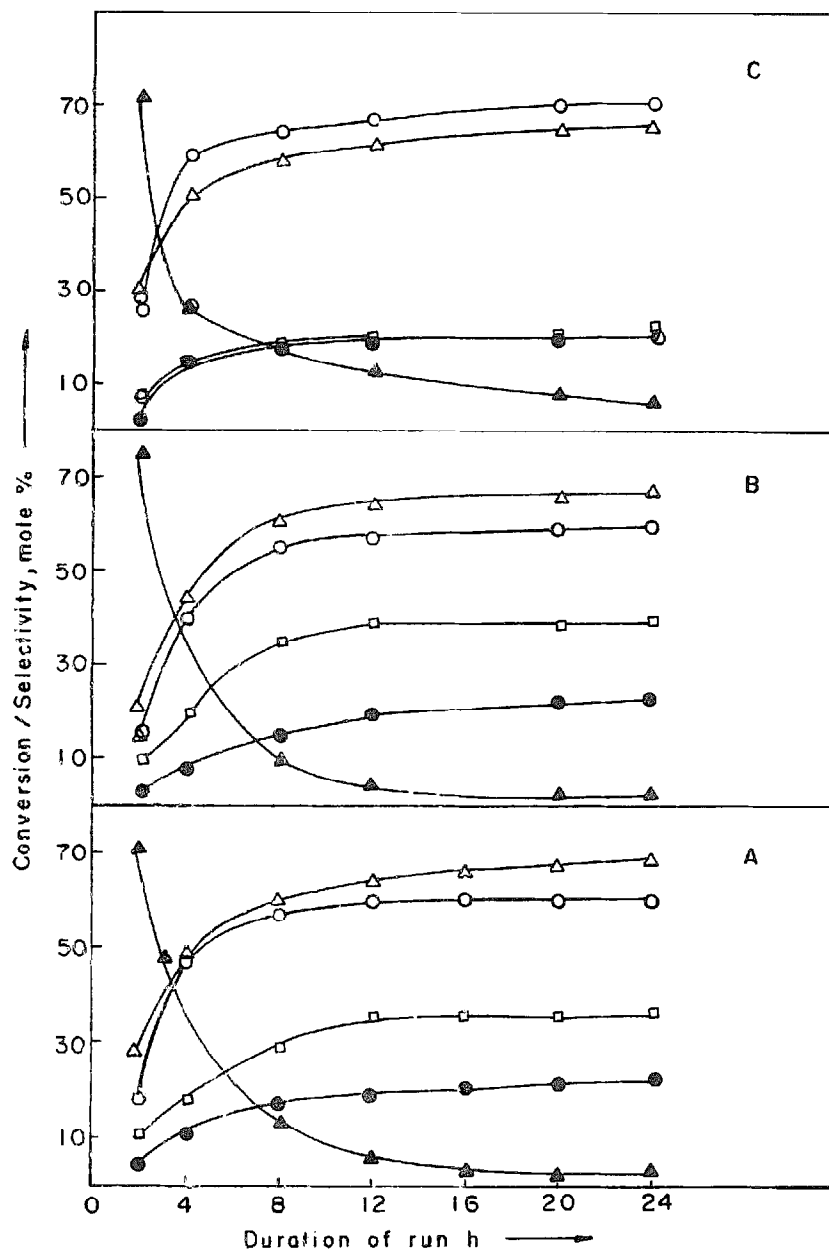
Fig. 2. The effect of mode of addition of aqueous H_2O_2 on the hydroxylation of phenol over Sn–silicalite-1 molecular sieve (Si/Sn mole ratio = 46) during 24 h of batch reaction at 348 K. A. Slow addition in 1 h; B. Slow addition in 6 h; and C. Addition in one lot. ● Phenol conversion; ▲ p-benzoquinone; □ hydroquinone; O catechol; and ▨ H_2O_2 efficiency.

that in all the samples the dispersion of the active Sn in the silicalite is fairly uniform and that any contribution from the external surface Sn species to the overall activity is constant. That the fairly well-dispersed Sn^{4+} ions are active in this reaction is seen from the results on amorphous Sn–silica sample which shows a H_2O_2 efficiency of 47% (Table 3). Since this sample is mostly mesoporous, a CAT to HQ ratio of 3 seems to be reasonable.

Further evidence to the role of Sn^{4+} in the sample is provided when the amount of the catalyst in the whole of the reaction mixture is varied. As seen from the data given in Table 4, with an increase in the catalyst to phenol ratio, the H_2O_2 yield increases and levels off at around 69 mole %. At low concentrations of the catalyst in the reaction mixture, the ortho to para product ratio is high and relatively more PBQ is found in the product as most of the reaction takes place on the

Table 2
Effect of H_2O_2 addition on the hydroxylation of phenol over Sn–Sil-1 [a]

Addition	H_2O_2 sel. [b] mole%	TON	Product distribution [c], mole%			
			PBQ	CAT	HQ	Tar [d]
1 h. slow	79.3	65.0	2.5	59.3	34.0	4.2
6 h. slow	77.2	63.5	1.5	57.3	38.2	3.0
one lot	75.8	60.6	4.0	68.8	22.2	5.0

[a] Reaction conditions: catalyst/phenol = 10 g mol^{-1} (Si/Sn = 46); phenol/H_2O_2 (mole) = 3 (26% aqueous solution); temperature = 348 K; solvent (water)/phenol = 20; reaction time = 24 h.
[b] H_2O_2 selectivity = mole% of H_2O_2 consumed in the formation of para-benzoquinone (PBQ), catechol (CAT) and hydroquinone (HQ) excluding tar.
[c] Break up (mole%) of products including tar.
[d] By independent TG analysis of the product.

external surface. Presumably, with the availability of additional catalyst up to a certain level, fresh active Sn sites (both external and within the channel) free of tar is responsible for the increased phenol conversion and stable product selectivity. The H_2O_2 is utilized in the formation of CAT and HQ, depleting its availability for further oxidation to quinone and tar. At still higher catalyst (Sn) concentrations, non-selective hydroxylations leading to other products restrict the peroxide efficiency to a maximum of about 69 mole% (Fig. 3 B). A H_2O_2 efficiency of less than 50% and a ortho to para product ratio of > 5 have been observed over a Sn–MFI (Si/Sn = 100) synthesized under fluoride medium [7].

3.4. The influence of solvents on hydroxylation

The influence of different solvents on the hydroxylation of phenol over Sn–Sil-1 is interesting and appears to be complex. In addition to water, we have used acetone, acetonitrile and methanol as solvent under similar conditions and the results are summarised in Table 5. Under the conditions given in Table 2, water appears to be the best of the four solvents studied. In methanol, the H_2O_2 yield (and hence the phenol conversion) is the lowest. In this respect, Sn–silicates are different from the titanosilicates (TS-1 and TS-2) which respond positively to different solvents

while shifting the selectivity between CAT and HQ [23,24], but are somewhat similar to vanadium silicate molecular sieves used in the hydroxylation of phenol [5]. In both acetone and methanol, vanadium silicates have been found to give very poor conversions. With TS-1, a high H_2O_2 efficiency (of the order of 80%) has been observed in methanol as solvent and acetone could be gainfully used to prevent accumulation of tar on the surface [24]. The solvents, however, depending on their nature may have a profound influence on the local environment of the active cation sites in these metallosilicates. Indeed, switching over from biphasic to triphasic conditions in such hydroxylation reactions is reported to cause an increase in the rate by several folds [25].

The observed difference between TS-1 and Sn–Sil-1 on the influence of different solvents on activity probably lies in the electrophilic behaviour of the isolated cation centers in the silicalite structure. Sn^{4+} species in Sn–Sil-1 samples are more acidic than Ti^{4+} ions in TS-1, as noticed from model cyclohexanol dehydration reaction [26]. Also, due to larger ionic radius, Sn^{4+} ions may assume higher coordination more easily than Ti^{4+} in order to relieve the strain within the structure. As expected for a coordinative interaction, the adsorption energy is likely to be small. We have tried to look into the coordination of Sn^{4+}

Table 3
Effect of Sn content of Sn–Sil-1 [a]

Si/Sn mole ratio	H_2O_2 sel., mole%	TON	Product distribution, mol%		
			PBQ	CAT	HQ
28	72.0	42.8	2.6	59.9	37.5
46	69.3	65.5	2.6	61.9	35.5
65	66.0	87.1	2.4	61.7	35.9
84	51.5	87.2	2.2	63.1	34.7
96	46.9	90.5	2.1	62.8	35.1
50 [b]	3.0	3.2	nd [d]	70.0	30.0
70 [c]	46.8	67.5	0.6	74.6	24.8
SnO_2	1.5	1.6	nd	65.0	35.0

[a] Reaction conditions and other details are as given in Table 2.
[b] Sn-impregnated silicalite-1
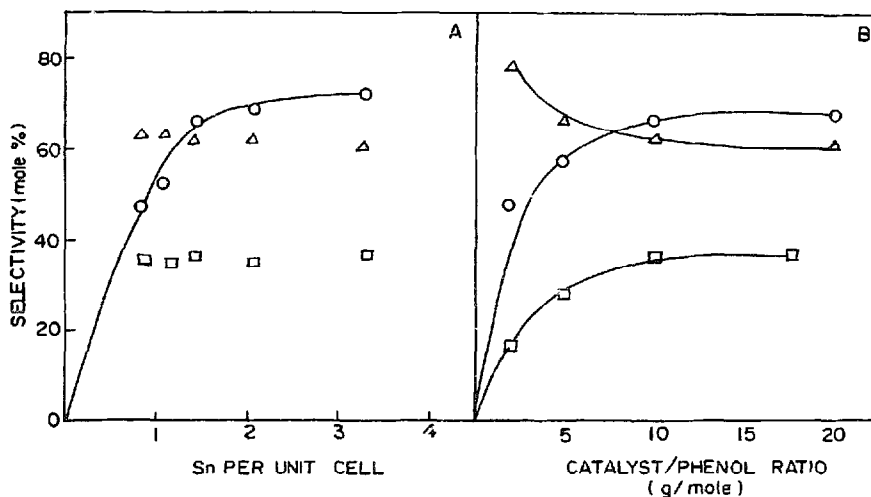[c] Sn–silica amorphous material.
[d] Not detected.

Fig. 3. Influence of Sn content in MFI–silicalite (A) and amount of catalyst (B) on H_2O_2 efficiency in the phenol hydroxylation reaction. ○ H_2O_2 efficiency; △ catechol; and □ hydroquinone.

Table 4
Effect of catalyst concentration [a] (Si/Sn mole ratio = 65)

Catalyst/PhOH g mol^{-1}	H_2O_2 sel, mole%	TON	Product distribution, mole%		
			PBQ	CAT	HQ
2	47.7	303.9	6.0	77.4	16.6
5	57.5	145.7	6.4	66.1	27.5
10	66.0	87.1	2.4	61.7	35.9
20	68.5	45.4	1.9	61.3	36.8

[a]Reaction conditions and other details are as given in Table 2.

Table 5
Effect of solvent on hydroxylation of phenol [a] (Si/Sn mole ratio = 65)

Solvent	H_2O_2 sel., mole%	TON	Product distribution, mole%		
			PBQ	CAT	HQ
Water	66.0	87.1	2.4	61.7	35.9
Acetonitrile	36.5	48.6	1.4	53.1	45.5
Acetone	15.3	20.2	2.1	65.2	32.7
Methanol	12.2	11.5	42.9	57.1	nd [b]

[a] Reaction condition and other details are as given in Table 2.
[b] Not detected.

species under the influence of the different solvent molecules. As mentioned earlier, the DR spectra of dehydrated Sn–Sil-1 samples show a single absorption at 205 ± 3 nm. On hydration or on treatment with solvents used in the phenol hydroxylation reaction, a shift in the UV–visible band to higher wavelength has been observed. After adsorption of H_2O, acetone, acetonitrile or methanol to a Sn–Sil-1 (100) sample, two additional peaks appeared in the DR spectrum. One at around 221 ± 3 nm is assigned to penta coordinated Sn species and the other at 255 ± 5 nm corresponds to hexa coordination around Sn species. The formation of a penta coordinated Sn having trigonal bipyramidal structure upon hydrolysis of four coordinated R_3SnX (X = Cl, Br or I) has earlier been reported by Swisher et al. [27]. The peak at 255 ± 5 nm is more pronounced with acetone than with other solvents. Qualitatively, the intensity of absorbance at 255 ± 5 nm decreases in the order, acetone > water > acetonitrile > methanol.

The tendency of the basic solvents to form coordinate bonds with acid center or the metal ion depends mainly on three factors, viz., the basicity or donor ability, the electrophilic behaviour and the polarity of the solvent. Gutmann [28] quantified the basicity in terms of donor number (DN) and the electrophilic behaviour as acceptor number (AN). With increasing AN, the nucleophilicity of the solvent reduces. The polarity is expressed in terms of e/e_0 where e and e_0 are the permittivity or dielectric constant of medium and vacuum, respectively. For the four solvents, these parameters are listed in Table 6. An increase in the DN to AN ratio will favour the formation of

Table 6
Physical properties of the solvents used [a]

Solvent	Donor number (DN)	Acceptor number (AN)	Polarity e/e_0	DN/AN
Acetone	17.0	12.5	20.7	1.36
Acetonitrile	14.1	19.3	36.0	0.73
Methanol	20.0	41.3	32.6	0.48
Water	18.0	54.8	81.7	0.33

[a] Data taken from Ref. [29]; see text for definitions.

coordination bond of a solvent with metal center, which for the four solvents is in the order, acetone > acetonitrile > methanol > water. This trend agrees with the UV-vis spectral results involving Sn^{4+} except in the case of water. This may be due to the high polarity (three times higher than other solvents) of water. The six-fold coordination of Sn in presence of solvent molecules (c, d and e) may be depicted as shown below:

c   d   e
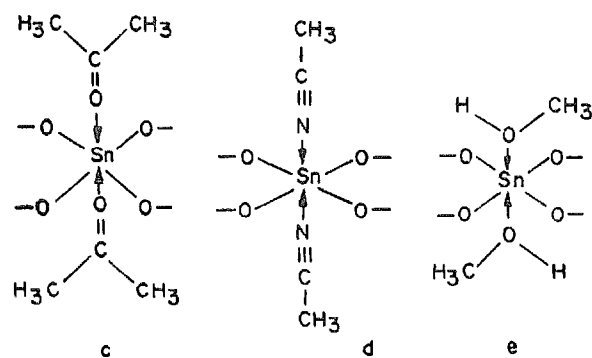
While stabilizing the active Sn site more effectively, acetone probably reduces the tendency of solvolysis of (c) type species in presence of trace amount of water (Sn-O-Si → Sn-OH + Si-OH) to form species (f). Consequently, the formation of hydroperoxy species like (g) from (f) in presence of H$_2$O$_2$ is not much favoured.

f   g
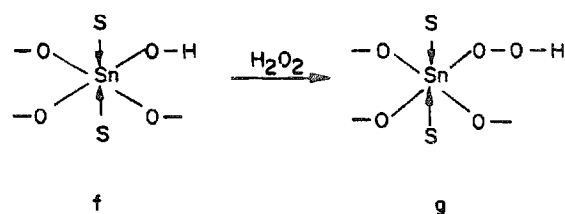
In addition, the steric effect may make the species (c) less sensitive to solvolysis. Acetonitrile is rel-

atively less prone to form a strong coordination bond with Sn^{4+} and hence is more effective than acetone in the oxidation reaction in presence of H$_2$O$_2$. As indicated, water is the best solvent because it is sufficiently polar to interact with Si-O-Sn species to give rise to Sn-O-H, which then forms the peroxo intermediate with H$_2$O$_2$. Methanol coordinates weakly with Sn but inhibits the oxidation reaction strongly. Being a protic solvent like water, methanol probably causes the cleavage of Si-O-Sn bond to form Si-OH and Sn-OMe, structures (h) or (i), which cannot react with H$_2$O$_2$ to form the Sn-hydroperoxide complex.

h

i
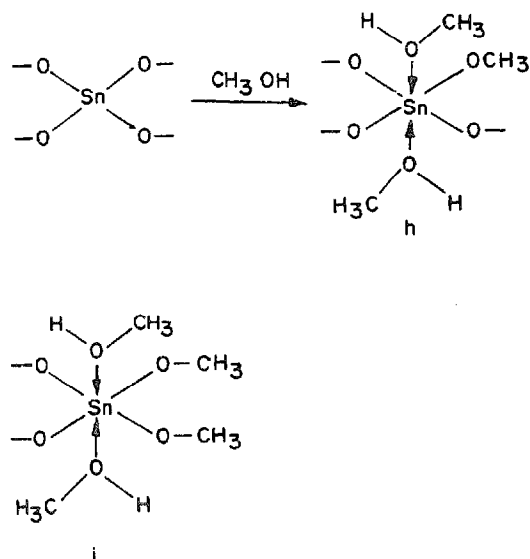
The Sn-O bonds in stannosiloxanes, for example, are highly reactive and undergo heterolytic cleavage in presence of water, alcohol, amine and mercaptans much more readily than Si-O bond owing to its higher polarity and lower π bond character [29]. Since the reaction takes place on the external surface also, methanol is likely to interact fast with surface -Sn-OH groups to form inactive - Sn-OMe species.

Some evidence for the formation of peroxide radical ion is provided by ESR spectral observations. The ESR spectra were recorded in a Bruker 200 D spectrometer at room temperature using a quartz cell wherein the catalyst was placed in presence of a liquid phase H$_2$O$_2$ and one of the solvents. In presence of H$_2$O$_2$/H$_2$O, both TS-1 and Sn-Sil-1 samples (Si/M = 100) give rise to an
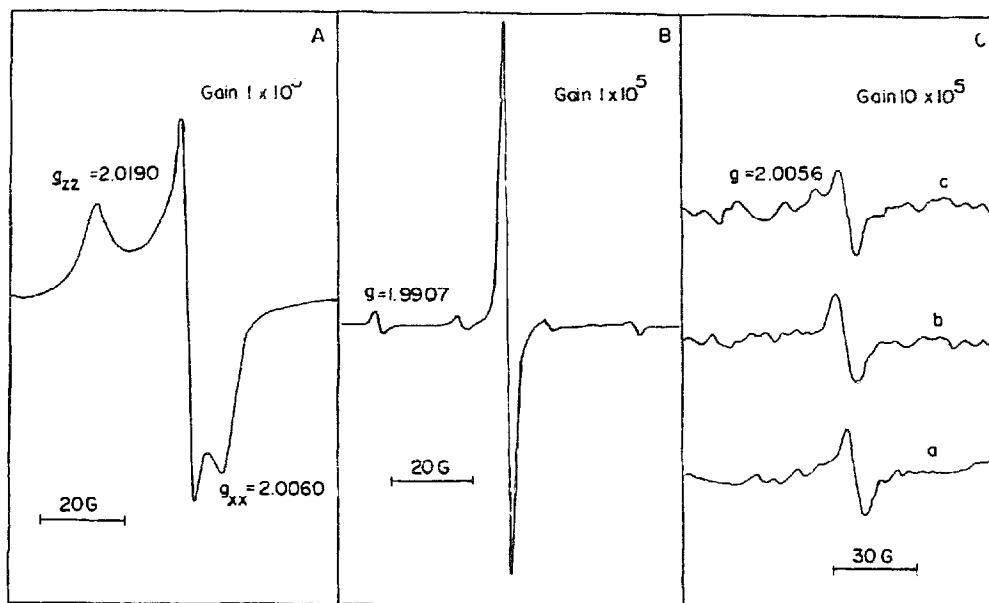
Fig. 4. EPR spectra of TS-1 and Sn–Sil-1 samples in presence of H_2O_2 and H_2O (A and B, respectively) and Sn–Sil-1 in presence of H_2O_2 and other solvents (C) acetonitrile (a), acetone (b) and methanol (c).

intense and anisotropic signal (Fig. 4 A and B). Geobaldo et al. [30] have earlier observed for TS-1 an intense EPR spectrum, where the principal g vectors (g_{zz} = 2.0238, g_{yy} = 2.0099 and g_{xx} = 2.0030) were associated with the formation of superoxide radical ion of Ti. A similar Sn–peroxide radical ion is most probably an intermediate in Sn–silicates. However, the difference between the two EPR signals (Fig. 4 A and B) may indicate significant difference in the type of intermediates that are formed with TS-1 and Sn–Sil-1 and hence the mechanism of oxidation on these two types of metallosilicates. Although detailed EPR studies on Sn–silicates are still in progress, there is an indication that the formation of the peroxide radical is inhibited in presence of other solvents, such as acetone, methanol and acetonitrile as seen from the attenuated EPR signals shown in Fig. 4 C. This observation lends support to our argument that the solvent molecules while stabilizing Sn^{4+} ions in six-fold coordination influence the rate of solvolysis of Sn–O–Si units in the silicate structure and subsequent formation of the peroxo species in presence of H_2O_2 to different extents.

4. Conclusions

Sn-containing MFI silicalites (Si/Sn > 30) have been found to be active in the hydroxylation of phenol using dilute H_2O_2 as oxidant. A good correlation between the activity and Sn content up to about 2.4 Sn per unit cell in the sample and a fairly stable product distribution corresponding to an *ortho* to *para* product ratio of 1.6 under optimum conditions suggest that isolated Sn^{4+} ions which are uniformly distributed on the external surface as well as within the channels are the active centers. Among different solvents used, water was found to be the most efficient. The isolated Sn^{4+} centers in Td configuration tend to coordinate strongly with solvent molecules such as acetone and acetonitrile and probably reduce the rate of solvolysis of the –(Si–O–Sn)– units and hence the formation of peroxo intermediate with H_2O_2. This is supported by EPR observations on the formation of peroxo radical ion.

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