

Hydroxylation of phenol over TS-2, a titanium silicate molecular sieve

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Abstract

The influence of different process parameters on the hydroxylation of phenol with H_2O_2 over the titanium silicate molecular sieve TS-2 has been investigated. Apart from the primary products *vis.*, *p*- and *o*-dihydroxybenzenes, the corresponding quinones are also formed. Higher Ti contents in the catalyst (TS-2) and higher catalyst concentrations lower the formation of the secondary oxidation products. Solvents have an influence on the relative amounts of the two dihydroxybenzenes in the product. H_2O_2 efficiency of up to 74% is obtainable at ~28% phenol conversion to dihydroxybenzenes.

Introduction

The titanium silicate molecular sieve, TS-1, [1, 2] with an MFI structure has been reported to catalyze a number of reactions, such as hydroxylation of aromatics [3, 4], selective oxidation of alkanes [5], ammoximation of cyclohexanone [6] and rearrangement of cyclohexanone oxime [7]. A more recent discovery is the titanium silicate molecular sieve, TS-2 [8, 9], which has an MEL structure. This material has also been reported to catalyze the ammoximation of cyclohexanone [10] and the selective oxidation of n-hexane [11].

The first commercial process utilizing titanium silicate (TS-1) as a catalyst was the hydroxylation of phenol to hydroquinone and catechol, introduced by Enichem, Italy [2, 12]. Some aspects of the TS-1-catalyzed hydroxylation reaction have been revealed recently [2, 12]. We have investigated the reaction using TS-2 as the catalyst, and present the results in this paper.

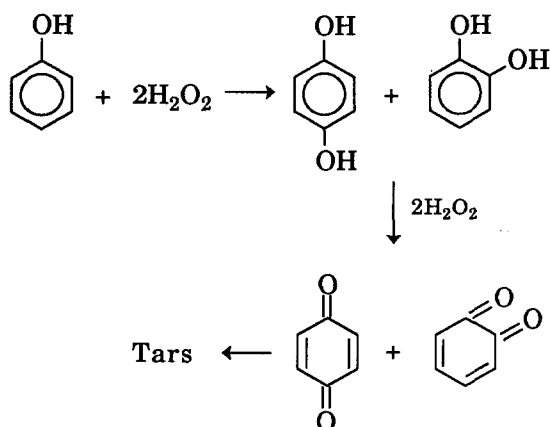
Experimental

The titanium silicate molecular sieve with MEL structure (TS-2) was synthesized by mixing tetrabutylammonium hydroxide, tetraethylorthosilicate and titanium butoxide and autoclaving the mixture at 443 K for 48 h. The details of the synthesis and characterization of this new titanium silicate have already been reported elsewhere [8, 9]. The as-synthesized TS-2 was filtered, washed, dried and calcined in dry air for 16 h at 823 K.

The catalytic runs were carried out batchwise in a four-necked glass flask (200 ml capacity) fitted with a mechanical stirrer, condenser, feed pump (Sage Instruments, USA) and a septum. The temperature of the reaction vessel was maintained using an oil bath. In a standard run, 10 g phenol, 20 g solvent and 1 g catalyst (particle size <300 mesh) were placed in the reaction vessel. The desired temperature was obtained before adding 4.6 g H_2O_2 (26% aqueous solution) through a feed pump. The products (0.2 ml) were taken out periodically by a microlitre syringe and diluted with the solvent before analysis by high resolution capillary GC (HP 5880).

Results and discussion

Though the major reaction is the hydroxylation of phenol, other side reactions also take place. These are the oxidation of the dihydroxybenzenes to quinones, the further oxidation of the quinones into tar and the decomposition of H_2O_2 . These reactions are shown below.



Like earlier reports [12], our studies also did not show the formation of *m*-dihydroxybenzene (resorcinol). We will now discuss the influence of various parameters on the above reactions.

Mode of addition of H_2O_2

As the desired dihydroxybenzenes are intermediates in a sequence of reactions (shown above) and H_2O_2 takes part in both their formation and destruction, its (H_2O_2) concentration in the reaction medium is an important factor determining the yield of the hydroxybenzenes. In other words, the mode of H_2O_2 addition could be important.

Three different modes of H_2O_2 addition were investigated: (1) addition of all H_2O_2 in one lot at the beginning of the reaction (Fig. 1(A)), (2) addition over a period of 1 h (Fig. 1(B)) and (3) slow addition over a period of 6 h (Fig. 1(C)).

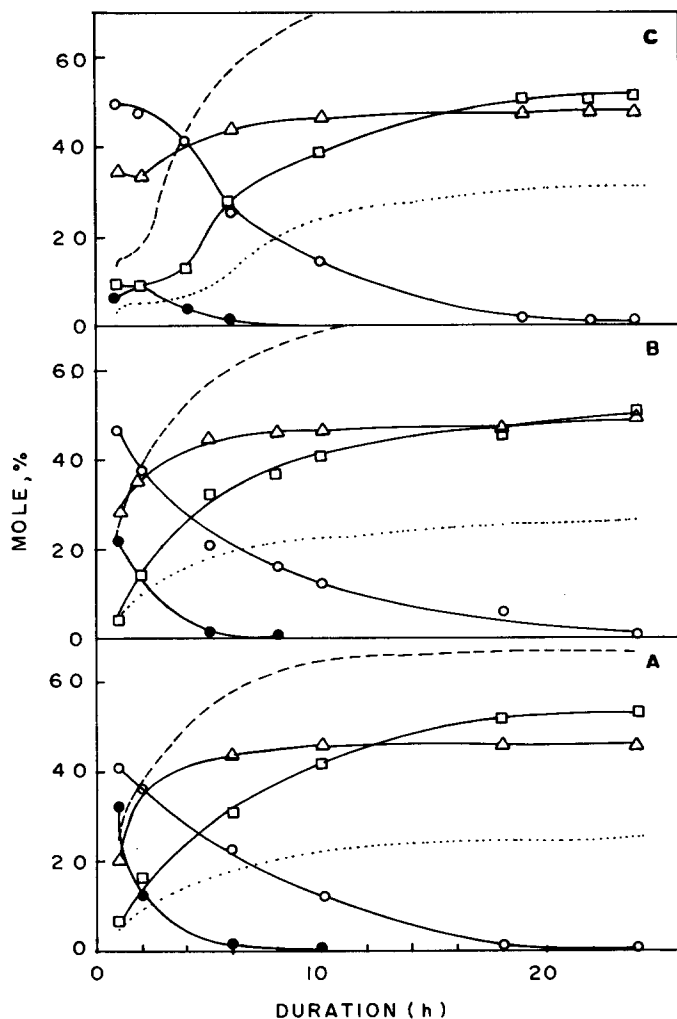


Fig. 1. Influence of mode of addition of H_2O_2 on product distribution. (A): Addition in one lot; (B): addition over 1 h; (C): addition over 6 h. (●) OBQ; (○) PBQ; (△) catechol; (□) hydroquinone; (---) H_2O_2 selectivity; (·····) phenol conversion. Reaction conditions, H_2O_2 selectivity and phenol conversion as defined in Table 1.

Studies were carried out at excess phenol conditions (phenol: H_2O_2 mole ratio = 3). In the early stages of the runs, the concentration of the secondary products (*o*-benzoquinone, OBQ and *p*-benzoquinone, PBQ) are considerably different in the three cases. However, after ~12 h, the product pattern, conversion levels and H_2O_2 selectivities are all only marginally different. The maximum H_2O_2 selectivity (defined as the mol.% of H_2O_2 consumed in the formation of dihydroxybenzenes and quinones) is 70% in the case of 1 h and 6 h additions, while it is slightly lower (66%) when the H_2O_2 is added in one lot. In the earlier stages of the run OBQ and PBQ are formed in

considerable amounts, though these react further to become tarry products (not estimated). OBQ is more reactive and disappears more rapidly than PBQ. It is also found that the sum of the *o*-products (catechol+OBQ) is more than the sum of the *p*-products (hydroquinone+PBQ) when H_2O_2 is in excess (added in one lot; see below).

Mode of addition:	Rapid	Slow	
	one lot	1 h	6 h
<i>o</i> - <i>p</i> -products ratio			
at 1 h	1.37	0.94	0.69
10 h	0.85	0.86	0.87

This suggests that hydroxylation at the *o*-position is more dependent on the concentration of H_2O_2 than is hydroxylation at the *p*-position.

The yields (conversion \times fraction in products) of OBQ and PBQ go through maxima with the duration of run, the maximum being reached earlier by OBQ. The maximum amount of quinones in the product is also higher at higher H_2O_2 levels in the system (see also later section on influence of H_2O_2 concentration).

Separate experiments were carried out to study the reaction of pure hydroquinone and catechol with H_2O_2 in the presence and absence of TS-2. These studies revealed the following:

- (1) Both dihydroxybenzenes are oxidized by H_2O_2 in the absence of any catalyst, catechol oxidation being more rapid.
- (2) TS-2 increases the rate of oxidation of the dihydroxybenzenes by H_2O_2 .
- (3) Tar formation takes place even in the absence of the catalyst, and the influence of the catalyst on tar formation is not clear.

The above studies (Fig. 1) have established that slow addition of H_2O_2 is preferable to addition in one lot. All further studies were therefore carried out with slow (1 h) addition of H_2O_2 .

Influence of Ti content of TS-2

The hydroxylation of phenol did not take place in the absence of catalyst. Negligible conversion was recorded in the presence of silicalite-2, TiO_2 and an amorphous mixture of TiO_2 and SiO_2 . The introduction of Ti into the silicalite lattice (TS-2), however, catalyzed the reaction, even at very low Ti contents. The influence of Ti content (of TS-2) on the reaction is presented in Table 1. The data were obtained after 24 h. Though the ratio of catechol to hydroquinone is not significantly affected by the Ti content, both conversion and selectivity increase with increasing Ti content.

Effect of catalyst concentration

Use of larger amounts of TS-2 increases conversion and selectivity and also lowers the amount of quinones in the product (Table 2). In fact, at a catalyst concentration of 20 g mol^{-1} of phenol, neither OBQ nor PBQ is

TABLE 1

Effect of titanium content of TS-2 on hydroxylation of phenol^a

Si/Ti ratio	H ₂ O ₂ selectivity ^b (%)	Phenol conversion ^c	Product distribution (mol.%) ^d		
			PBQ	CAT	HQ
29	70.0	26.8	0.9	49.3	49.8
48	64.0	24.3	1.1	49.7	49.2
70	51.1	19.6	1.0	49.5	49.5
124	39.2	15.0	0.5	50.3	49.2

^aReaction conditions: catalyst = 10 g mol⁻¹ phenol [TS-2 (Si/Ti) = 29]; phenol/H₂O₂ (mole) = 3.0; H₂O₂: 26% aqueous solution; temp. = 342 K; solvent = acetone (20 ml); reaction time = 24 h.

$${}^b\text{H}_2\text{O}_2 \text{ selectivity} = \frac{\text{H}_2\text{O}_2 \text{ (mols) consumed in formation of dihydroxybenzenes (DHB) and quinones}}{\text{total H}_2\text{O}_2 \text{ (mols) added}} \times 100$$

^cPhenol converted for formation of DHB and quinones.

^b, ^cConsumption for tar formation excluded.

^dBreak-down (in mol.%) of products excluding tars. PBQ = *p*-benzoquinone; CAT = catechol; HQ = hydroquinone.

TABLE 2

Effect of catalyst amount^a

Catalyst amount (g mol ⁻¹ phenol)	H ₂ O ₂ selectivity ^b	Phenol conversion ^c	Product distribution (mol.%) ^d			
			OBQ	PBQ	CAT	HQ
2	23.0	4.6	25.5	42.4	22.8	9.3
5	47.8	14.8	6.5	22.1	41.4	30.0
10	70.0	26.8	0.0	0.9	49.3	49.8
20	72.3	27.2	0.0	0.0	48.4	51.6

^aReaction conditions as in Table 1, except amount of catalyst varied.

^b, ^c, ^d As in Table 1.

present in the product, while large amounts of OBQ and PBQ are present at and below a catalyst concentration of 5 g mol⁻¹ of phenol. Figure 2(A) presents the results (at different run durations) at a catalyst loading of 20 g mol⁻¹ phenol. Corresponding data for a catalyst loading of 10 g mol⁻¹ phenol are reported in Fig. 1(B). Comparing the two figures, we note that the yield of quinones decreases more rapidly with time when more catalyst is present. This is due to the faster rate of conversion of phenol to dihydroxybenzenes at higher catalyst loadings, depleting the H₂O₂ available for further oxidation (quinones and tar). Consequently, the H₂O₂ selectivity is also higher (74%) at 20 g than at 10 g catalyst loading (70%).

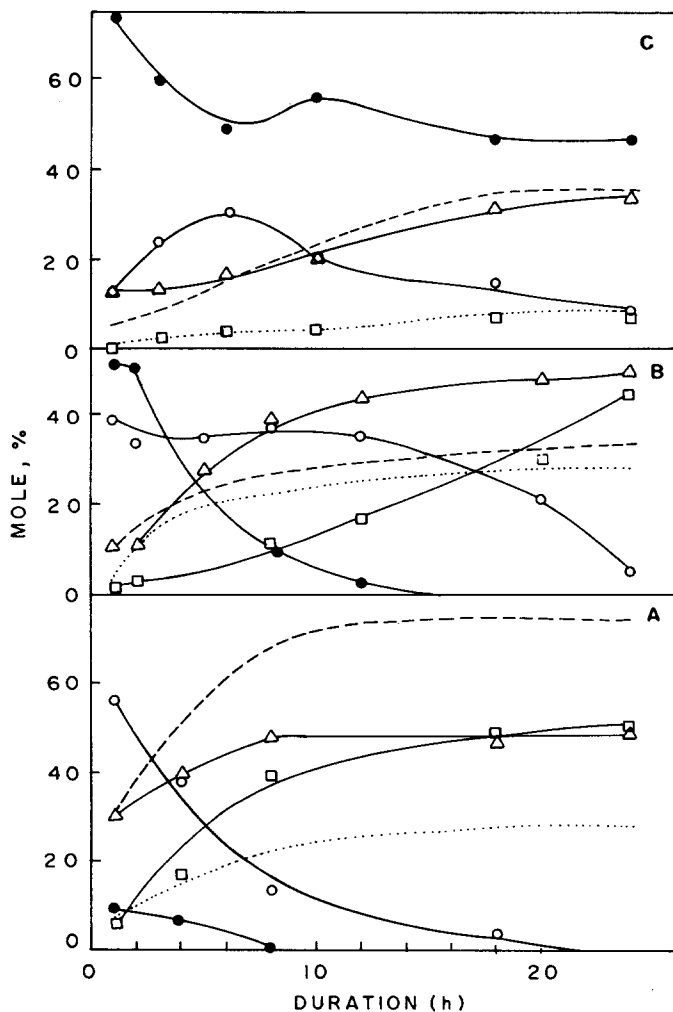


Fig. 2. Influence of duration of run on product distribution. (A) Higher catalyst content (20 g mol^{-1} phenol), (B) longer duration of H_2O_2 addition (phenol: H_2O_2 mole ratio = 1), (C) lower reaction temperature (310 K), (●) OBQ; (○) PBQ; (△) catechol; (□) hydroquinone; (---) H_2O_2 selectivity; (.....) phenol conversion; Conditions: Mode of H_2O_2 addition = 1 h, acetone = 20 ml, (A) Temp. (K) = 342; phenol: H_2O_2 (molar) ratio = 3; (B) Temp. (K) = 342; phenol: H_2O_2 (molar) ratio = 1; (C) Temp. (K) = 310; phenol: H_2O_2 (molar) ratio = 3.

Influence of H_2O_2 concentration

The results show (Table 3) that for maximum useful utilization of H_2O_2 (H_2O_2 selectivity) and for minimum quinones formation, the phenol: H_2O_2 (molar) ratio must be kept as high as possible. However, lower H_2O_2 concentrations lead to lower phenol conversions. The influence of a higher H_2O_2 content (phenol: H_2O_2 molar ratio = 1) on the product composition at different run durations is presented in Fig. 2(B). At the higher H_2O_2 con-

TABLE 3

Effects of H₂O₂ concentrations; other conditions as in Table 1

Phenol:H ₂ O ₂ (mole) ratio	H ₂ O ₂ selectivity	Phenol conversion	Product distribution (mol.%)		
			PBQ	CAT	HQ
1	27.5	26.1	5.4	49.4	45.0
3	70.0	26.8	0.9	49.3	49.8
5	75.9	17.4	0.0	51.7	48.3

TABLE 4

Effects of temperature; other conditions as in Table 1

Temperature (K)	H ₂ O ₂ selectivity	Phenol conversion	Product distribution (mol.%)			
			OBQ	PBQ	CAT	HQ
310	35.4	9.3	9.4	47.8	34.3	8.5
326	58.2	19.3	1.6	16.5	44.2	37.7
342	70.0	26.8	0.0	0.9	49.3	49.8

centration, not only are more quinones produced, they also persist in the product for a much longer duration (compare Fig. 2(B) and 1(B)). These observations are similar to those made during studies on the mode of H₂O₂ addition (Fig. 1). The *o*-/*p*-product ratio is also higher when H₂O₂ content is greater (see below):

<i>o</i> -/ <i>p</i> -product ratio	phenol:H ₂ O ₂ (molar) ratio	
	1	3
at 1 h	1.56	0.94
6 h	1.14	0.86

Influence of temperature

The results of the studies carried out in the temperature range 310 to 342 K are presented in Table 4. Both conversion and H₂O₂ consumption increase with temperature. The catechol/hydroquinone ratio (at the end of 24 h) is found to be dependent on temperature, the ratio being 4.08 at 310 K and 0.98 at 342 K.

At 310 K, significant quantities of OBQ and PBQ are present in the product even at the end of 24 h. Again the ratio of the *o*-/*p*-products is much higher at 310 K (7.49 after 1 h and 3.10 after 10 h) when compared to the values observed at 342 K (0.94 and 0.86) (Figs. 2(C) and 1(B)).

Influence of solvents

Acetone was used as the solvent in all the experiments reported earlier. Studies were also carried out using other solvents (Table 5). The solvent affects both the conversion and H₂O₂ efficiency. Similarly, the catechol/hydroquinone ratios are also influenced by the solvent, the ratios being 0.66 in methanol, 0.99 in acetone and 1.90 in 2-butanone. The amount of PBQ in the product is 5.8% in the case of 2-butanone and nil in the case of methanol. Earlier workers [12] have also reported the influence of solvents (methanol and acetone) on the hydroxylation of phenol over TS-1.

Mechanism of phenol hydroxylation

The hydroxylation of phenol exclusively at the *o*- and *p*-positions suggests the reaction to be an electrophilic substitution, probably involving (OH)⁺ species. We can now envisage the reaction to take place as follows:

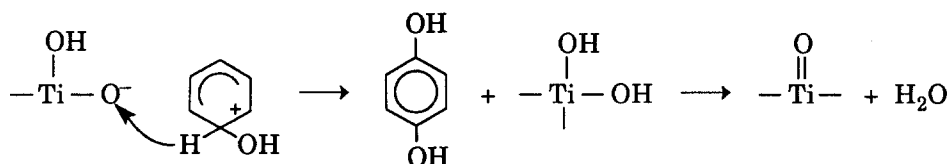
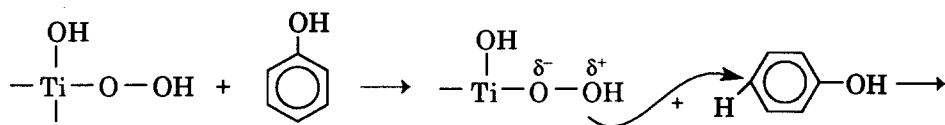
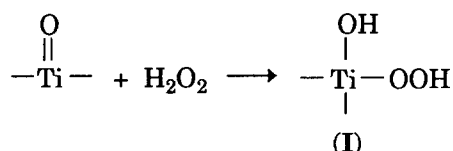


TABLE 5

Effect of solvent; other conditions as in Table 1

Solvent	H ₂ O ₂ selectivity	Phenol conversion	Product distribution (mol.%)		
			PBQ	CAT	HQ
acetone	70.0	26.8	0.9	49.3	49.8
methanol	66.2	25.4	0.0	39.7	60.3
acetonitrile	41.0	15.4	1.9	51.4	46.7
2-butanone	46.9	17.1	5.8	61.7	32.5

The interaction of H_2O_2 with TS-1 has been reported, by earlier workers [1, 13], to produce titanium hydroxyperoxo complexes of the type shown (I). The formation of such species in the case of TS-2 also is very likely.

However, in the early stages of the reaction, especially in the presence of excess H_2O_2 or at lower temperatures, the amount of *o*-products formed is more than the amount of *p*-products. In the hydroxylation of phenol with H_2O_2 in the presence of Fenton's reagent (Fe^{2+} ions), which is known to proceed by a free radical mechanism [14], the yield of *o*-products is generally more than twice the yield of *p*-products [15]. It is, therefore, likely that both ionic and radical-type mechanisms are operative during hydroxylation over TS-2, the importance of one mechanism over the other being dependent on the reaction conditions.

Conclusions

The titanium silicate molecular sieve, TS-2, catalyzes the hydroxylation of phenol to *o*- and *p*-dihydroxybenzenes with H_2O_2 . The reaction is found to be catalyzed specifically by Ti ions in the molecular sieve. Higher phenol: H_2O_2 (molar) ratios and higher catalyst loadings lead to better utilization of the H_2O_2 and higher conversion levels. The *o*:-*p*-dihydroxybenzene ratio in the product is influenced by the reaction temperature, the phenol: H_2O_2 (molar) ratio and the solvent.

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