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Catalytic Properties of Crystalline Titanium Silicalites

II. Hydroxylation of Phenol with Hydrogen Peroxide over TS-1 Zeolites

The major commercial process utilizing titanium zeolites as catalysts is the oxidation of phenol to hydroquinone and catechol by Enichem, Italy. Hydroxylation of phenol and benzene has frequently been used as a test reaction to characterize the presence/absence of Ti^{4+} ions in framework positions of TS-1 and TS-2 titanium zeolites (*1–13*). Although this reaction is in commercial practice, the details of the influence of various reaction parameters on activity, yield, and selectivity of the TS-1 zeolites have not yet been reported in the open literature. In our previous paper (Part I of this series (*11*)), we had reported the synthesis and physicochemical characterization of titanium silicalites containing amounts of titanium in lattice positions much higher than those reported in the prior art literature. We had also found that the catalytic activity of these materials could be enhanced significantly by increasing their titanium content. In the present note, we report detailed studies on the influence of various reaction parameters that affect the performance of these catalysts in this industrially important process.

The details about the synthesis and characterization of the titanium silicalite (TS-1) samples are given in Ref. (*11*). The catalytic runs were carried out batchwise in a 200-ml glass reactor as described earlier (*11–13*).

1. Influence of titanium content: Table 1 illustrates the influence of titanium content on phenol conversion and product distribution. The composition and physicochemical properties of these samples are given in Tables 1 and 2 of Part I of this series (*11*). Phenol conversion increases with titanium content. Pure silicalite-1, TiO_2 (both amorphous and crystalline), amorphous titanium silicates, and physical mixtures of silicalite-1 and TiO_2 were inactive in this reaction suggesting that titanium ions associated with the MFI framework structure are responsible for the observed catalytic activity. The relative concentration of hydroquinone (HQ) and catechol (CA) is rather insensitive to titanium content. Further detailed studies on the influence of various reaction parameters were carried out with the sample of composition $Ti/(Ti + Si) = 0.042$ with a Si/Ti ratio of 23. The sample consisted of cuboid crystals of dimension 0.5–1.0 μm.

2. The influence of catalyst concentration: Hydroxylation did not occur in the absence of the catalyst (Table 2). As the concentration of the catalyst was increased, both the phenol conversion and the efficiency in the utilization of H_2O_2 (for the production of dihydroxybenzenes) increased and attained constant values beyond 5% (g cat/g phenol). The balance was decomposed to $H_2O + \frac{1}{2} O_2$. This latter reaction predominates in the absence of adequate amount of catalyst. The titanium zeolite ensures that the H_2O_2 is utilized for the hydroxylation reaction rather than for the nonselective decomposition. An interesting observation is the significant formation of *para*-benzoquinone (PBQ) at low catalyst concentrations (Table 2). Most of the further experiments described below were carried out at 10% (g cat/g phenol).

3. The influence of reaction time: Low residence times caused incomplete conversion of phenol as well as low H_2O_2 efficiencies (Table 3). Moreover, the concentration of *para*-benzoquinone in the product was also higher. There were no significant

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TABLE 1

Hydroxylation of Phenol on Titanium Silicalites, TS-1, and Influence of Ti Content

	Ti/(Ti + Si), mole					
	0	0.010	0.021	0.042	0.056	0.091
Phenol conv. (% theor.)	0	60	78	87	90	93
H_2O_2 effective conv. (%)[a]	0	55	70	80	83	85
		Product (wt%)				
Hydroquinone	0	45	47	47	46	46
Catechol	0	55	53	53	54	52
p-Benzoquinone	0	0	0	0	0	2

Note. Solvent: acetone; temp., K = 330; phenol/H_2O_2, mole = 3; reaction time, h = 6; catalyst/phenol (g/g), % = 10.

[a] To dihydroxybenzenes and quinones; the balance remained either unreacted or decomposed to water and oxygen.

changes beyond 6 h. Hence, in all further experiments, the residence time was kept constant at 6 h.

4. Influence of solvent: The influence of various solvents is illustrated in Table 4. Acetone and methanol had similar high (82 and 84%, respectively) phenol conversion values while 2-butanone and acetonitrile had similar but lower values (48 and 51%, respectively). The H_2O_2 efficiency also followed a similar trend (75 and 81% vs 43 and 48% for the former and latter pair of solvents, respectively). The influence of the solvent on the product distribution is more complex. The two ketones (acetone and 2-butanone) have similar values of *ortho*-selectivity (57 and 60, respectively). In 2-butanone and acetonitrile solvents, wherein phenol conversion was low, *para*-benzoquinone was observed in the products.

5. Influence of temperature: The formation of *para*-benzoquinone, significant at low temperatures becomes negligible above 310 K. The temperature coefficient of conversion is higher in acetone than in methanol. While catechol is the predominant dihydroxybenzene over the entire temperature range in acetone, it was the predominant species in methanol only below 340 K.

TABLE 2

The Influence of Catalyst Concentration

Catalyst conc. (g cat./g phenol) (%)	0	1	2	5	10	20
Phenol Conv., (% theor.)	0	18	42	84	87	87
H_2O_2 eff. conv. (%)	0	13	37	77	80	80
Products (wt%)						
Hydroquinone	0	0	17	40	47	47
Catechol	0	20	33	60	53	53
p-Benzoquinone	0	80	50	0	0	0

Note. Catalyst: TS-1 (Si/Ti = 23); solvent: acetone; temp., K = 330; Phenol/H_2O_2, mole = 3; reaction time, h = 6.

TABLE 3

Influence of Reaction Time

Reaction Time (h)	1	3	6	20
Phenol conv. (% theor.)	21	87	96	99
H_2O_2 eff. conv. (%)	20	80	85	86
Products (wt.%)				
Hydroquinone	0	33	47	47
Catechol	30	47	53	53
p-Benzoquinone	70	20	0	0

Note. Catalyst: TS-1 (Si/Ti = 23); solvent: acetone; temp., K = 330; Phenol/H_2O_2, mole = 3; catalyst/phenol (g/g), % = 10.

TABLE 4

Influence of Solvent

Solvent	Phenol conv. (% theor.)	H_2O_2 eff. conv. (%)	Products (wt%)[a]		
			HQ	CAT	PBQ
Acetone	82	75	43	57	0
2-Butanone	48	43	37	60	3
Acetonitrile	51	48	32	52	16
Methanol	84	81	65	35	0

Note. Catalyst: TS-1 (Si/Ti = 23); solvent: acetone; temp., K = 330; Phenol/H_2O_2, mole = 3; Reaction time, h = 6; catalyst/phenol (g/g), % = 10.

[a] HQ, hydroquinone; CAT, catechol; PBQ, *para*-benzoquinone.

6. Influence of the method of addition of H_2O_2: When H_2O_2 was heated at 330 K in the absence of phenol and the catalyst for 6 h about 15–17% of H_2O_2 was found to decompose to H_2O and O_2. Similar values were obtained when H_2O_2 was heated in the presence of the catalyst alone. Thus, the nonselective decomposition of H_2O_2 was purely a thermal effect and is not catalyzed by the titanium zeolite. The results of two methods of addition of H_2O_2 are shown in Table 5. In the first method, the entire quantity of the requisite H_2O_2 was added to the reaction mixture at 298 K and the system was then slowly warmed to the reaction temperature (330 K). The reaction was then continued for 6 h. In the second method, the phenol–catalyst mixture was first heated to 330 K and the requisite H_2O_2 was then added dropwise at 330 K over a period of 1 h. Phenol conversion, H_2O_2 efficiency, and hydroquinone formation are more in the latter case. An interesting feature of Table 5 is the much larger formation (91 vs 20%) of *para*-benzoquinone at the end of the first hour when the entire H_2O_2 is added at 298 K and the effective concentration of H_2O_2 is much higher (than when H_2O_2 was added dropwise).

TABLE 5

Influence of the Method of Addition of H_2O_2

Method of addition of H_2O_2:	Total addition at 298 K		Dropwise addition at 330 K	
Reaction time (h):	1	6	1	6
Phenol conv (% theor.)	12	90	15	82
H_2O_2 eff. conv. (%)	17	81	23	75
Products (wt%)				
Hydroquinone	2	47	14	43
Catechol	7	53	66	57
p-Benzoquinone	91	0	20	0

Note. Catalyst: TS-1 (Si/Ti = 23); solvent: acetone; temp., K = 330; Phenol/H_2O_2, mole = 3; catalyst/phenol (g/g), % = 10.

7. The influence of phenol/H_2O_2 ratio: Both the phenol conversion and effective utilization of H_2O_2 increase at higher phenol/H_2O_2 molar ratios (Table 6). The ratio of hydroquinone/catechol is insensitive to variations in phenol/H_2O_2 ratio.

A significant novel finding of this study is the formation of *para*-benzoquinone at low phenol conversion levels. The conversion of *para*-benzoquinone, which appears to be a primary product, to hydroquinone, is a reduction reaction. The inertness/role of the solvents in this reactions is being investigated. A more detailed study of this phenomenon will be published later.

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TABLE 6

Influence of H_2O_2 Concentration

Phenol/H_2O_2 (mole)	1	2	3	4	5
Phenol conv. (% theor.)	36	68	82	92	90
H_2O_2 eff. conv. (%)	28	58	75	77	87
Products (wt%)					
Hydroquinone	5	43	43	47	45
Catechol	51	47	57	53	55
p-Benzoquinone	44	10	0	0	0

Note. Catalyst: TS-1 (Si/Ti = 23); solvent: acetone; temp., K = 330; Reaction time, h = 6; catalyst/phenol (g/g), % = 10.

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