ISSN 1070-4272, Russian Journal of Applied Chemistry, 2011, Vol. 84, No. 4, pp. 640–648. © Pleiades Publishing, Ltd., 2011. Original Russian Text © V.V. Potekhin, V.A. Kulikova, V.V. Vasil'ev, E.G. Kohina, and V.M. Potekhin, 2011, published in Zhurnal Prikladnoi Khimii, 2011, Vol. 84, No. 4, pp. 603–611.

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Hydroxylation of Phenol with Hydrogen Peroxide in Protic and Aprotic Solvents on TS-1 Catalyst

V. V. Potekhin^a, V. A. Kulikova^b, V. V. Vasil'ev^c, E. G. Kohina^b, and V. M. Potekhin^b

^a Himtek Engineering Private Joint-Stock Company, St. Petersburg, Russia
^b St. Petersburg State Institute of Technology, St. Petersburg, Russia
^c St. Petersburg State Engineering and Economic University, St. Petersburg, Russia

Received June 22, 2010

Abstract—Hydroxylation of phenol with a 25% aqueous solution of hydrogen peroxide in polar protic and aprotic solvents on TS-1 heterogeneous catalyst under various conditions was studied. The major reaction products (hydroquinone, pyrocatechol) and their ratio were determined. A kinetic model describing the hydroxylation in accordance with the Rideal–Eley mechanism was chosen.

DOI: 10.1134/S1070427211040148

Major researchers' attention is given today to micro- and mesoporous titanium silicalite catalysts on which selective oxidation of organic compounds can be performed [1, 2]. In particular, such microporous catalyst as TS-1 found use for the synthesis of hydroquinone and pyrocatechol by hydroxylation of phenol with hydrogen peroxide in aqueous-acetone solution [2]. The hydroquinone/pyrocatechol ratio was close to unity. The reaction is not regioselective.

It is reported in [3–7] that solvents used in hydroxylation of phenol with hydrogen peroxide affect the hydroquinone/pyrocatechol ratio. For example, in aqueous acetone the reaction yields hydroquinone and pyrocatechol in approximately equivalent ratio, whereas in aqueous methanol the hydroxylation occurs with preferential formation of hydroquinone. However, possible causes of the regioselectivity in hydroxylation of aromatic compounds on micro- and mesoporous titanium silicalite catalysts are not discussed. Data on the influence exerted on the regioselectivity by the solvent (protic or aprotic, polar or nonpolar) and hydroxylation conditions are also limited.

In this study we examined the reaction kinetics and the solvent effect on the regioselectivity of phenol hydroxylation with hydrogen peroxide on TS-1. As solvents we used methanol, acetone, acetonitrile, 1,4-dioxane, and their mixtures with water.

EXPERIMENTAL

In our experiments we used methanol [chemically pure grade, 99.5%, GOST (State Standard) 6995–77], acetone (analytically pure grade, GOST 2603–79), acetonitrile [chemically pure grade, 99.85%, TU (Technical Specification) SOMR2-040–06], 1,4-dioxane (analytically pure grade, GOST 10455–80), phenol (analytically pure grade, 99.5%), and 35% aqueous solution of hydrogen peroxide. The catalyst, TS-1, was prepared according to [8] and had the following characteristics: TiO₂ content 2.6%, specific micropore volume 0.140 cm³ g⁻¹, mean particle size 10–100 μ m (determined with a JSM-35CF scanning electron microscope, JEOL). X-ray diffraction analysis showed that TS-1 contained no anatase phase.

Experiments were performed in a temperaturecontrolled glass reactor with continuous shaking to ensure the kinetic control of the reaction. In all the experiments, the reaction mixture volume was constant: 10 ml. The conditions were varied: initial H_2O_2 concentration, from 0.12 to 1.65 M; catalyst amount, from 0.4 to 1.0 g; initial phenol concentration, from 1.78 to 2.1 M; and temperature, from 40 to 60°C. Experiments were performed in aqueous solvents at the water content from 3 to 33 vol %.

The content of hydrogen peroxide in the reaction mixture was determined by iodometric titration. The phenol hydroxylation products were determined with a Khromos GKh-1000 chromatograph.

Kinetic studies were performed with TS-1 catalyst with a particle size of $10-100 \mu m$, with which the external and internal diffusion did not control the phenol hydroxylation with hydrogen peroxide [9, 10].

Figure 1 shows the kinetic curves of the H_2O_2 consumption in phenol hydroxylation in a methanol solution on TS-1 under various conditions. As can be seen, at the initial hydrogen peroxide concentration of 0.52 M, initial phenol concentration of 1.78 M, and temperature of 40–60°C, the decomposition of hydrogen peroxide appreciably increased. The reaction order with respect to hydrogen peroxide varied from zero to unity with the conversion. In the examined temperature range, at a hydrogen peroxide conversion $X(H_2O_2) < 50\%$, the reaction order was zero, which indicates that the forming products do not affect the process kinetics. At the hydrogen peroxide conversion $X(H_2O_2) > 50\%$, first order was observed.

The zero reaction order with respect to hydrogen peroxide was also confirmed by the method of initial concentrations. At the initial hydrogen peroxide concentration varied from 0.36 to 1.3 M and constant temperature of 60°C (Fig. 1, curves I-3), the initial rate of the H₂O₂ consumption r_0 remained constant, (2.2 ± 0.1) × 10⁻⁴ mol g⁻¹ min⁻¹, irrespective of the hydrogen peroxide concentration $c(H_2O_2)$, which corresponded to the rate constant of a pseudo-zero-order reaction. The initial rate was also found to be independent of the catalyst amount.

The temperature dependence of the initial rates r_0 of H₂O₂ consumption is satisfactorily linearized in the Arrhenius coordinates log r_0 -1/T and is characterized by the activation energy of the overall process $E_{\text{eff}} = 47 \pm 5 \text{ kJ mol}^{-1}$.

The major products of phenol hydroxylation with hydrogen peroxide in methanol are hydroquinone and pyrocatechol (Table 1).

As seen from Table 1, the process is regioselective with preferential formation of hydroquinone. The hydroquinone/pyrocatechol concentration ratio decreases from 4.5 to 3.5 as the temperature is increased from 40 to 60°C. At increased ratio between the initial

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 84 No. 4 2011



Fig. 1. Kinetic curves of H_2O_2 consumption in hydroxylation of phenol in methanol. Initial phenol concentration 1.78 M. (*c*) Hydrogen peroxide concentration and (τ) time; the same for Figs. 3 and 4. Initial H_2O_2 concentration, M: (*1*) 0.36, (*2*) 0.70, (*3*) 1.30, and (*4*–6) 0.52. Temperature, °C: (*1*–3) 60, (*4*) 40, (5) 50, and (*6*) 60. Catalyst amount, wt %: (*1*–3) 1.0 and (*4*–6) 4.0.

concentrations of hydrogen peroxide and phenol and elevated temperatures, benzoquinone is also formed (Table 2), and the catalyst is noticeably deactivated as H_2O_2 is consumed. The catalyst deactivation is due to formation of tarry products which are sorbed on the surface and in pores of the catalyst. In particular, *p*-benzoquinone is the product of hydroquinone

Table 1. Hydroxylation of phenol in methanol. $c_0(H_2O_2) = 0.52$, $c_0(C_6H_5OH) = 1.78$ M; $m_c = 4.0$ wt %; $\tau = 6$ h

Compound	Relative content in products, wt %, at indicated temperature				
	40	50	60		
Phenol	87.8	87.0	85.0		
Hydroquinone	10.0	10.2	11.7		
Pyrocatechol	2.2	2.8	3.3		

Table 2. Hydroxylation of phenol in methanol. $c_0(H_2O_2) = 1.65$, $c_0(C_6H_5OH) = 1.78$ M; $m_c = 10$ wt %; $\tau = 5$ h

Compound	Relative content in products, wt %, at indicated temperature				
	40	50	60		
Phenol	96.4	89.7	85.0		
Hydroquinone	0.5	2.0	3.2		
Pyrocatechol	2.3	7.6	11.0		
Benzoquinone	0.8	0.7	0.8		



Fig. 2. Kinetic curves of H_2O_2 consumption in hydroxylation of phenol in aqueous acetone. Initial concentrations, M: phenol 2.1 and acetone 11.3; catalyst content 4.0 wt %; 40°C. (*c*) Hydrogen peroxide concentration, (τ) time, and (r_0) initial reaction rate. Initial H_2O_2 concentration, M: (1) 0.12, (2) 0.23, (3) 0.35, and (4) 0.47. (5) Variation of the initial reaction rate in relation to the initial H_2O_2 concentration.

oxidation with hydrogen peroxide, and the colored tarry product is formed by condensation of highly reactive *o*-benzoquinone, the product of pyrocatechol oxidation.

We also found that, when the reaction is performed at 40°C and $c_0(C_6H_5OH)/c_0(H_2O_2)$ ratio close to unity, the hydrogen peroxide decomposition follows a zeroorder equation. At the hydrogen peroxide conversion exceeding 36%, the phenol hydroxylation rapidly decelerated; the selectivity was about 28%. The reaction solution acquired a dark cherry color.

At the ratio $c_0(C_6H_5OH)/c_0(H_2O_2) > 3$, the hydrogen peroxide decomposition at the start of the reaction also followed zero order, but the hydroxylation occurred with practically complete consumption of hydrogen peroxide (Fig. 1, curves 4-6), and the selectivity of the hydroquinone and pyrocatechol formation with respect to H₂O₂ exceeded 85%. However, at elevated temperatures and the ratio $c_0(C_6H_5OH)/c_0(H_2O_2) > 3$ preserved, the hydroxylation selectivity decreased (for example, at 60°C it was about 70%). This is apparently due to the fact that the rate of the hydrogen peroxide consumption in methanol with the formation of methanol oxidation products and molecular oxygen ($E_{eff} = 72 \pm 5 \text{ kJ mol}^{-1}$) increases with temperature more rapidly than does the parallel reaction of the phenol hydroxylation in the same solvent ($E_{eff} = 47 \pm 5 \text{ kJ mol}^{-1}$).

Similar temperature dependence of the selectivity

of the phenol hydroxylation with hydrogen peroxide is observed in polar aprotic solvents (acetone, acetonitrile) and their mixtures with water at the ratio $c_0(C_6H_5OH)/c_0(H_2O_2) > 3$.

Figure 2 shows the kinetic curves of the hydrogen peroxide consumption in hydroxylation of phenol in aqueous acetone at 40°C and various initial concentrations of hydrogen peroxide. The dependence of the initial rate of the hydrogen peroxide consumption on its concentration (Fig. 2, curve 5) is described by a curve with saturation. The reaction rate is proportional to the H₂O₂ concentration, and at $c(H_2O_2)$ from 0 to 0.25 M the reaction is first-order with respect to H₂O₂. At $c(H_2O_2) > 0.3$ M, the reaction rate is independent of the H₂O₂ concentration, i.e., the kinetics of the hydrogen peroxide consumption follows a zero-order law.

The temperature dependence of the initial rate of the H₂O₂ consumption at $c(H_2O_2) > 0.3$ M is linearized in the coordinates log r_0-1/T and corresponds to the activation energy of the overall process of the phenol hydroxylation in aqueous acetone of 38 ± 5 kJ mol⁻¹.

Thus, the nature of the solvent (protic methanol or aprotic acetone) does not affect the range of hydrogen peroxide concentrations in which the H_2O_2 consumption follows the zero- or first-order law. This fact may be due to significant difference in the adsorption equilibrium constants for H_2O_2 and the solvent, including water and reaction products, on active sites of the titanium silicalite catalyst. However, the concentration ratio of the components in the reaction system should be taken into account.

The major products of phenol hydroxylation in aqueous acetone are hydroquinone and pyrocatechol (Table 3).

An increase in the initial concentration of hydrogen peroxide leads to an increase in the H_2O_2 conversion and selectivity of formation of hydroquinone and pyrocatechol. The hydroquinone/pyrocatechol ratio varies insignificantly and is in the range (1.1-1.2): 1. At the initial concentration of hydrogen peroxide exceeding 0.4 M, tarry products start to form, the reaction solution becomes colored, and the catalyst activity decreases, which was also noted above for the hydroxylation of phenol in methanol.

It should be noted that, in phenol hydroxylation in aqueous acetone, in contrast to the oxidation in methanol, the regioselectivity with respect to hydroquinone decreased by a factor of more than 3.

HYDROXYLATION OF PHENOL WITH HYDROGEN PEROXIDE

Initial H ₂ O ₂ concentration,	Relati	ve content in produ	H ₂ O ₂ conversion %	Selectivity with	
М	phenol	hydroquinone	pyrocatechol		respect to H_2O_2 , %
0.12	98.7	0.7	0.6	95.0	74.0
0.23	93.5	3.7	2.8	93.0	75.0
0.35	89.5	5.8	4.7	85.0	82.0
0.47	88.5	6.6	4.9	72.0	84.0

Table 3. Hydroxylation of phenol in aqueous acetone. 40°C, $c_0(C_6H_5OH) = 2.1 \text{ M}$, $c_0(H_2O) = 13 \text{ vol }\%$, $\tau = 6 \text{ h}$

Table 4. Hydroxylation of phenol in aqueous acetone. 40°C, $c_0(H_2O_2) = 0.47$, $c_0(C_6H_5OH) = 2.1$ M; $m_c = 4$ wt %; $\tau = 6$ h

		Relative content in products				Selectivity with
Water, vol % phenol	phenol	hydroquinone	pyrocatechol	hydroquinone/pyrocatechol	conversion, %	respect to H_2O_2 , %
		wt %		ratio		
3.0	93.7	3.3	3.0	1.1	49.4	55.0
8.0	91.3	4.9	3.9	1.3	58.2	65.0
13.0	89.4	5.3	4.9	1.1	71.9	68.0
23.0	87.2	6.9	5.9	1.2	85.0	69.0
33.0	82.7	9.1	8.2	1.1	95.5	83.0

Introduction of water into the reaction solution noticeably affects the rate of the hydrogen peroxide consumption and the selectivity of formation of dihydric phenols (Table 4). The major products of phenol hydroxylation in aqueous acetone at the water concentration from 3 to 33 vol % are hydroquinone and pyrocatechol.

As seen from Fig. 3 and Table 4, an increase in the water content in the reaction mixture leads to an increase not only in the H_2O_2 conversion, but also in the reaction selectivity with respect to hydroquinone and pyrocatechol. At the same time, the hydroquinone/pyrocatechol ratio remains practically constant, (1.1–1.2) : 1, i.e., the regioselectivity does not change. Thus, introduction of water into the reaction zone favors acceleration of phenol hydroxylation to dihydric phenols and decreases the contribution of the concurrent reaction of the hydrogen peroxide decomposition with the formation of molecular oxygen.

In phenol hydroxylation, with an increase in the temperature from 40 to 60°C, the yields of hydroquinone and pyrocatechol ncrease, but the selectivity of formation of hydroquinone and pyrocatechol decreases (Table 5).

The phenol oxidation at temperatures exceeding 50°C and high H_2O_2 conversions is accompanied by noticeable formation of tars which are deposited on the surface and in pores of the catalyst. The reaction solution



Fig. 3. Kinetic curves of H_2O_2 consumption in hydroxylation of phenol in aqueous acetone. Initial concentrations, M: phenol 2.1 and H_2O_2 0.47; catalyst content 4.0 wt %; 40°C. Initial H_2O concentration, M: (1) 1.6, (2) 4.4, (3) 7.2, (4) 12.7, and (5) 18.3. Initial acetone concentration, M: (1) 12.7, (2) 12.0, (3) 11.3, (4) 9.9, and (5) 8.6.

	Relativ	e content in products		Selectivity with	
<i>T</i> , °C	phenol	hydroquinone	pyrocatechol	H_2O_2 conversion, %	respect to H_2O_2 , %
40	89.6	5.4	5.0	72.0	84.0
50	84.7	8.3	7.0	87.0	80.0
55	84.3	8.6	7.1	93.0	80.0
60	83.0	9.0	8.0	97.0	77.0

Table 5. Hydroxylation of phenol in aqueous acetone. 40–60°C, $c_0(H_2O_2) = 0.47$, $c_0(C_6H_5OH) = 2.1$ M; $m_c = 4$ wt %; $c_0(H_2O) = 13$ vol %; $\tau = 6$ h

becomes cherry-colored, and the catalyst becomes inactive. To enhance the catalyst activity, it is necessary to repeatedly (3–5 times) wash the spent catalyst with the solvent.

The hydrogen peroxide consumption in phenol hydroxylation in an acetonitrile solution on TS-1 catalyst at 40–60°C occurs faster than in aqueous acetone (water concentration 3 vol %). As seen from Fig. 4, the reaction order with respect to H₂O₂ varies with the hydrogen peroxide conversion. At the H₂O₂ conversion of up to 50%, zero order is observed. At higher conversions, the hydrogen peroxide consumption follows the first-order law. From the initial rates of the hydrogen peroxide consumption at different temperatures in the examined range, we determined the effective activation energy of the process, $E_{\rm eff} = 34 \pm 5$ kJ mol⁻¹.

As in the case of phenol hydroxylation in aqueous acetone, decomposition of hydrogen peroxide in acetonitrile is mainly accompanied by hydroxylation of phenol into hydroquinone and pyrocatechol in (1.2-1.3): 1 ratio (Table 6).

In the process, the selectivity of the formation of hydroquinone and pyrocatechol with respect to

Table 6. Hydroxylation of phenol with hydrogen peroxide in acetonitrile. $c_0(H_2O_2) = 0.52$, $c_0(C_6H_5OH) = 1.78$ M; $m_c = 4$ wt %; $\tau = 6$ h

Compound	Relative content in products, wt %, at indicated temperature, °C			
	40	50	60	
Phenol	83.2	86.2	86.2	
Hydroquinone	9.2	7.8	7.4	
Pyrocatechol	7.6	6.0	6.4	

hydrogen peroxide varies from 81 (at 40°C) to 70% (at 60°C), with the regioselectivity remaining constant. Irrespective of temperature, hydrogen peroxide at its conversion no higher than 50% is mainly consumed (to more than 80%) for phenol hydroxylation. Then the process noticeably decelerates (as in the case of hydroxylation in methanol and aqueous acetone), which is due to formation of tarry products which are sorbed on the surface and in pores of TS-1 catalyst.

The experiments on phenol hydroxylation with hydrogen peroxide in a low-polarity aprotic solvent, 1,4-dioxane, at 40–60°C [$c_0(H_2O_2) = 0.52$, $c_0(C_6H_5OH) = 1.78$ M; $m_c = 4$ wt %] gave negative results. Only at 60°C hydroquinone and pyrocatechol formed in a small amount (less than 2%), although the hydrogen peroxide consumption was noticeable.

The hydrogen peroxide consumption in a 1,4-dioxane solution containing phenol is mainly accompanied by the solvent oxidation with the effective activation energy of 51 ± 5 kJ mol⁻¹, calculated from the initial rates of the



Fig. 4. Kinetic curves of H_2O_2 consumption in hydroxylation of phenol in acetonitrile. Initial concentrations, M: phenol 1.78 and H_2O_2 0.52; catalyst content 4.0 wt %. Temperature, °C: (1) 40, (2) 50, and (3) 60.

 H_2O_2 transformation. Low degree of hydroxylation is due to low concentration of phenol in the pore volume of TS-1 catalyst.

Thus, the following conclusions can be made. In polar protic and aprotic solvents (methanol, acetone, acetonitrile) causing decomposition of H_2O_2 with the formation of O_2 and oxidative decomposition of the solvents to 10–15%, phenol undergoes selective hydroxylation to dihydric phenols at 40–60°C with an aqueous solution of hydrogen peroxide on the surface and in pores of TS-1 microporous catalyst. The regioselectivity (about 80% with respect to hydroquinone) was observed when the reaction was performed in methanol or aqueous methanol, whereas in aqueous acetone and acetonitrile no regioselectivity of the hydroxylation was observed.

Water in a definite concentration interval exerts a noticeable positive effect on the rate and selectivity of phenol hydroxylation.

When the reaction of phenol with hydrogen peroxide is performed in 1,4-dioxane at 40–60°C, practically no hydroxylation of phenol is observed, and hydrogen peroxide is mainly consumed for the oxygen formation and solvent oxidation.

The phenol hydroxylation on active four-coordinate titanium sites is preceded by fast reversible processes of adsorption of solvent S (water, methanol, acetone, acetonitrile) and dissociative chemisorption of hydrogen peroxide (Scheme 1).

Hydrogen peroxide is actively chemisorbed on the catalytic center of titanium, possibly containing the solvent, with the formation of hydroperoxide and peroxide complexes [1, 11, 12].

It is suggested in the literature [1, 11] that, in a protic solvent, in particular, in alcohol, the hydroperoxy group is stabilized by the alcohol molecule sorbed on the catalytic site with the formation of five-coordinate Ti(IV):



The possibility of formation of radical species II_R from complex II is also noted:



This species, along with complexes I, I_S , and II, actively participates in oxidation reactions with oxygen transfer to the substrate.

Presumably, in phenol hydroxylation, complexes II and II_R are more active than I and I_S , because phenol hydroxylation with hydrogen peroxide in methanol occurs with a higher activation energy than in aqueous acetone and acetonitrile solutions. Excess water favors the formation of titanium peroxy complex [12].

Scheme 1. Chemisorption of hydrogen peroxide on titanium sites of TS-1 catalyst.







It is known that the regioselectivity is influenced by the activity of the species attacking the substrate and by steric and polar factors. In particular, the regioselectivity, as a rule, increases with a decrease in the activity of the attacking species. Apparently, the phenol hydroxylation with hydrogen peroxide in protic and aprotic solvents involves peroxy species of different activities.

The limiting step of the process, phenol hydroxylation,

is accompanied by the reaction of the oxygen atom of hydrogen peroxide, activated with Ti(IV) (structures I, I_S or II, II_R), with the incident phenol molecule from the bulk of solution (Scheme 2).

Increased regioselectivity of phenol hydroxylation in methanol, compared to aqueous acetone and acetonitrile, is associated with lower reactivity of the oxygen atom in complexes I and I_S , compared to II and I_R , and with

solvation of the OH group of phenol with the solvent

which sterically hinders the hydroxylation in the *o*-position of the aromatic ring.

The observed mechanism, taking into account the kinetics of phenol hydroxylation with hydrogen peroxide, corresponds to the kinetic model of the Rideal–Eley mechanism, described by the rate equation

$$r = \frac{kb_{\rm H_{2}O_{2}}c_{\rm H_{2}O_{2}}(1 + \Sigma b_{\rm S}c_{\rm S})c_{\rm C_{2}H_{5}OH}}{1 + b_{\rm H_{2}O_{2}}c_{\rm H_{2}O_{2}}(1 + \Sigma b_{\rm S}c_{\rm S}) + \Sigma b_{\rm S}c_{\rm S} + b_{\rm C_{2}H_{5}OH}c_{\rm C_{2}H_{5}OH}}$$

where k is the rate constant of the hydroxylation on the active four-coordinate titanium site; $b(H_2O_2)$, H_2O_2 adsorption equilibrium constant; b_s , adsorption equilibrium constant of solvent S (including H_2O); $c(H_2O_2)$, $c(C_6H_5OH)$, and c_s are the concentrations of H_2O_2 , C_6H_5OH , and solvent S (including H_2O), respectively.

At low hydrogen peroxide conversion, when $b(H_2O_2)c(H_2O_2) >> 1 + \Sigma b_S c_S (c(H_2O_2) > 0.3 \text{ M})$, the phenol hydroxylation rate is independent of the H_2O_2 concentration (zero reaction order with respect to hydrogen peroxide).

At a high conversion of hydrogen peroxide, corresponding to $c(H_2O_2) < 0.2$ M at $1 + \Sigma b_S c_S > b(H_2O_2)c(H_2O_2)(1 + b_S c_S)$, the hydroxylation rate becomes proportional to the H₂O₂ concentration (first reaction order with respect to hydrogen peroxide):

$$r = \frac{kb_{\rm H_{2}O_{2}}c_{\rm H_{2}O_{2}}c_{\rm C_{2}H_{5}OH}}{1 + \Sigma b_{\rm S}c_{\rm S}}$$

Assuming that the hydroxylation on TS-1 follows the Langmuir–Hinshelwood mechanism, i.e., that the reaction of the adsorbed hydrogen peroxide and phenol molecules takes place, the rate equation will be given in the form

$$r = \frac{kb_{\rm H_2O_2}c_{\rm H_2O_2}(1 + \Sigma b_{\rm S}c_{\rm S})b_{\rm C_2H_5OH}c_{\rm C_2H_5OH}}{[1 + b_{\rm H_2O_2}c_{\rm H_2O_2}(1 + \Sigma b_{\rm S}c_{\rm S}) + \Sigma b_{\rm S}c_{\rm S} + b_{\rm C_2H_5OH}c_{\rm C_2H_5OH}]^2}.$$

In this case, at $b(H_2O_2)c(H_2O_2)(1 + \Sigma b_S c_S) >> 1 + b(C_6H_5OH)c(C_6H_5OH) + \Sigma b_S c_S$, which corresponds

to low conversion of hydrogen peroxide and its high initial concentration, the reaction product with respect to H_2O_2 should be negative, equal to -1, which is not the case. Apparently, because of steric hindrance in catalyst micropores, phenol cannot be sorbed on the same active site of titanium together with hydrogen peroxide, with the subsequent hydroxylation of the aromatic ring. Hydroxylation is not observed, either, if hydrogen peroxide and phenol are sorbed on TS-1 active catalytic sites remote from each other. Therefore, the most probable pathway is the reaction of complexes **I**, **I**_S and **II**, **II**_R with an incident phenol molecule from the bulk of solution, which corresponds to the Rideal– Eley kinetics.

CONCLUSIONS

(1) Selective hydroxylation of phenol with an aqueous H_2O_2 solution at 40–60°C and molar ratio $c_0(C_6H_5OH)/c_0(H_2O_2) > 3$ on TS-1 into hydroquinone and pyrocatechol occurs in polar protic and aprotic solvents resistant to oxidation (methanol, acetone, acetonitrile), with practically complete conversion of H_2O_2 . In a protic solvent (methanol and aqueous methanol), phenol undergoes regioselective oxidation with preferential formation of hydroquinone (about 80%). At a temperature exceeding 60°C and initial H_2O_2 concentration in the solution exceeding 0.4 M, the process selectivity appreciably decreases, with the catalyst deactivation.

(2) An increase in the water concentration in the reaction solution favors an increase in the rate of phenol hydroxylation with hydrogen peroxide and in the reaction selectivity.

(3) The kinetics of phenol hydroxylation with hydrogen peroxide at 40–60°C in protic and aprotic organic solvents on TS-1 is described by the Rideal–Eley kinetic model. At the hydrogen peroxide concentration in the reaction solution below 0.3 M, the phenol hydroxylation rate is proportional to the H₂O₂ concentration, and at $c(H_2O_2) > 0.3$ M the reaction rate reaches a maximum.

(4) In a dioxane solution, the phenol hydroxylation with hydrogen peroxide at 40–60°C does not occur. Hydrogen peroxide is consumed in redox reactions with the formation of molecular oxygen and products of 1,4-dioxane oxidation.

REFERENCES

- 1. Notari, B., Adv. Catal., 1996, vol. 41, pp. 253-334.
- 2. Kholdeeva, O.A. and Trukhan, N.N., *Usp. Khim.*, 2006, vol. 75, no. 5, pp. 460–481.
- 3. US Patent 5683952.
- 4. European Patent Appl. 86200663.2.
- 5. Tuel, A. and Ben Taarit, Y., *Appl. Catal. A: General*, 1993, vol. 102, pp. 69–77.
- 6. Perego, C., Carati, A., Ingallina, P., et al., *Appl. Catal. A: General*, 2001, vol. 221, pp. 63–72.
- 7. Kumar, R. and Bhaumik, A., Micropor. Mesopor. Mater.,

1998, vol. 21, pp. 497-504.

- Clerici, M.G., Bellussi, G., and Romano, U., J. Catal., 1991, vol. 129, pp. 159–167.
- 9. Pol, A.J.H.P. van der, Verduyn, A.J., and Hoff, J.H.C. van, *Appl. Catal. A: General*, 1992, vol. 92, pp. 113–130.
- 10. Pol, A.J.H.P. van der, Verduyn, A.J., and Hoff, J.H.C. van, *Appl. Catal. A: General*, 1993, vol. 106, pp. 97–113.
- 11. Bellussi, G., Carati, A., Clerici, M., et al., *J. Catal.*, 1992, vol. 133, pp. 220–230.
- Bonino, F., Damin, A., and Ricchiardi, G., J. Phys. Chem., 2004, vol. 108, pp. 3573–3583.