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Chemical Engineering Journal 116 (2006) 179–186

Chemical Engineering Journal

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Chemical kinetics of hydroxylation of phenol catalyzed by TS-1/diatomite in fixed-bed reactor

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Received 11 May 2005; received in revised form 30 November 2005; accepted 5 December 2005

Abstract

The chemical kinetics of hydroxylation of phenol with 30% H_2O_2 over the TS-1/diatomite catalyst in a fixed-bed reactor system was studied at 50–90 °C. The rate of hydroxylation of phenol was found to increase with increase in temperature, phenol and hydrogen peroxide concentrations. Simultaneously, the rate of decomposition of hydrogen peroxide also increased with increase in temperature and hydrogen peroxide concentration. Based on our analysis, the consuming rate of phenol, formation rate of catechol and hydroquinone and the rate of decomposition of hydrogen peroxide can be described as: $r_{\mathrm{P}} = 7.18 \times 10^3\,\mathrm{e}^{-(42.0/RT)} C_{\mathrm{P}}^{1.06} C_{\mathrm{H_2O_2}}^{0.34}$, $r_{\mathrm{CAT}} = 3.92 \times 10^3\,\mathrm{e}^{-(42.1/RT)} C_{\mathrm{P}}^{1.09} C_{\mathrm{H_2O_2}}^{0.33}$, $r_{\mathrm{HQ}} = 3.13 \times 10^3\,\mathrm{e}^{-(41.9/RT)} C_{\mathrm{P}}^{1.04} C_{\mathrm{H_2O_2}}^{0.35}$ and $r_{\mathrm{H_2O_2}} = 1.75 \times 10^7\,\mathrm{e}^{-(57.8/RT)} C_{\mathrm{H_2O_2}}^{0.75}$, respectively. Based on the Eley–Rideal mechanism for an adsorption of single molecule, the reaction kinetic model of hydroxylation of phenol has been founded, that is $r = (kK_1 C_{\mathrm{H_2O_2}} C_{\mathrm{P}})/(1 + K_1 C_{\mathrm{H_2O_2}} + K_2 C_{\mathrm{P}} + K_3 C_{\mathrm{Prod}})$, which is in agreement with the experimental data.

Keywords: TS-1/diatomite catalyst; Hydroxylation of phenol; Chemical kinetics; Reaction mechanism; Fixed-bed reactor

1. Introduction

As a novel catalytic material, titanium silicalite-1 (TS-1) has attracted much attention last decade, because of its unique catalytic properties for the selective oxidations of organic compounds, such as aromatic hydroxylation, epoxidation of alkenes, ammoximation of cyclohexanone and oxidation of alkanes and alcohols [1–4] by hydrogen peroxide as an oxidant. Among of them, the hydroxylation of phenol is one of the most important and promising chemical processes. In contrast with a mass of researches on the synthesis and characterization of TS-1 in recent years, very few papers were reported to study the reaction kinetics catalyzed by TS-1, especially in the fixed-bed reactor system that is more important and useful than batch reactor system for its commercial application. Maspero and Romano [5] have studied the oxidation kinetics of alcohols over the TS-1 catalyst in the batch reactor, and Gao et al. [6] have reported the kinetics investigation of the epoxidation of allyl chloride on TS-1 zeolite. However, to our knowledge there is not any report of the chemical kinetics of hydroxylation of phenol.

Recently, we have found that the supported TS-1 on diatomite catalyst has good catalytic performance for the hydroxylation of phenol in the fixed-bed reactor (FBR) operated continuously [7]. Compared with the batch process, the FBR continuous process has many advantages, such as to be free from tiresome operations of the catalyst filtration and makeup, and easy operation in large scale. In order to develop the FBR hydroxylation process, the intrinsic kinetics and mechanism of hydroxylation of phenol over the supported TS-1 catalyst in the fixed-bed reactor were investigated in detail in this paper.

2. Experimental

2.1. Preparation of TS-1/diatomite catalyst

TS-1 was prepared by hydrothermal synthesis using tetraethylothosilicate (TEOS) as silicon source, tetrabutyorthotitanate (TBOT) as titanium source, and tetrapropylammonium hydroxide (TPAOH) as template. 20.0 g TEOS was hydrolyzed with 24.0 g TPAOH solution (20% in H_2O, Aldrich),

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doi:10.1016/j.cej.2005.12.001

and then the solution of 1.008 g TBOT in 20 mL dry isopropyl alcohol was added drop-wise under stirring. Subsequently, 8.0 g TPAOH solution and 18.6 g deionized water were added. The molar composition of the matrix gel was SiO_2:0.03TiO_2:0.32TPAOH:25H_2O. After heated to 80 °C and kept for 3 h to remove isopropyl alcohol, the gel was transferred into a stainless steel autoclave with PTFE liner and crystallized at 170 °C for 3 days under static condition. The solid obtained was filtered, washed with deionized water, dried overnight at 120 °C and calcined at 550 °C for 6 h. The average crystal size of TS-1 is about 0.25 μm measured by scanning electron microscopy (SEM).

The TS-1/diatomite catalyst was prepared by mixing TS-1 powder with diatomite ($SiO_2\% \geq 85.0$, $Al_2O_3\% \leq 3.5$, $Fe_2O_3\% \leq 1.5$; TS-1/diatomite = 3/2, wt) homogeneously, then pressed and crushed to 0.30–0.45 mm grains.

2.2. Hydroxylation of phenol

The hydroxylation of phenol was carried out in the continuous flow fixed-bed glass reactor (Ø10 mm), and the catalyst was packed in the isothermal region of reactor. The mixture solution of phenol, H_2O_2 (30 wt.%) and solvent (acetone) was fed to the bottom of reactor by a micropump. The reaction products were analyzed by PE Autosystem XL gas chromatograph with flame ionization detector and PE-2 capillary column (25 m × 0.32 mm × 1.0 μm, 5% methyl benzene silicone). The concentration of H_2O_2 was determined by an iodometric titration. The conversion of phenol and H_2O_2 and the selectivity of product are defined as follows:

$$X_{\text{phenol}} = \frac{n^0_{\text{phenol}} - n_{\text{phenol}}}{n^0_{\text{phenol}}} \tag{1}$$

$$X_{H_2O_2} = \frac{n^0_{H_2O_2} - n_{H_2O_2}}{n^0_{H_2O_2}} \tag{2}$$

$$S_{\text{DHB}} = \frac{n_{\text{CAT}} + n_{\text{HQ}}}{n^0_{H_2O_2} - n_{H_2O_2}} \tag{3}$$

X_{phenol}, $X_{H_2O_2}$ and S_{DHB} denote the conversion of phenol, the conversion of H_2O_2 and the selectivity of dihydroxybenzene based on H_2O_2, respectively. n^0 and n denote the initial molar amount and the final molar amount, respectively. CAT and HQ represent catechol and hydroquinone, respectively.

The conversion of phenol (X_P) was controlled to be less than 10%. Although the conversion of H_2O_2 is larger than 10% in some experiments, the reaction order is quite small, as will be shown later, and therefore the change in reaction rate is less than ±10% of the mean value, even with H_2O_2 conversion as high as 40%. With such small change in reaction rate the differential reactor approach can be employed with an acceptable error, and the reaction rate of each reactant can be calculated as follows:

$$r_P = F_0 C^0_P \frac{X_P}{W} \tag{4}$$

$$r_{\text{CAT}} = F_0 \frac{C_{\text{CAT}}}{W} \tag{5}$$

$$r_{\text{HQ}} = F_0 \frac{C_{\text{HQ}}}{W} \tag{6}$$

$$r_{H_2O_2} = F_0 C^0_{H_2O_2} \frac{X_{H_2O_2}}{W} \tag{7}$$

Here, r_P, r_{CAT}, r_{HQ} and $r_{H_2O_2}$ denote the consuming rate of phenol, formation rate of catechol and hydroquinone and the consuming rate of H_2O_2, respectively (mol h^{-1} g^{-1}); F_0 represents the feed velocity (L h^{-1}); C^0_P and $C^0_{H_2O_2}$ denote the initial concentration of phenol and H_2O_2 (mol L^{-1}) in the feed; C_{CAT} and C_{HQ} denote the concentration of catechol and hydroquinone (mol L^{-1}) in the outlet reaction solution, respectively; W represents the amount of catalyst (g).

3. Results and discussion

We have found that the conversion of phenol and selectivity to products over the TS-1/diatomite catalyst in the fixed-bed reactor system is nearly unchanged in a period of 10 h [8], and as the time on stream is longer than 10 h, the activity and selectivity would drop slightly. Therefore, all the kinetic experiments were carried out under steady-state conditions and the kinetic data were measured after the reaction run for 1 h.

3.1. Exclusion of the internal and external diffusion limitations

It is well known that the limitations of the internal and external diffusion must be excluded before measuring the data of intrinsic kinetics. The results in Table 1 show that the conversion of phenol is changed hardly by the particle size of catalyst when its particle size is less than 0.30–0.45 mm, that is to say, the effect of an internal diffusion on the catalytic reaction may be ignored. Therefore, the catalyst with the size of 0.30–0.45 mm was used in the kinetic experiment.

Fig. 1 reveals the effect of the space velocity of feed on the conversion of phenol. When $W/F_0 < 1.000 \times 10^{-2}$ g h mL^{-1}, the two lines of X_P versus W/F_0 overlap nearly, that is to say, the influence of an external diffusion on the catalytic reaction may be ignored. Therefore, W/F_0 was controlled at less than 1.000×10^{-2} g h mL^{-1} in this kinetic experiment.

Table 1
Effect of the catalyst size on the performance of TS-1/diatomite for hydroxylation of phenol at 80 °C

Catalyst size (mm)	X_P (%)
0.9–2.0	6.21
0.45–0.9	8.41
0.30–0.45	8.77
0.20–0.30	8.72

$C^0_P = 4.973$ mol L^{-1}; $C^0_{H_2O_2} = 1.656$ mol L^{-1}; W = 0.80 g.

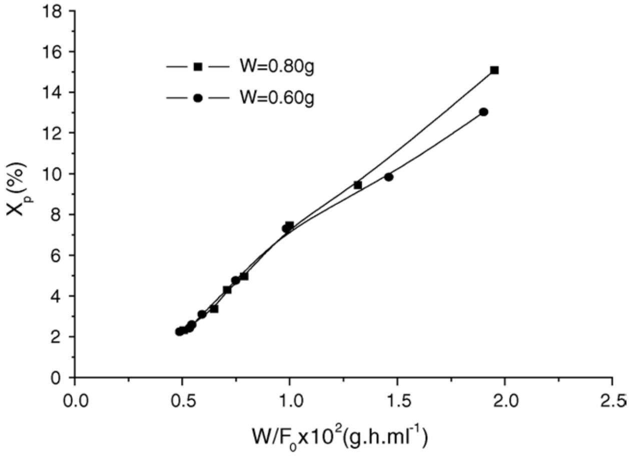
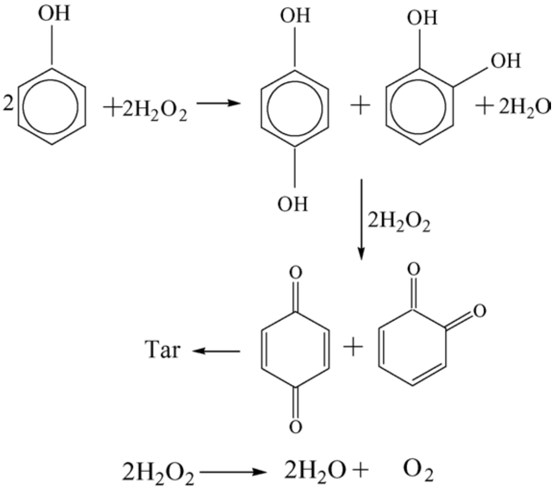


Fig. 1. Effect of the space velocity on the performance of TS-1/diatomite for hydroxylation of phenol at 80 °C.



Scheme 1. Schematic diagram of the main and side reactions in the oxidation of phenol with H_2O_2.

3.2. Hydroxylation of phenol

The possible reactions in the oxidation of phenol by H_2O_2 are shown in Scheme 1 [9]. However, catechol, hydroquinone and *p*-benzoquinone (PBQ) were detected in our study on kinetics factors. The similar products were also obtained by other researchers [4,10] in the hydroxylation of phenol catalyzed by TS-1. The tar formation can be neglected in this paper, based on the facts of a very low conversion of phenol (less than 10%) and very short reaction time (less than 2 h). The method of carbon balance was used to verify the error of total carbon mass of phenol and products between in the inlet and outlet of reactor, and it was found that this error was less than 5%.

3.2.1. Effect of the phenol concentration

In the study of the oxidation of phenol, we observed when the molar ratio of phenol/H_2O_2 was less than 1 (the amount of H_2O_2 was excessive), the serious decomposition of H_2O_2 and the further oxidation of dihydroxybenzenes to tar would occur; the higher the reaction temperature, the more serious the side reactions above became. Therefore, the molar ratio of phenol/H_2O_2 was controlled at more than 1 in this paper, in which the tar formation may be negligible.

The effects of the reaction temperature and phenol concentration on the hydroxylation of phenol are shown in Table 2. The results show that the conversion of phenol and the selectivity to dihydroxybenzene increase with an increase of the reaction temperature. When the inlet concentration of phenol varies from 1.989 to 4.973 mol L^{-1}, the change of the phenol conversion is unobvious. The reason is possibly the excessive amount of phenol as compared with H_2O_2. However, the conversion of H_2O_2 and the selectivity to dihydroxybenzene increases greatly with an increase of the phenol concentration. This is due to the molar ratio of H_2O_2/phenol decreases with the increase of phenol concentration, and the utilization efficiency of H_2O_2 increases at lower molar ratio of H_2O_2/phenol [9], as a result, the selectivity to dihydroxybenzene increases. Fig. 2 displays the effect of the phenol concentration on the rate of hydroxylation of phenol. It is found that the rate of hydroxylation of phenol increases significantly with increase in reaction temperature and phenol concentration, and the rate of hydroxylation of phenol is near first order with respect to the concentration of phenol.

3.2.2. Effect of the H_2O_2 concentration

The effects of the H_2O_2 concentration and reaction temperature on the hydroxylation of phenol are shown in Table 3. The results show that the conversion of phenol and the selectivity to dihydroxybenzene increase with a rise of the reaction temperature. Increasing the inlet concentration of H_2O_2 makes

Table 2
Effect of the phenol concentration on the hydroxylation of phenol on TS-1/diatomite[a]

C_P^0 (mol L^{-1})	Reaction temperature (°C)														
	50			60			70			80			90		
	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)
1.989	1.27	1.03	4.40	2.38	1.52	4.81	3.57	2.75	5.62	6.01	4.75	12.92	8.15	11.73	18.66
2.984	1.29	1.78	4.78	2.21	3.11	8.39	3.56	5.31	8.89	5.92	10.88	15.71	8.36	15.91	19.24
3.481	1.45	2.96	7.12	2.24	4.89	8.64	3.79	7.27	12.10	6.88	15.20	16.85	8.66	19.10	20.09
4.476	1.35	4.66	7.75	2.93	6.09	11.50	3.72	10.43	13.36	5.53	18.01	16.91	8.47	23.32	21.32
4.973	1.30	7.05	11.27	2.73	8.12	12.80	3.96	11.65	15.91	6.91	19.56	17.34	8.77	30.09	21.70

[a] $C_{H_2O_2}^0 = 1.656$ mol L^{-1}.

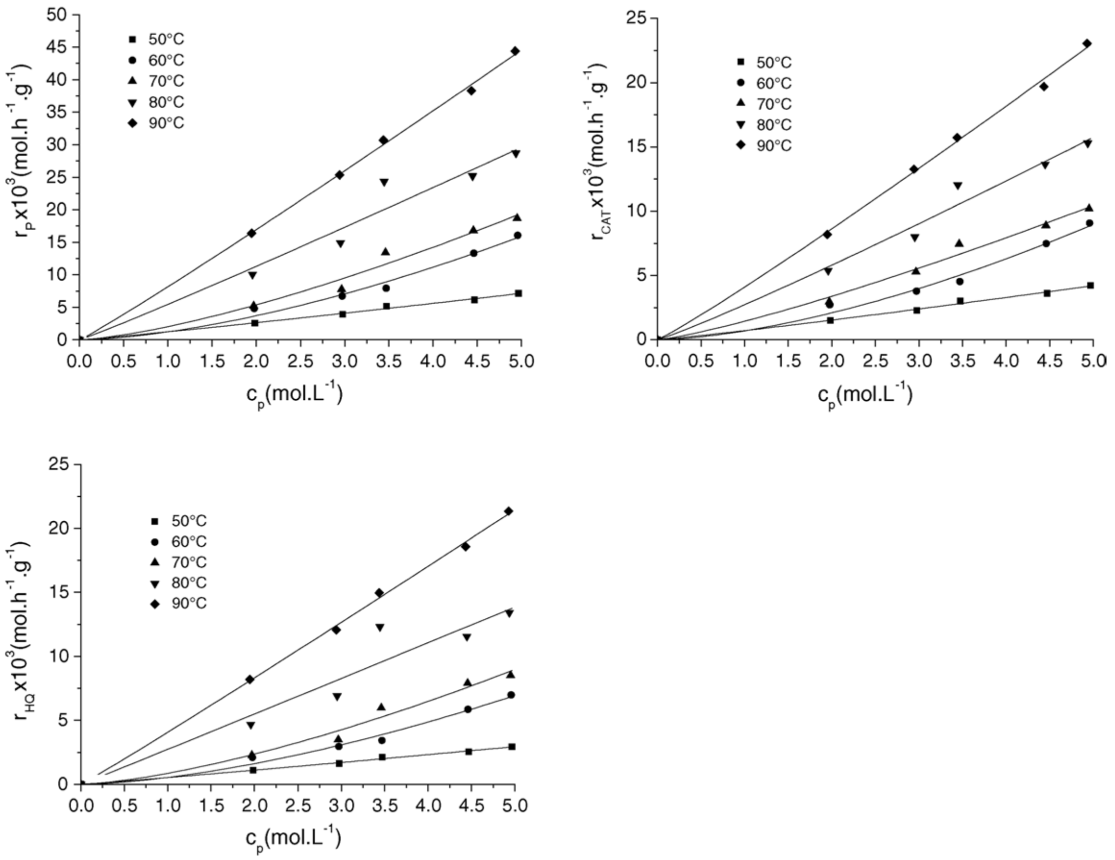


Fig. 2. Effect of the phenol concentration and reaction temperature on the rate of hydroxylation over TS-1/diatomite (C_P denotes the average concentration of phenol between inlet and outlet; $C^0_{H_2O_2} = 1.656\,mol\,L^{-1}$).

the conversion of phenol to increase, and the selectivity to dihydroxybenzene and the conversion of hydrogen peroxide to decrease. The rate of hydroxylation of phenol is plotted against the concentration of H_2O_2 in Fig. 3. It is shown that with the increase of H_2O_2 concentration or reaction temperature the rate of hydroxylation of phenol increases, and however, the slope of the curves decreases gradually. This suggests that the reaction rate is between zero order and first order with respect to the concentration of hydrogen peroxide, that is to say, it is about zero order at higher H_2O_2 concentration and about first order at lower H_2O_2 concentration.

3.2.3. *Effect of the CAT, HQ and PBQ concentration*

In order to investigate the influence of the main products (CAT and HQ) and by-products (PBQ) on the hydroxylation reaction, some CAT, HQ or PBQ were added into the feedstock. The results in Table 4 show that the effects of the concentration of CAT, HQ or PBQ on the conversion of phenol and H_2O_2 are unobvious. This implies that the adsorptions of products on the surface of catalyst are weak, and the products formed desorb quickly from the surface of catalyst and have not an influence on the adsorption of the reactants on the active sites of catalyst.

Table 3
Effect of the H_2O_2 concentration on the hydroxylation reaction over TS-1/diatomite[a]

$C^0_{H_2O_2}$ (mol L^{-1})	Reaction temperature (°C)														
	50			60			70			80			90		
	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	X_P (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)
0.4129	0.76	10.30	16.34	1.37	14.21	18.00	2.60	19.22	22.04	4.21	31.20	23.58	5.43	40.11	24.44
0.8258	1.15	9.45	15.07	1.98	11.97	17.32	3.43	17.67	19.18	4.98	28.52	19.57	6.78	36.30	22.38
1.239	1.28	8.23	11.32	2.03	10.02	13.73	3.63	12.45	16.21	5.89	25.60	19.46	7.66	34.39	22.01
1.656	1.30	7.05	11.27	2.73	8.12	12.76	3.96	11.65	15.91	6.91	19.56	17.34	8.77	30.09	21.70
2.064	1.46	6.88	9.12	3.20	7.81	10.27	4.61	9.34	15.81	7.62	15.84	16.20	9.33	27.40	17.97

[a] $C^0_P = 4.973\,mol\,L^{-1}$.

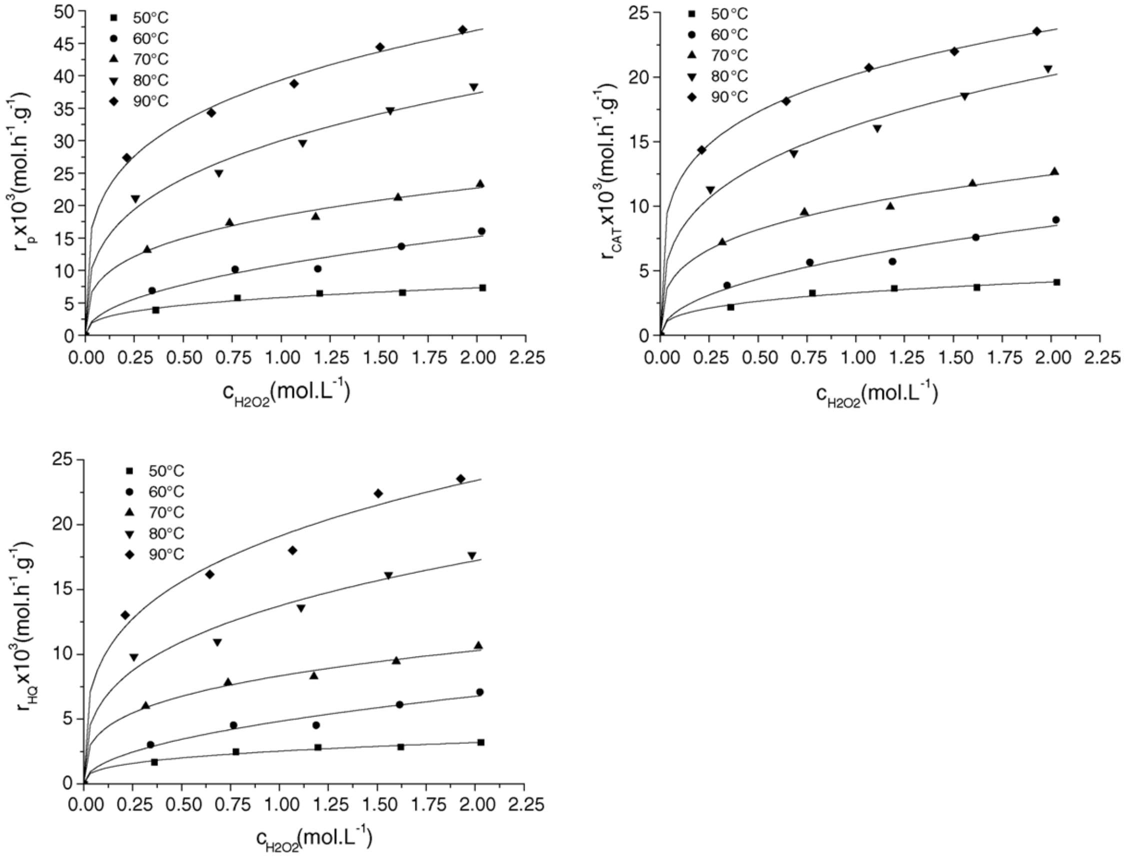


Fig. 3. Effect of the H_2O_2 concentration and reaction temperature on the rate of hydroxylation on TS-1/diatomite ($C_{H_2O_2}$ denotes the average H_2O_2 concentration between inlet and outlet; $C_P^0 = 4.973\,\mathrm{mol\,L^{-1}}$).

3.3. Decomposition of hydrogen peroxide

The decomposition rate of hydrogen peroxide is plotted against the concentration of H_2O_2 at different reaction temperature as shown in Fig. 4. The results show that the decomposition rate increases greatly with increasing the reaction temperature or the concentration of H_2O_2. However, the slopes of curves decrease slightly with an increase of H_2O_2 concentration. The rate of H_2O_2 decomposition is between zero order and first order with respect to the concentration of hydrogen peroxide.

3.4. Kinetic model

An exponential function is usually used to describe the kinetic equation and is convenient for the engineering application. The kinetic equations of hydroxylation of phenol and decomposition of H_2O_2 may be proposed as follows:

$$\text{Hydroxylation of phenol}: \quad r_i = k_0\,\mathrm{e}^{-(E/RT)} C_{\mathrm{P}}^{a} C_{\mathrm{H_2O_2}}^{b}, \quad (i = \text{Phenol, CAT, HQ}) \tag{8}$$

Table 4
Effect of the product concentrations on the catalytic hydroxylation of phenol at 80 °C

C_P^0 (mol L^{-1})	$C_{H_2O_2}^0$ (mol L^{-1})	C_{CAT}^0 (mol L^{-1})	C_{HQ}^0 (mol L^{-1})	C_{PBQ}^0 (mol L^{-1})	X_P (%)	$X_{H_2O_2}$ (%)
4.973	1.656	0	0	0	6.91	19.56
4.973	1.656	0.2125	0	0	7.05	20.71
4.973	1.656	0.4250	0	0	6.88	18.99
4.973	1.656	0.5100	0	0	7.15	19.72
4.973	1.656	0	0.2125	0	6.83	19.26
4.973	1.656	0	0.3188	0	7.11	20.01
4.973	1.656	0	0.4250	0	6.49	19.60
4.973	1.656	0	0	0.01515	6.39	20.82
4.973	1.656	0	0	0.06490	6.64	17.98
4.973	1.656	0	0	0.08659	6.67	18.22

CAT, catechol; HQ, hydroquinone; PBQ, *p*-benzoquinone.

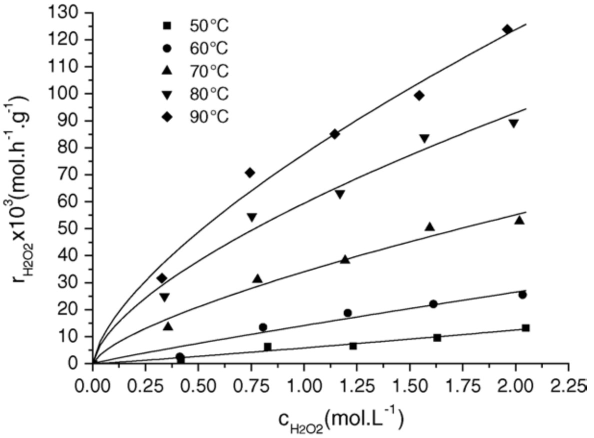


Fig. 4. Effect of H_2O_2 concentration and the reaction temperature on the decomposition rate of hydrogen peroxide on TS-1/diatomite ($C_{H_2O_2}$ denotes the average H_2O_2 concentration between inlet and outlet).

$$\text{Decomposition of } H_2O_2: \quad r_{H_2O_2} = k_0\, e^{-(E/RT)} C^{a}_{H_2O_2} \tag{9}$$

Here, k_0 represents the pre-exponential factor. E represents the activation energy. The model parameters in Eqs. (8) and (9) were estimated by linear regression according to the experiment data above using the OriginPro7.0 software, and the results estimated are listed in Table 5. After the estimated values of kinetics parameters are putted in the Eqs. (8) and (9), r_i and $r_{H_2O_2}$ can be described as follows:

$$r_P = 7.18 \times 10^3\, e^{-(42.0/RT)} C_P^{1.06} C_{H_2O_2}^{0.34} \tag{10}$$

$$r_{CAT} = 3.92 \times 10^3\, e^{-(42.1/RT)} C_P^{1.09} C_{H_2O_2}^{0.33} \tag{11}$$

$$r_{HQ} = 3.13 \times 10^3 e^{-(41.9/RT)} C_P^{1.04} C_{H_2O_2}^{0.35} \tag{12}$$

$$r_{H_2O_2} = 1.75 \times 10^7\, e^{-(57.8/RT)} C_{H_2O_2}^{0.75} \tag{13}$$

3.5. Catalytic reaction mechanism

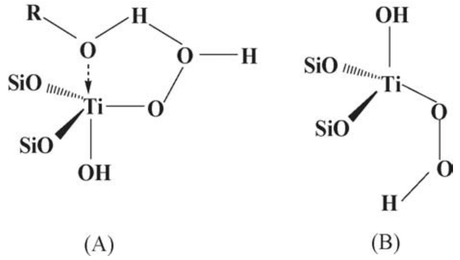
3.5.1. Hydroxylation of phenol

In the liquid–solid catalytic reaction, the solvent often plays an important role on it and participates in the cycle of catalytic reaction. It is well known there is a strong interaction between TS-1 and aqueous H_2O_2 to form the titanium-peroxo compounds. The titanium-peroxo compounds account for the catalytic activity of TS-1 and are the actual oxygen donors in the TS-1-catalyzed reactions [3,11]. In the protic solvents, such as methanol or H_2O, the titanium-peroxo species interacts with solvent molecules to form a five-ring intermediate described as Scheme 2-A. But in the aprotic solvents, such as acetone, the titanium-peroxo species exists in the form as Scheme 2-B [12,13]. Those phenomena imply that the interaction between TS-1 and aprotic solvent is weak. Besides, there are also a little of H_2O in the reaction system, but its amount is lower compared with the solvent acetone. So the adsorption of water on the surface of TS-1 can be neglected. The adsorption of phenol on zeolites is mainly physical adsorption [14,15], so the adsorption of phenol on the TS-1 catalyst is much weaker than the chemisorption of H_2O_2.

Table 5
Estimated values of kinetics parameters in the Eqs. (8) and (9)

i	k_0	E (kJ mol^{-1})	a	b	R^2
Phenol	7.18×10^3	42.0	1.06	0.34	0.967
CAT	3.92×10^3	42.1	1.09	0.33	0.964
HQ	3.13×10^3	41.9	1.04	0.35	0.961
H_2O_2	1.75×10^7	57.8	0.75	–	0.968

R^2, correlation coefficient.



Scheme 2.

According to the assumption mentioned above and the experiment results, the surface reaction of hydroxylation of phenol may be described as follows:

$$[\text{Cat}] + H_2O_2 \overset{K_1}{\rightleftharpoons} [\text{Cat} \cdot H_2O_2] \quad (\text{fast}) \tag{i}$$

$$[\text{Cat}] + P \overset{K_2}{\rightleftharpoons} [\text{Cat} \cdot P] \quad (\text{fast}) \tag{ii}$$

$$[\text{Cat} \cdot H_2O_2] + P \xrightarrow{k} [\text{Cat} \cdot \text{Prod}] \quad (\text{slow}) \tag{iii}$$

$$[\text{Cat} \cdot \text{Prod}] \overset{K_3}{\rightleftharpoons} [\text{Cat}] + \text{Prod} \quad (\text{fast}) \tag{iv}$$

Here, [Cat] represents the active sites of catalyst; $[\text{Cat} \cdot H_2O_2]$, $[\text{Cat} \cdot P]$ and $[\text{Cat} \cdot \text{Prod}]$ represent the adsorbed H_2O_2, phenol or product, respectively; K_1, K_2 and K_3 represent the adsorption equilibrium constant, and k represents the reaction rate constant. The results above show that the rate of hydroxylation is correlative to the concentration of reactants and increases with the concentration of phenol or H_2O_2. That is to say, the adsorption of reactants (reaction formula (i) and (ii)) or desorption of products (reaction formula (iv)) is not the rate determining step. In other words, the catalytic reaction on the surface (reaction formula (iii)) is the rate-determining step.

According to the discussion about the catalytic reaction above, the catalytic hydroxylation of phenol over TS-1/diatomite should accord with the Eley–Rideal mechanism, in which H_2O_2 adsorbed and molecular phenol participate in the hydroxylation reaction. The rate expression can be obtained as the Eq. (14) based on the Eley–Rideal isotherms

$$r = \frac{kK_1 C_{H_2O_2} C_P}{1 + K_1 C_{H_2O_2} + K_2 C_P + K_3 C_{\text{Prod}}} \tag{14}$$

Based on the experiment results that the adsorption of products on the catalyst is weak; the value of $K_3 C_{\text{Prod}}$ should be very small and can be ignored. So the Eq. (14) can be simplified into

Table 6
Kinetic equations based on the mechanisms proposed

Model	Assumptions and kinetic equations
Eley–Rideal	$r=\frac{kK_1C_{H_2O_2}C_P}{1+K_1C_{H_2O_2}+K_2C_P+K_3C_{Prod}}$ (H_2O_2 adsorbed, phenol free, surface reaction controlling)
Langmuir–Hinshelwood	$r=\frac{kK_1K_2C_{H_2O_2}C_P}{(1+K_1C_{H_2O_2}+K_2C_P+K_3C_{Prod})^2}$ (Phenol and H_2O_2 adsorbed on the Ti active sites, surface reaction controlling)

the Eq. (15)

$$r=\frac{kK_1C_{H_2O_2}C_P}{1+K_1C_{H_2O_2}+K_2C_P} \tag{15}$$

The adsorption of H_2O_2 on the active sites of TS-1 is much stronger than that of phenol, so that $K_1 \gg K_2$. The rate expression of the Eq. (15) can be further simplified to the Eq. (16)

$$r=\frac{kK_1C_{H_2O_2}C_P}{1+K_1C_{H_2O_2}} \tag{16}$$

When the concentration of phenol is kept constant, the Eq. (16) is a typical hyperbolic equation. If the concentration of H_2O_2 is very low, $K_1C_{H_2O_2} \ll 1$, the hydroxylation rate is first order to the concentration of H_2O_2; if its concentration is very high, $K_1C_{H_2O_2} \gg 1$, the hydroxylation rate is zero order to the concentration of H_2O_2. For the middle concentration of H_2O_2, the reaction order is between zero and unity. This is coincident with the experiment results above.

When the concentration of H_2O_2 is kept constant, the Eq. (16) can be simplified to $r=\lambda C_P$. Because λ is a constant, the rate of hydroxylation is first order with respect to the concentration of phenol, which is also agreement with the experiment results.

In order to justify further the feasibility of the Eley–Rideal model proposed, another kinetic equation is proposed based on Langmuir–Hinshelwood mechanism, as shown in Table 6. The ideal model will be selected based on the regression results.

Table 7
Parameters of kinetic equations

Model	Eley–Rideal	Langmuir–Hinshelwood
k	$3.09\times10^5\ \exp\left(-\frac{5.12\times10^4}{RT}\right)$	$4.01\times10^5\ \exp\left(-\frac{4.02\times10^4}{RT}\right)$
K_1	$7.20\times10^{-3}\ \exp(\frac{1.71\times10^4}{RT})$	$9.55\times10^{-3}\ \exp\left(\frac{1.18\times10^4}{RT}\right)$
K_2	$7.02\times10^{-3}\ \exp\left(\frac{8.16\times10^3}{RT}\right)$	$2.75\times10^{-3}\ \exp\left(\frac{1.01\times10^4}{RT}\right)$

Table 8
Statistical tests of kinetic models

Model	Q ($\times10^3$)	R^2
Eley–Rideal	9.94	0.985
Langmuir–Hinshelwood	20.6	0.909

Q, the square sum of residuals; R^2, the correlation coefficient.

According to the above experiment results the adsorption of products on the catalyst is weak; the value of K_3C_{Prod} should be very small and can be ignored. Therefore, there are the reaction rate constant (k) and two adsorption equilibrium constants (K_1, K_2) in each kinetic equation. It is assumed that the influence of temperature on the reaction rate constant and adsorption equilibrium constant accords with the Arrhenius Equation and Van't Hoff equations, respectively [16]. Based on the kinetics data of the hydroxylation of phenol, the parameters of two equations were estimated by a non-linear regression using the statistical software of MATLAB. The results of the regression are shown in Table 7.

The reaction rates of hydroxylation of phenol were calculated according to the estimated parameters of two models, and the calculated reaction rate is plotted against the experimental reaction rate as shown in Fig. 5. The statistical tests of kinetic models are listed in Table 8. The results of Fig. 5 and Table 8 show that the Eley–Rideal mechanism fits the experimental data well, and the Langmuir–Hinshelwood mechanism is in poor agreement with the experimental data.

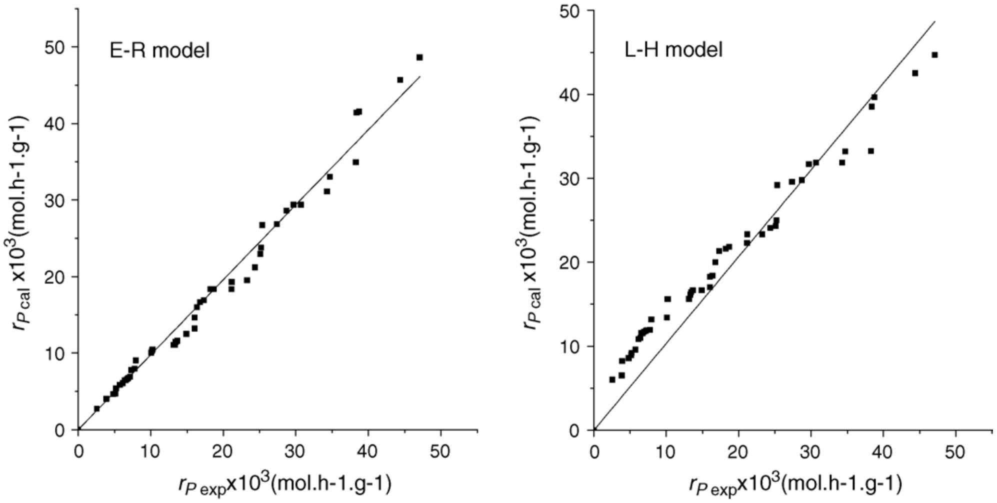


Fig. 5. Reaction rate of hydroxylation of phenol tested vs. calculated. $r_{P\,exp}$, the reaction rate tested; $r_{P\,cal}$, the reaction rate calculated.

3.5.2. Decomposition of H_2O_2

The surface reaction mechanism of H_2O_2 decomposition is described as follows:

$$[\mathrm{Cat}] + \mathrm{H_2O_2} \overset{K_1'}{\rightleftharpoons} [\mathrm{Cat} \cdot \mathrm{H_2O_2}] \quad \text{(fast)} \tag{v}$$

$$[\mathrm{Cat} \cdot \mathrm{H_2O_2}] \xrightarrow{k'} [\mathrm{Cat} \cdot \mathrm{Prod}] \quad \text{(slow)} \tag{vi}$$

$$[\mathrm{Cat} \cdot \mathrm{Prod}] \overset{K_2'}{\rightleftharpoons} [\mathrm{Cat}] + \mathrm{Prod} \quad \text{(fast)} \tag{vii}$$

As it is assumed that step (vi) is rate determining, the rate expression of Eq. (17) is obtained

$$r = \frac{k' K_1' C_{\mathrm{H_2O_2}}}{1 + K_1' C_{\mathrm{H_2O_2}} + K_2' C_{\mathrm{Prod}}} \tag{17}$$

On account of the strong chemical adsorption of H_2O_2 on TS-1, so that $K_1' C_{\mathrm{H_2O_2}} \gg K_2' C_{\mathrm{Prod}}$ and Eq. (17) can be simplified to Eq. (18). It is shown that the decomposition rate of H_2O_2 is between zero order and first order with respect to the concentration of hydrogen peroxide, which is in agreement with the experiment values

$$r = \frac{k' K_1' C_{\mathrm{H_2O_2}}}{1 + K_1' C_{\mathrm{H_2O_2}}} \tag{18}$$

4. Conclusions

The factors affecting the hydroxylation of phenol catalyzed by the TS-1/diatomite catalyst in the fixed-bed reactor system, as well as their kinetic characteristics are obtained. The rate of hydroxylation of phenol increases with the increase of reaction temperature, phenol concentration and H_2O_2 concentration. The rate of hydroxylation of phenol is near first order toward the concentration of phenol, and zero to first order toward the concentration of H_2O_2. Meanwhile, the rate of H_2O_2 decomposition increases also with the increase of reaction temperature and H_2O_2 concentration, and is 0.75 with respect to the concentration of hydrogen peroxide. Based on the Eley–Rideal mechanism for an adsorption of single molecule, the reaction kinetic model of hydroxylation of phenol is founded, which is in agreement with the experimental results.

Acknowledgements

This study was supported financially by the Commission of Science and Technology of Shanghai Municipality (No. 03DJ14006).

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