

Kinetic modelling of phenol hydroxylation using titanium and tin silicalite-1s: Effect of tin incorporation

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Abstract

Effects of tin incorporation in titanium silicalite-1 (TS-1) on the kinetic modelling of phenol hydroxylation to dihydroxybenzenes with aqueous hydrogen peroxide have been investigated. The modelling of the hydroxylation reaction was from the results of a batch reactor, minimizing mass transfer conditions. The kinetic analysis indicates that under the same reaction conditions, titanium-tin silicalite-1 (Ti-Sn-S-1) gave a higher phenol conversion rate than TS-1. This was attributed to the Sn active sites. Incorporation of tin influences the initiation of intermediate reactions of products with hydrogen peroxide. Tin increases the rate of benzoquinone conversion to tar; however, it does not affect hydroquinone and catechol reactions. A Langmuir–Hinshelwood-type mechanism model was used to fit the proposed phenol hydroxylation and parallel reactions of products with the observed rate data. The intrinsic kinetic constants were found to be proportional to the concentration of reactants and the Ti and Sn active sites. The surface reaction yielded the best fit of the model for reactions in the system. It however failed to predict the outcome of the catechol reaction using TS-1, in which the catechol adsorption on the Ti active site was rate-limiting. The model fitted to the experimental data generated in this study was determined to provide the best values for the kinetic parameters. The effect of temperature on the hydroxylation rate is also documented in further detail.

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1. Introduction

Hydroxylation of phenol (PH) has attracted considerable attention in the industry in recent years due to the products generated from this reaction, i.e. hydroquinone (HQ) and catechol (CT). These compounds are used in a broad range of applications, such as photographic developers, polymerization inhibitors, rubber antioxidants, food antioxidants, and pharmaceuticals [1]. Since Taramasso et al. reported a new invention of framework substituted microporous materials titanium silicalite-1 (TS-1) [2], a new route of PH hydroxylation using hydrogen peroxide (H₂O₂ or HP) as an oxidant was made possible [3]. The nature of solvents [4], the catalyst properties (external surface, pore size, and crystal size) [5,6], and the framework titanium content [7,8], have been identified as the key parameters for this

reaction. Consequently, the identification and characterization of active sites [9,10] or the experimental determination of the conversion and selectivity data [11,12] have been reported in the literatures. However, few studies have examined the mechanistic details of PH hydroxylation using a kinetic analysis. Such analysis is fundamental for determining the design and industrial operating conditions of an optimized large scale catalytic reactor.

An attempt was made by WilkenhÖner et al. to develop a kinetic rate expression for the PH hydroxylation reaction [6]. They monitored the rates of disappearance of PH and H₂O₂ and appearance of desired products, HQ and CT, and fitted the data with a power law model in which the reaction orders correspond to both reactant concentrations. They concluded that the pore structure and the external surface of TS-1 play an important role on the PH conversion and the product formation rates. However, statistical analyses of the experimental data generated using their models were not proven.

Recently we reported that a bimetallic framework titanium-tin silicalite-1 (Ti-Sn-S-1) performed with higher catalytic

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Nomenclature

C_i	concentration of the component “ i ” (mol l^{-1})
k, K	symbols used for kinetic constants
S_{BET}	catalyst surface area ($\text{m}^2 \text{g}^{-1}$)
t	reaction time (s)
T	reaction temperature ($^{\circ}\text{C}$)
W	catalyst weight (g)
X_i	partial conversion

activity for PH hydroxylation than TS-1 (at the same Si/Ti ratio), estimated 26% [13]. The optimal tin content provides for a faster adsorption of the reactants, especially H_2O_2 , due to a higher Lewis acid property of tin than titanium in silicalite-1 molecule. The same paper also reported experimental data showing the influence of the solvent, the catalyst pore structure, and the tin incorporation on the time evolution of the conversion and selectivity of the PH hydroxylation with dilute H_2O_2 . In this work, an extensive calculation was performed of the equilibrium concentration using a Langmuir–Hinshelwood approach. The scope of this paper is to investigate the effect of tin incorporated in TS-1 framework on the kinetics of PH hydroxylation and intermediate reactions of products compared with using TS-1. These estimations were made under the same conditions as mentioned in the previous report. The objectives of the present work are to combine the reported kinetic data and to reexamine the kinetic analysis in order to represent the time-dependent reaction rate and establish a plausible reaction mechanism for the selective hydroxylation of PH using TS-1 or Ti-Sn-S-1.

2. Experimental

2.1. Catalyst preparation and characterization

TS-1, obtained from National Chemical Laboratory (NCL), Pune, India, was prepared based on the literature recipe [11]. Ti-Sn-S-1 was synthesized according to the ref. [14]. The characterization data of these catalysts are shown elsewhere [13]. The surface area, porosity, UV, IR, and XRD spectra, crystallinity, tetrahedral tin and titanium location, acidity, etc., are documented.

2.2. PH hydroxylation and intermediate reaction of products

The hydroxylation reaction was carried out in a 100 ml, water jacketed, three-necked, glassflask fitted with a condenser and a mechanical stirrer. The stirring rate was kept constant and controlled at a speed ensuring intrinsic kinetic observation. The temperature was controlled by a thermostated water bath (LAUDA ecoline RE 206). To initiate the reaction, H_2O_2 (30 wt%, Aldrich) was added all at once to the mechanically well stirred aqueous solution of PH (99.5 wt%, Aldrich) which contained catalyst at the desired reaction temperature. Typically, 1 wt% of catalyst based on the total solution was used. Although,

most of the open and patent literature describes GC methods for analysis [3–5,7,8,11–13], our earlier study indicated that the GC methodology was not reliable. This is because a hot GC injection port can cause secondary reactions which will change the product composition. Therefore, in this study, the reaction products were collected and analyzed using a HPLC (Hewlett Packard, Series 1050). The HPLC was equipped with a C-18 column (Altima, Alltech) using 40 vol% of acetonitrile in 0.1 vol% of aqueous phosphoric acid solution as a mobile phase and a UV detector operating at 254 nm. The tar formation was calculated based on mass balance. The H_2O_2 consumption was determined by iodometric titration (ASTM Test Method D 2340-96).

For the concentration effects, the reactions were carried out with different molar ratios of PH to H_2O_2 as follows: 3 to 1, 2 to 1, 1 to 1, 1 to 2, and 1 to 3.

The temperature effects were studied by carrying out the reaction at different temperatures: 50, 60, 70, and 80°C .

The intermediate reactions of hydroxylation products were carried out in the same conditions as mentioned for PH except using HQ (>99 wt%, Aldrich), CT (>99 wt%, Aldrich), or benzoquinone (BQ, 98 wt%, Aldrich) instead.

3. Results and discussion

3.1. Mass transfer considerations

The effect of stirring rate on the rate of reaction was studied in the range of 600–1200 rpm under standard conditions. It was observed that the initial rate of PH hydroxylation was independent of the stirring rate above 800 rpm. Beyond 1000 rpm, a vortex flow pattern occurred. This indicates that the resistance to mass transfer from the liquid phase to the solid surface is absent at 800–1000 rpm. In order to ascertain the absence of pore diffusion, catalysts having different crystal sizes (particle sizes) in the range of 120–200 nm were tested for their initial hydroxylation rate, at 1000 rpm stirring rate. It was found that there was no affect in regards to particle size of the catalyst, on the initial rate of reaction. The effectiveness factor is unity. From this data, the conclusion was made that the intrinsic kinetics could be derived from the experimental data. Thus, all further experiments were carried out at stirring rate of 1000 rpm.

3.2. Effect of tin incorporation on PH hydroxylation

Catalytic activities on PH and H_2O_2 conversions compared when using TS-1 and Ti-Sn-S-1 are shown in Fig. 1. The results indicate that under the same conditions, Ti-Sn-S-1 shows considerably higher activity than TS-1. This result was obtained for every studied PH to H_2O_2 molar ratio; however, the selectivity of the desired products when using Ti-Sn-S-1 and TS-1 were almost the same, 60% to HQ and 35% to CT. Moreover, the conversions of PH and H_2O_2 with these two catalysts were strongly influenced by the initial concentrations and the reaction time while the distributions of the preferred products were roughly independent of these factors. In addition to HQ and CT, BQ and tar (TA) were produced in these systems, at an estimated 5% selectivity. This indicates that the tin incorporation affects

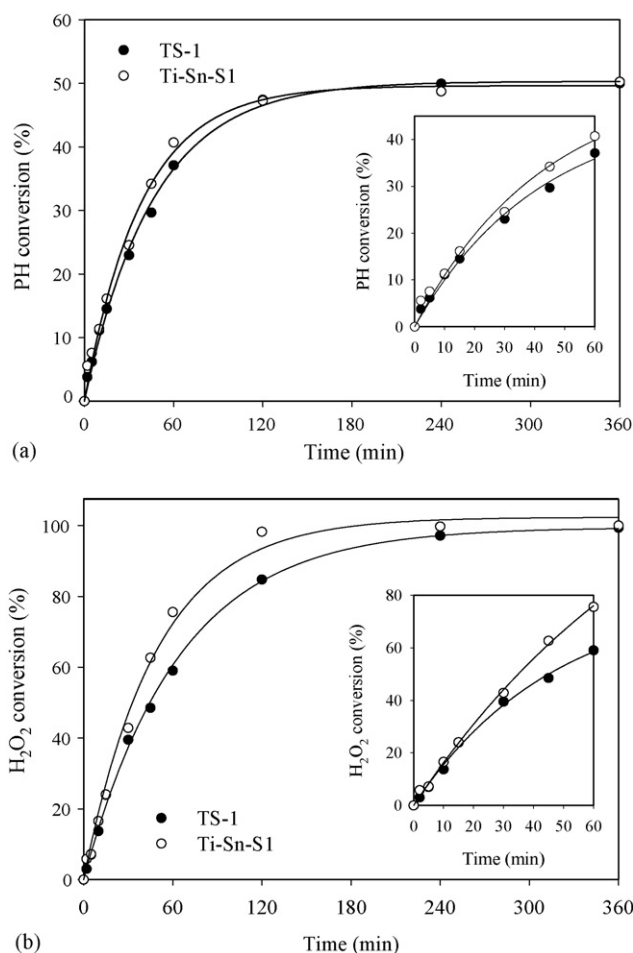


Fig. 1. Comparison of (a) PH and (b) H₂O₂ conversions using TS-1 and Ti-Sn-S-1 in water at 60 °C (PH:H₂O₂ = 2:1).

the PH and H₂O₂ conversion rates but not the overall product selectivity.

3.3. Effect of tin incorporation on the intermediate reactions of products

During PH hydroxylation, the products produced in the system are also active for reaction with H₂O₂ in the presence of catalyst. Fig. 2 shows the reaction of these products with H₂O₂ under the same conditions of PH hydroxylation.

Fig. 2(a and b) show the comparison results of BQ reactions with different H₂O₂ molar ratios using TS-1 and Ti-Sn-S-1, respectively, in water at 60 °C. BQ converted to TA with 100% selectivity over the range of the studied conditions with TS-1 and Ti-Sn-S-1. It is clearly seen that the conversion of BQ strongly depends on concentrations of both BQ and H₂O₂ but not reaction time. However, when using Ti-Sn-S-1 as a catalyst, BQ conversion was affected by the reactant concentrations more than using TS-1. Additionally, the reaction did not take place without H₂O₂ or a catalyst. It can be concluded from these results that tin incorporation only affects the BQ conversion but not the TA selectivity.

The reactions of HQ, using TS-1 and Ti-Sn-S-1 with different H₂O₂ molar ratios in water at 60 °C, were also studied. The

results are shown in Fig. 2(c and d). BQ was the only product produced during the reaction with TS-1 and Ti-Sn-S-1, despite very low HQ conversion. When using TS-1 as a catalyst, the reactant concentrations had more effect on HQ conversion than using Ti-Sn-S-1. The HQ conversions using TS-1 and Ti-Sn-S-1 were not influenced by the reaction time.

Fig. 2(e and f) shows the CT reactions using TS-1 and Ti-Sn-S-1 with different H₂O₂ molar ratios under the specified conditions. The reactions were only selective to TA in which TS-1 gave a higher CT conversion than Ti-Sn-S-1. Furthermore, the results indicated that CT conversions using TS-1 and Ti-Sn-S-1 were affected by reactant concentrations, but not the reaction time. It should be noted that the CT reaction did not occur in the absence of H₂O₂ or catalyst.

3.4. Effect of tar formation on the reaction rate

Although TA was highly produced from two reactions, BQ and CT (Fig. 2), it was not favored in the PH hydroxylation system. TA can plug catalyst pores resulting in lower catalyst activity [6], consequently retarding reaction rates. To verify this, the reactions of PH, BQ, HQ, and CT with H₂O₂ using spent catalysts (tar-plugged TS-1 and tar-plugged Ti-Sn-S-1) were carried out.

Fig. 3 shows the comparison of PH conversion with H₂O₂ (a) between using TS-1 and spent TS-1 and (b) between using Ti-Sn-S-1 and spent Ti-Sn-S-1, in water at 60 °C. PH conversion was extremely low with spent catalyst compared with fresh one. The reaction rate of PH significantly decreased with spent catalyst. Furthermore, it was found that no conversions were observed in the reactions of BQ, HQ, and CT with these spent catalysts (not shown). These results support our belief that the produced TA can plug the catalyst pores then decrease the catalyst activity, and therefore the reaction rate. Thus, a constant conversion in the reactions of intermediate products was observed (Fig. 2), allowing one the determination of constant overall product selectivity. Nevertheless, these intermediate reactions influence the reaction mechanism.

3.5. Kinetic models

3.5.1. Reaction pathway

From these results, the parallel-sequential reaction scheme can be drawn as shown in Scheme 1. PH reacts with H₂O₂, which then irreversibly converts to BQ, HQ, and CT. Subsequently these products change under hydroxylation conditions; BQ and CT change to TA, and HQ changes to BQ. Since the rates of H₂O₂ decomposition and non-catalytic PH hydroxylation are insignificant under the studied conditions, they are of little consequence to the kinetic model.

3.5.2. Reaction mechanism

Based on the reaction pathway, a series of mechanistic hypotheses were proposed. A possible mechanism for catalytic PH hydroxylation using TS-1 was formulated in which the products formed as a consequence of a sequence of elementary reaction steps, shown in Scheme 2. Both H₂O₂ (HP) and PH

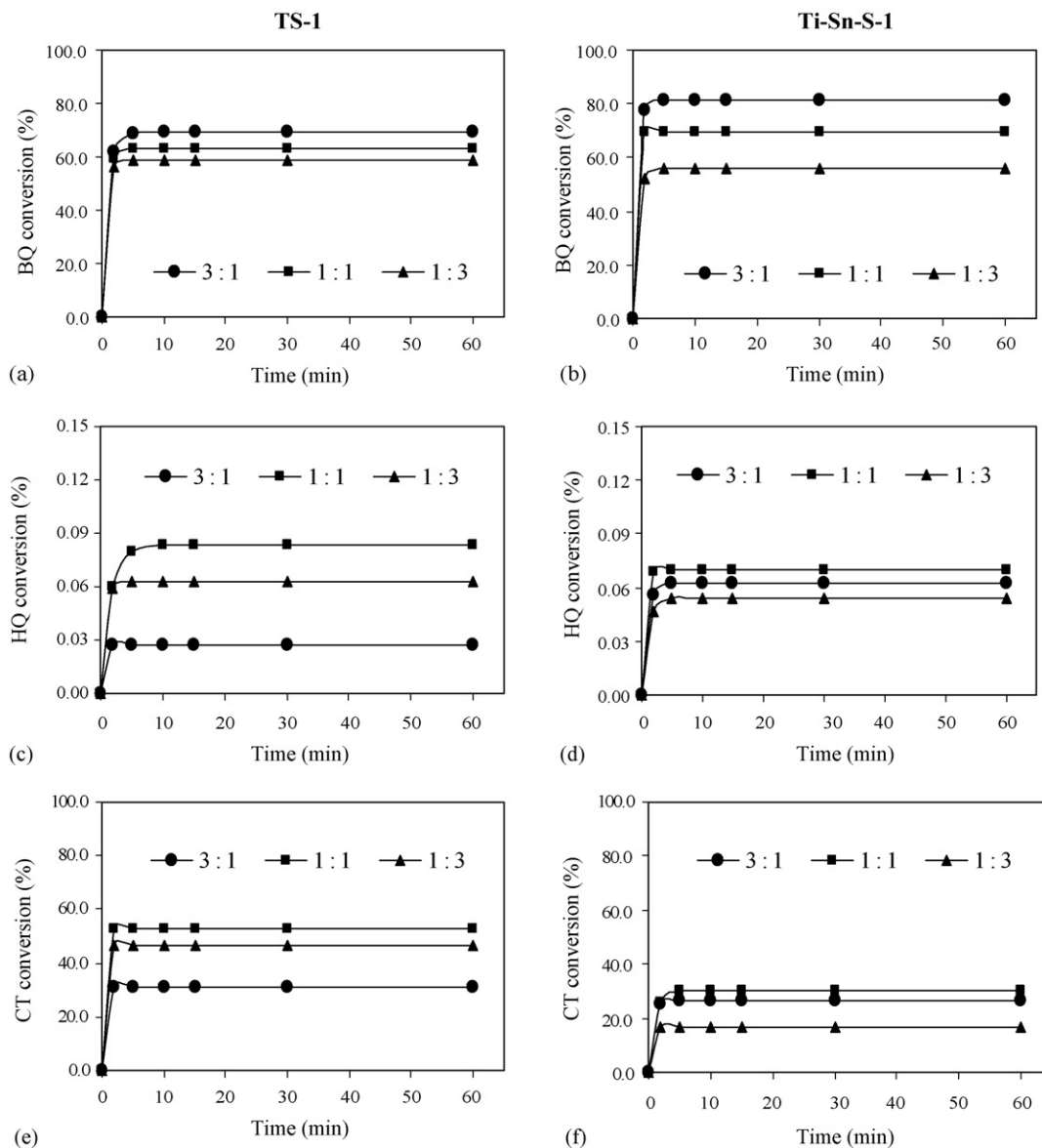


Fig. 2. Effect of tin incorporation on the intermediate reaction of products with different H_2O_2 molar ratios (reactant: H_2O_2) using TS-1 and Ti-Sn-S-1 in water at 60°C : (a and b) BQ reactions, (c and d) HQ reactions, (e and f) CT reactions.

adsorb on the Ti active site (S), step (1) and (2). The interaction of sites with HP gives a titanium-hydroperoxo group [9]. Subsequently, the interacted HP molecule further reacts with the activated PH to form the products, step (3) to step (5). The products are also activated by H_2O_2 under the hydroxylation conditions, step (6) to step (8) show these reactions. The catalytic cycle is finally ended with desorption of products in step (9) to step (12).

For Ti-Sn-S-1, the reaction mechanism is almost the same as TS-1 except the addition of the tin active site (S') adsorption with the reactants, PH and HP, and the irreversible reactions of these adsorbed active sites on the catalyst surface, as shown in Scheme 3.

The systematic efforts of kinetic model derivations using the classical Langmuir–Hinshelwood approach were conducted. The two hypotheses were introduced to evaluate the kinetic equations on a theoretical basis: (1) the existence of a rate-limiting

step and (2) the assumption of a stationary state approximation for the unstable intermediate appearing in the mechanism (Pseudo-Steady-State Hypothesis (PSSH)) application. In this work, we considered the adsorption or the surface reaction as the rate-limiting step as the rate of desorption for the product is very rapid, under the studied conditions.

For TS-1, the selective rate equation derived from the assumption that the adsorption of a reactant on the Ti active site is the rate-limiting step is: for HP adsorption as the rate-limiting step;

$$-r_i = \frac{k_i C_{\text{HP}}}{1 + K_{\text{IS}} C_i} \quad (1)$$

for PH (or BQ, HQ, and CT) adsorption as the rate-limiting step;

$$-r_i = \frac{k_i C_i}{1 + K_{\text{HPS}} C_{\text{HP}}} \quad (2)$$

where “ i ” is PH, BQ, HQ or CT and S is available Ti active site.

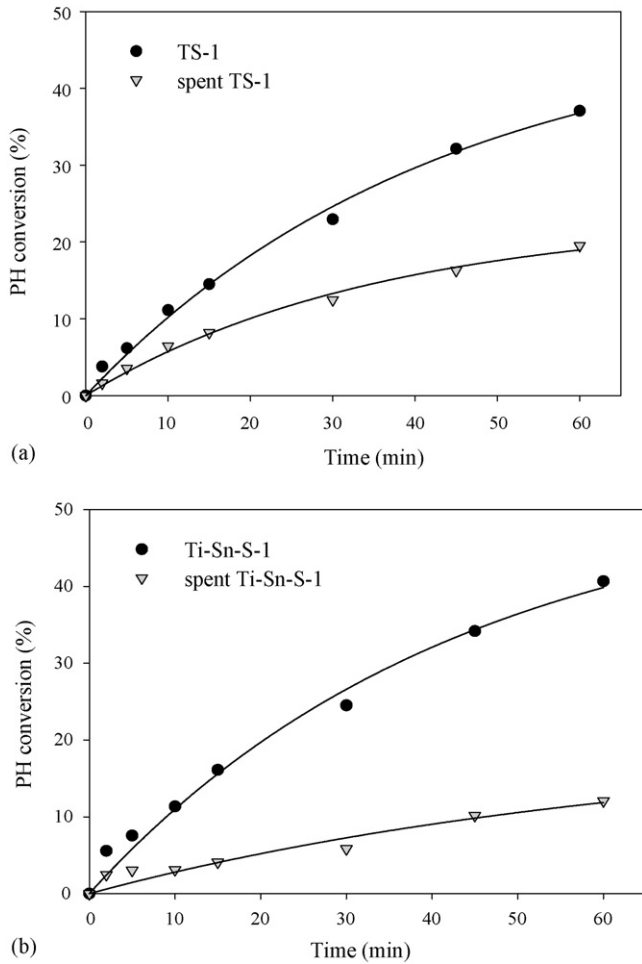
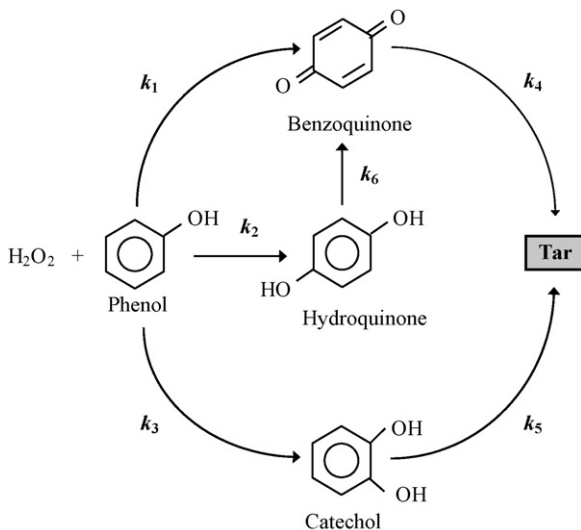
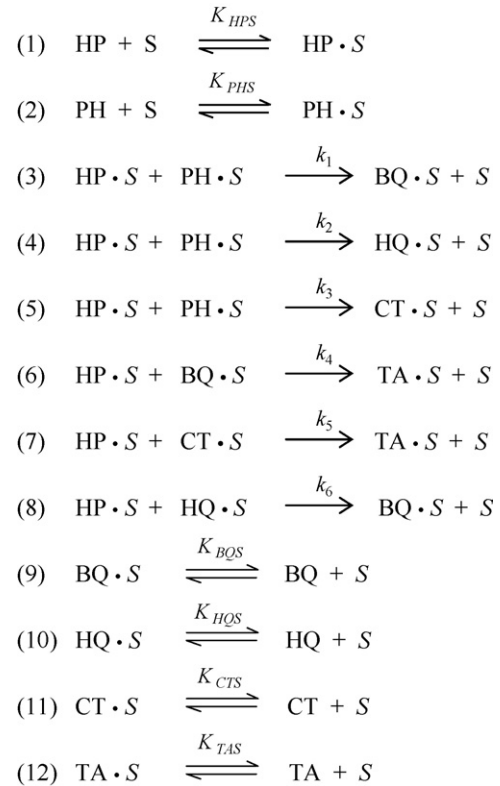


Fig. 3. Comparison of PH conversion with H_2O_2 (a) between using TS-1 (BET area $403 \text{ m}^2 \text{ g}^{-1}$, total pore volume $0.32 \text{ cm}^3 \text{ g}^{-1}$) and spent TS-1 (BET area $194 \text{ m}^2 \text{ g}^{-1}$, total pore volume $0.22 \text{ cm}^3 \text{ g}^{-1}$), and (b) between using Ti-Sn-S-1 (BET area $404 \text{ m}^2 \text{ g}^{-1}$, total pore volume $0.40 \text{ cm}^3 \text{ g}^{-1}$) and spent Ti-Sn-S-1 (BET area $232 \text{ m}^2 \text{ g}^{-1}$, total pore volume $0.37 \text{ cm}^3 \text{ g}^{-1}$), in water at 60°C (PH: $\text{H}_2\text{O}_2 = 2:1$).



Scheme 1. Reaction pathway for PH hydroxylation with H_2O_2 using TS-1 and Ti-Sn-S-1.



Scheme 2. Mechanistic scheme for PH hydroxylation and intermediate reactions of its products with H_2O_2 using TS-1: HP represents H_2O_2 and S represents the catalytic Ti active sites available.

For the assumption that both PH and HP are adsorbed on the active site and that surface reaction between adsorbed PH and adsorbed HP is the rate-limiting step, the following rate expression is obtained:

$$-r_i = \frac{k_i C_i C_{\text{HP}}}{(1 + K_{\text{HPS}} C_{\text{HP}} + K_{\text{IS}} C_i)^2} \quad (3)$$

where “ i ” is PH, BQ, HQ or CT and S is available Ti active site.

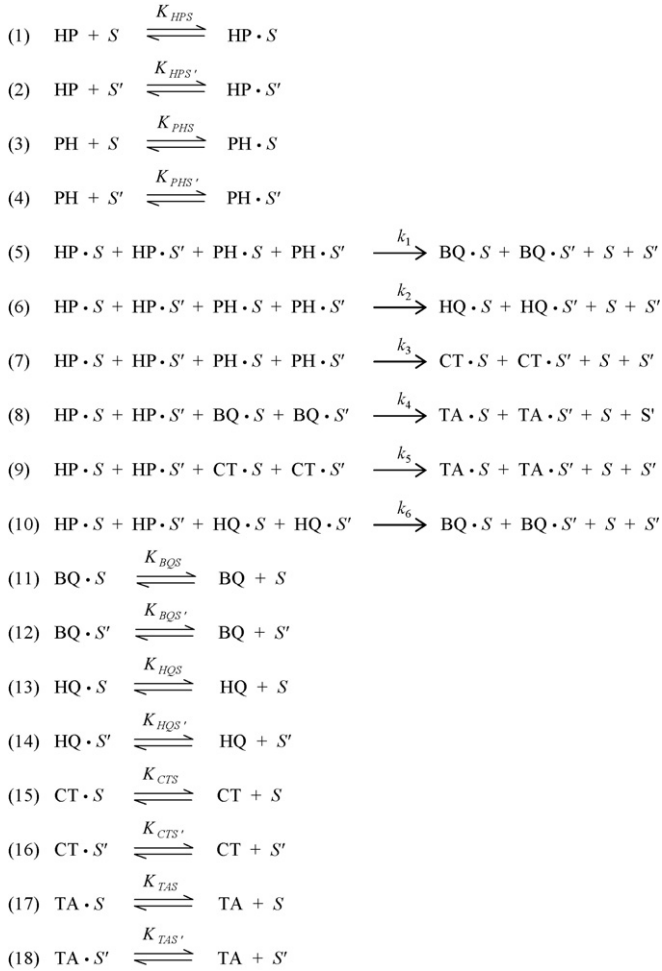
For Ti-Sn-S-1, the rate equation which the adsorption of reactant on the active site Ti and Sn is the rate-limiting step is similar to Eqs. (1) and (2). However, for surface reaction as the rate-limiting step, the adsorbed PH and HP on Sn active sites are also involved in the rate equation as follows:

$$-r_i = \frac{k_i C_i^2 C_{\text{HP}}^2}{(1 + K_{\text{HPS}} C_{\text{HP}} + K_{\text{IS}} C_i)^2 (1 + K_{\text{HPS}'} C_{\text{HP}} + K_{\text{IS}'} C_i)^2} \quad (4)$$

where “ i ” is PH, BQ, HQ or CT, S the available Ti active site, and S’ is available Sn active site.

3.5.3. Kinetic calculation

Designating conversions of PH through the reactions (1)–(3) (based on Scheme 1) are $X_{\text{PH,BQ}}$, $X_{\text{PH,HQ}}$, and $X_{\text{PH,CT}}$, respectively. The conversions of BQ and CT to TA as in reactions (4) and (5) (Scheme 1) are assigned as $X_{\text{BQ,TA}}$, and $X_{\text{CT,TA}}$, respectively. And for HQ conversion to BQ, reaction (6) in Scheme 1, is given by $X_{\text{HQ,BQ}}$. Concentration of components in the system



Scheme 3. Mechanistic scheme for PH hydroxylation and intermediate reactions of its products with H₂O₂ using Ti-Sn-S-1: HP represents H₂O₂, S represents the catalytic Ti active site available and S' represents the Sn active site available.

at any reaction time in batch reactor will be

$$C_{\text{PH}} = C_{\text{PH0}}(1 - X_{\text{PH,BQ}} - X_{\text{PH,HQ}} - X_{\text{PH,CT}}),$$

$$C_{\text{H}_2\text{O}_2} = C_{\text{H}_2\text{O}_20}(1 - X_{\text{H}_2\text{O}_2,\text{overall}})$$

$$C_{\text{BQ}} = C_{\text{PH0}}(X_{\text{PH,BQ}} - X_{\text{BQ,TA}}) + C_{\text{HQ}}X_{\text{HQ,BQ}},$$

$$C_{\text{HQ}} = C_{\text{PH0}}(X_{\text{PH,HQ}} - X_{\text{HQ,BQ}})$$

$$C_{\text{CT}} = C_{\text{PH0}}(X_{\text{PH,CT}} - X_{\text{CT,TA}}),$$

$$C_{\text{TA}} = C_{\text{BQ}}X_{\text{BQ,TA}} + C_{\text{CT}}X_{\text{CT,TA}}$$

Finally, the differential equation form for the reaction is

$$\frac{dC_i}{dt} = -r_i \times W \times S_{\text{BET}}$$

where C_i is the concentration of component “ i ” at any time (mol l^{-1}), r_i the reaction rate of component “ i ” ($\text{mol l}^{-1} \text{m}^{-2} \text{s}^{-1}$), W the catalyst weight (g), and S_{BET} is the catalyst surface area ($\text{m}^2 \text{g}^{-1}$).

3.5.4. Parameter estimation

The kinetic parameters, i.e. the rate constant (k_i) and the equilibrium constant (K_j), were determined based on the experimental data. The POLYMATH non-linear regression analysis [15] was applied for this purpose. The procedure is that assuming the common equilibrium constants and then determining the kinetic constant based on the simulation [16]. Further varying these values until find their best value that minimizes the sum of squares (σ^2). The criteria used to evaluate the best rate equation are based on the agreement between the calculated and experimentally obtained conversions and the statistic significance, F -test and t -test [17].

A summary of rate equations and parameters evaluated using POLYMATH program for the reactions using TS-1 and Ti-Sn-S-1 with the 95% confidence limits is shown in Tables 1–4. For PH, HQ, and BQ reactions using TS-1 (Tables 1 and 2), the Langmuir–Hinshelwood kinetic rate expression which involved

Table 1
Summary of rate expressions and kinetic parameters for the PH hydroxylation using TS-1

Eq.	Rate expression	Rate parameter	95% confidence limits	$F_{0.95}$ value	$t_{0.95}$ value
1	$r_1 = r_{\text{BQ}} = \frac{k_{\text{BQ}}C_{\text{PH}}C_{\text{HP}}}{(1+K_{\text{HPS}}C_{\text{HP}}+K_{\text{PHS}}C_{\text{PH}})^2}$	$k_{\text{BQ}} = k_1 = 3.05 \times 10^{-6}$ $K_{\text{HPS}} = 3.75$ $K_{\text{PHS}} = 5.56$	$\pm 9.59 \times 10^{-7}$ ± 3.42 ± 4.21	9.08×10^{-10}	0.56
2	$r_2 = r_{\text{HQ}} = \frac{k_{\text{HQ}}C_{\text{PH}}C_{\text{HP}}}{(1+K_{\text{HPS}}C_{\text{HP}}+K_{\text{PHS}}C_{\text{PH}})^2}$	$k_{\text{HQ}} = k_2 = 9.21 \times 10^{-5}$ $K_{\text{HPS}} = 3.75$ $K_{\text{PHS}} = 5.56$	$\pm 1.26 \times 10^{-5}$ ± 3.42 ± 4.21	9.38×10^{-12}	0.43
3	$r_3 = r_{\text{CT}} = \frac{k_{\text{CT}}C_{\text{PH}}C_{\text{HP}}}{(1+K_{\text{HPS}}C_{\text{HP}}+K_{\text{PHS}}C_{\text{PH}})^2}$	$k_{\text{CT}} = k_3 = 5.44 \times 10^{-5}$ $K_{\text{HPS}} = 3.75$ $K_{\text{PHS}} = 5.56$	$\pm 9.89 \times 10^{-6}$ ± 3.42 ± 4.21	4.03×10^{-11}	0.40
	$-r_{\text{PH,overall}} = \frac{k_{\text{PH}}C_{\text{PH}}C_{\text{HP}}}{(1+K_{\text{HPS}}C_{\text{HP}}+K_{\text{PHS}}C_{\text{PH}})^2}$	$k_{\text{PH}} = 1.55 \times 10^{-4}$ $K_{\text{HPS}} = 3.75$ $K_{\text{PHS}} = 5.56$	$\pm 1.61 \times 10^{-5}$ ± 3.42 ± 4.21	0.99	-1.29

Note: k_1 , k_2 , k_3 , and k_{PH} in the unit of $\text{l mol}^{-1} \text{m}^{-2} \text{s}^{-1}$; K_{HPS} and K_{PHS} in unit of l mol^{-1} ; tabulated $F_{0.95}$ value = 6.39; tabulated $t_{0.95}$ value = 3.18.

Table 2
Summary of rate expressions and kinetic parameters for the intermediate reactions of products using TS-1

Eq.	Rate expression	Rate parameter	95% confidence limits	$F_{0.95}$ value	$t_{0.95}$ value
4	$r_4 = -r_{BQ} = \frac{k'_{BQ} C_{BQ} C_{HP}}{(1 + K_{HP,S} C_{HP} + K_{BQ,S} C_{BQ})^2}$	$k'_{BQ} = k_4 = 3.39 \times 10^{-4}$ $K_{HP,S} = 3.75$ $K_{BQ,S} = 11.82$	$\pm 2.62 \times 10^{-4}$ ± 3.42 ± 5.34	5.33	1.91
5	$r_5 = -r_{CT} = \frac{k'_{CT} C_{CT}}{1 + K_{HP,S} C_{HP}}$	$k'_{CT} = k_5 = 2.17 \times 10^{-5}$ $K_{HP,S} = 3.75$	$\pm 1.78 \times 10^{-5}$ ± 3.42	0.56	2.05
6	$r_6 = -r_{HQ} = \frac{k'_{HQ} C_{HQ} C_{HP}}{(1 + K_{HP,S} C_{HP} + K_{HQ,S} C_{HQ})^2}$	$k'_{HQ} = k_6 = 6.95 \times 10^{-7}$ $K_{HP,S} = 3.75$ $K_{HQ,S} = 1.91$	$\pm 1.37 \times 10^{-7}$ ± 3.42 ± 1.86	0.54	-1.25

Note: k_4 and k_6 in the unit of $l \text{ mol}^{-1} \text{ m}^{-2} \text{ s}^{-1}$; k_5 in unit of $\text{m}^{-2} \text{ s}^{-1}$; $K_{HP,S}$, $K_{BQ,S}$, and $K_{HQ,S}$ in unit of $l \text{ mol}^{-1}$; tabulated $F_{0.95}$ value = 19.00; tabulated $t_{0.95}$ value = 4.30.

the surface reaction between the adsorbed HP and the adsorbed reactant “*r*” (PH, HQ or BQ) on the active sites Ti (HP·S, PH·S, HQ·S, and BQ·S) yielded the best statistical and meaningful data. The calculated $F_{0.95}$ value (comparing the regression sum of squares to the residual sum of squares) is the highest among the rival rate equations, which using different assumptions (Eqs. (1) and (2)), and exceeds the tabulated $F_{0.95}$ value. Furthermore, the calculated $F_{0.95}$ value comparing between the data from the chosen model and the replicated experiments ($F_{0.95}$ value in the table) is much lower than the tabulated $F_{0.95}$ value. This indicates that the selected model is statistically adequate and provides the parameters satisfying the physicochemical constraints, positive, and statistically, significantly different from zero.

Besides the $F_{0.95}$ values, the $t_{0.95}$ values (compared between the model predicted and the experimental data) are also shown in the tables. The calculated $t_{0.95}$ values for every rate equation are in the interval of the accepted $t_{0.95}$ value based on the statistical *t*-test table. This indicates that each of these kinetic parameters represent our experimental data.

For CT reaction using TS-1, the statistical significance exhibited that the adsorption of CT on the active site Ti as the rate-limiting step gave the best fit. This can be explained by limitation of CT adsorption on TS-1 due to the shape selectivity effect, the steric restrictions in the transition state and different diffusivity of *ortho*- and *para*-product due to the large cross-section of CT [18].

Table 3
Summary of rate expressions and kinetic parameters for the PH hydroxylation using Ti-Sn-S-1

Eq.	Rate expression	Rate parameter	95% confidence limits	$F_{0.95}$ value	$t_{0.95}$ value
1	$r_1 = r_{BQ} = \frac{k_{BQ} C_{PH}^2 C_{HP}^2}{(1 + K_{HP,S} C_{HP} + K_{PH,S} C_{PH})^2 (1 + K_{HP,S'} C_{HP} + K_{PH,S'} C_{PH})^2}$	$k_{BQ} = k_1 = 4.50 \times 10^{-3}$ $K_{HP,S} = 3.75$ $K_{PH,S} = 5.56$ $K_{HP,S'} = 9.63$ $K_{PH,S'} = 17.34$	$\pm 1.50 \times 10^{-3}$ ± 3.42 ± 4.21 ± 9.48 ± 15.57	1.74×10^{-8}	0.47
2	$r_2 = r_{HQ} = \frac{k_{HQ} C_{PH}^2 C_{HP}^2}{(1 + K_{HP,S} C_{HP} + K_{PH,S} C_{PH})^2 (1 + K_{HP,S'} C_{HP} + K_{PH,S'} C_{PH})^2}$	$k_{HQ} = k_2 = 1.10 \times 10^{-1}$ $K_{HP,S} = 3.75$ $K_{PH,S} = 5.56$ $K_{HP,S'} = 9.63$ $K_{PH,S'} = 17.34$	$\pm 2.67 \times 10^{-2}$ ± 3.42 ± 4.21 ± 9.48 ± 15.57	1.09×10^{-10}	-0.55
3	$r_3 = r_{CT} = \frac{k_{CT} C_{PH}^2 C_{HP}^2}{(1 + K_{HP,S} C_{HP} + K_{PH,S} C_{PH})^2 (1 + K_{HP,S'} C_{HP} + K_{PH,S'} C_{PH})^2}$	$k_{CT} = k_3 = 6.31 \times 10^{-2}$ $K_{HP,S} = 3.75$ $K_{PH,S} = 5.56$ $K_{HP,S'} = 9.63$ $K_{PH,S'} = 17.34$	$\pm 1.76 \times 10^{-2}$ ± 3.42 ± 4.21 ± 9.48 ± 15.57	6.92×10^{-11}	0.99
	$-r_{PH,overall} = \frac{k_{PH} C_{PH}^2 C_{HP}^2}{(1 + K_{HP,S} C_{HP} + K_{PH,S} C_{PH})^2 (1 + K_{HP,S'} C_{HP} + K_{PH,S'} C_{PH})^2}$	$k_{PH} = 1.82 \times 10^{-1}$ $K_{HP,S} = 3.75$ $K_{PH,S} = 5.56$ $K_{HP,S'} = 9.63$ $K_{PH,S'} = 17.34$	$\pm 1.37 \times 10^{-1}$ ± 3.42 ± 4.21 ± 9.48 ± 15.57	1.23	1.35

Note: k_1 , k_2 , k_3 and k_{PH} in the unit of $l^3 \text{ mol}^{-3} \text{ m}^{-2} \text{ s}^{-1}$; $K_{HP,S}$, $K_{HP,S'}$, $K_{PH,S}$, and $K_{PH,S'}$ in unit of $l \text{ mol}^{-1}$; tabulated $F_{0.95}$ value = 6.39; tabulated $t_{0.95}$ value = 3.18.

Table 4
Summary of rate expressions and kinetic parameters for the intermediate reactions of products using Ti-Sn-S-1

Eq.	Rate expression	Rate parameter	95% confidence limits	$F_{0.95}$ value	$t_{0.95}$ value
4	$r_4 = -r_{BQ} = \frac{k'_{BQ} C_{BQ}^2 C_{HP}^2}{(1 + K_{HPS} C_{HP} + K_{BQS} C_{BQ})^2 (1 + K_{HPS'} C_{HP} + K_{BQS'} C_{BQ})^2}$	$k'_{BQ} = k_4 = 5.33 \times 10^{-1}$ $K_{HPS} = 3.75$ $K_{BQS} = 11.82$ $K_{HPS'} = 9.63$ $K_{BQS'} = 3.34$	$\pm 3.56 \times 10^{-1}$ ± 3.42 ± 5.34 ± 9.48 ± 1.58	1.24	1.99
5	$r_5 = -r_{CT} = \frac{k'_{CT} C_{CT}^2 C_{HP}^2}{(1 + K_{HPS} C_{HP} + K_{CTS} C_{CT})^2 (1 + K_{HPS'} C_{HP} + K_{CTS'} C_{CT})^2}$	$k'_{CT} = k_5 = 1.58 \times 10^{-1}$ $K_{HPS} = 3.75$ $K_{CTS} = 2.75$ $K_{HPS'} = 9.63$ $K_{CTS'} = 1.49$	$\pm 2.80 \times 10^{-2}$ ± 3.42 ± 1.86 ± 9.48 ± 1.46	2.00	-0.36
6	$r_6 = -r_{HQ} = \frac{k'_{HQ} C_{HQ}^2 C_{HP}^2}{(1 + K_{HPS} C_{HP} + K_{HQS} C_{HQ})^2 (1 + K_{HPS'} C_{HP} + K_{HQS'} C_{HQ})^2}$	$k'_{HQ} = k_6 = 1.82 \times 10^{-4}$ $K_{HPS} = 3.75$ $K_{HQS} = 1.91$ $K_{HPS'} = 9.63$ $K_{HQS'} = 0.17$	$\pm 8.09 \times 10^{-5}$ ± 3.42 ± 1.86 ± 9.48 ± 0.13	2.76	-2.10

Note: k_4 , k_5 , and k_6 in the unit of $l^3 \text{ mol}^{-3} \text{ m}^{-2} \text{ s}^{-1}$; K_{HPS} , $K_{HPS'}$, K_{BQS} , $K_{BQS'}$, K_{CTS} , $K_{CTS'}$, K_{HQS} , and $K_{HQS'}$ in unit of $l \text{ mol}^{-1}$; tabulated $F_{0.95}$ value = 19.00; tabulated $t_{0.95}$ value = 4.30.

Using Ti-Sn-S-1 as a catalyst for the PH hydroxylation, the Langmuir–Hinshelwood rate expression with the surface reaction between the adsorption of PH and HP on the active sites Ti and Sn, PH·S, PH·S', HP·S, and HP·S', gave the best statistically adequate parameters (Table 3). Additionally, the surface reaction as the rate-determining step provided the best results for the intermediate reactions of products using Ti-Sn-S-1 as a catalyst (Table 4). For CT reaction with Ti-Sn-S-1, the tin incorporation decreases the limit of CT adsorption due to the increasing of catalyst pore size [13], thus less shape selectivity effect than using TS-1.

Fig. 4 shows the parity plot of the fractional conversion of PH: (a) with TS-1 and (b) with Ti-Sn-S-1. It shows excellent agreement over the range of PH conversions when random deviation from the diagonal line is observed. These results confirm the absence of systematic error in the analysis.

Fig. 5 shows the concentration plots of the components in the system during the reaction with TS-1 and Ti-Sn-S-1 under standard conditions compared between the values from the model prediction and the experimental data. The results show a good fit between these two data confirming that the kinetic model can describe the catalytic PH hydroxylation with these two catalysts. However, some deviations at high conversion are visible. A possible explanation for such behavior is that the kinetic resolution was not accounted by the model, only the primary reactions were considered while the secondary reactions were neglected.

3.6. Effect of tin incorporation on the kinetics of PH hydroxylation and the intermediate reactions of products

Tin incorporation in TS-1 framework enhanced PH hydroxylation rate through the higher adsorptions of PH and HP on the tin active sites than the titanium ones, as a result of kinetic analysis

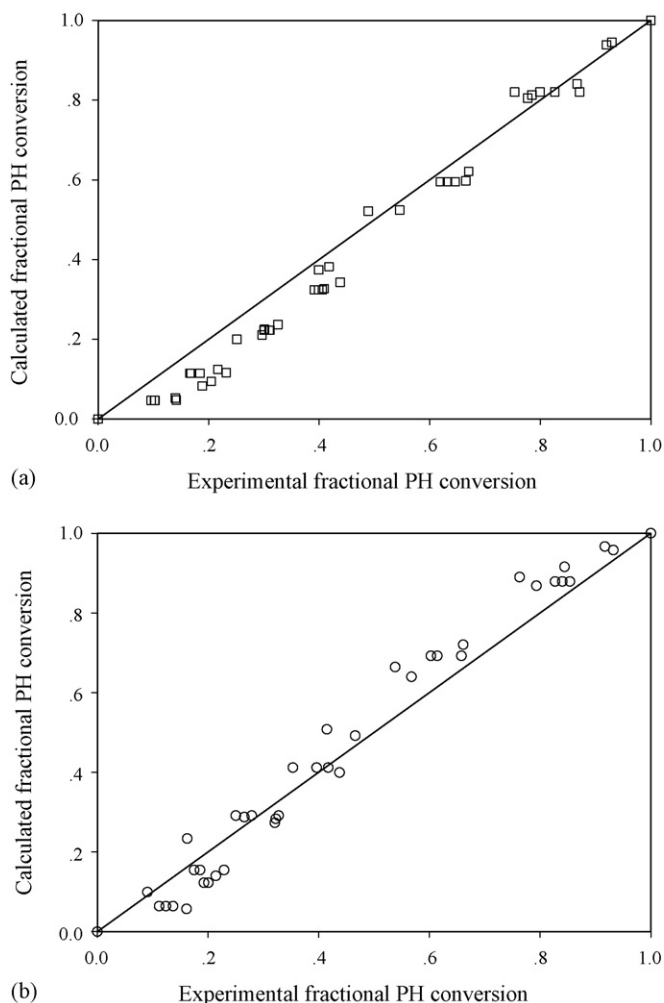


Fig. 4. Parity plot for the fractional PH conversion (a) with TS-1 and (b) with Ti-Sn-S-1.

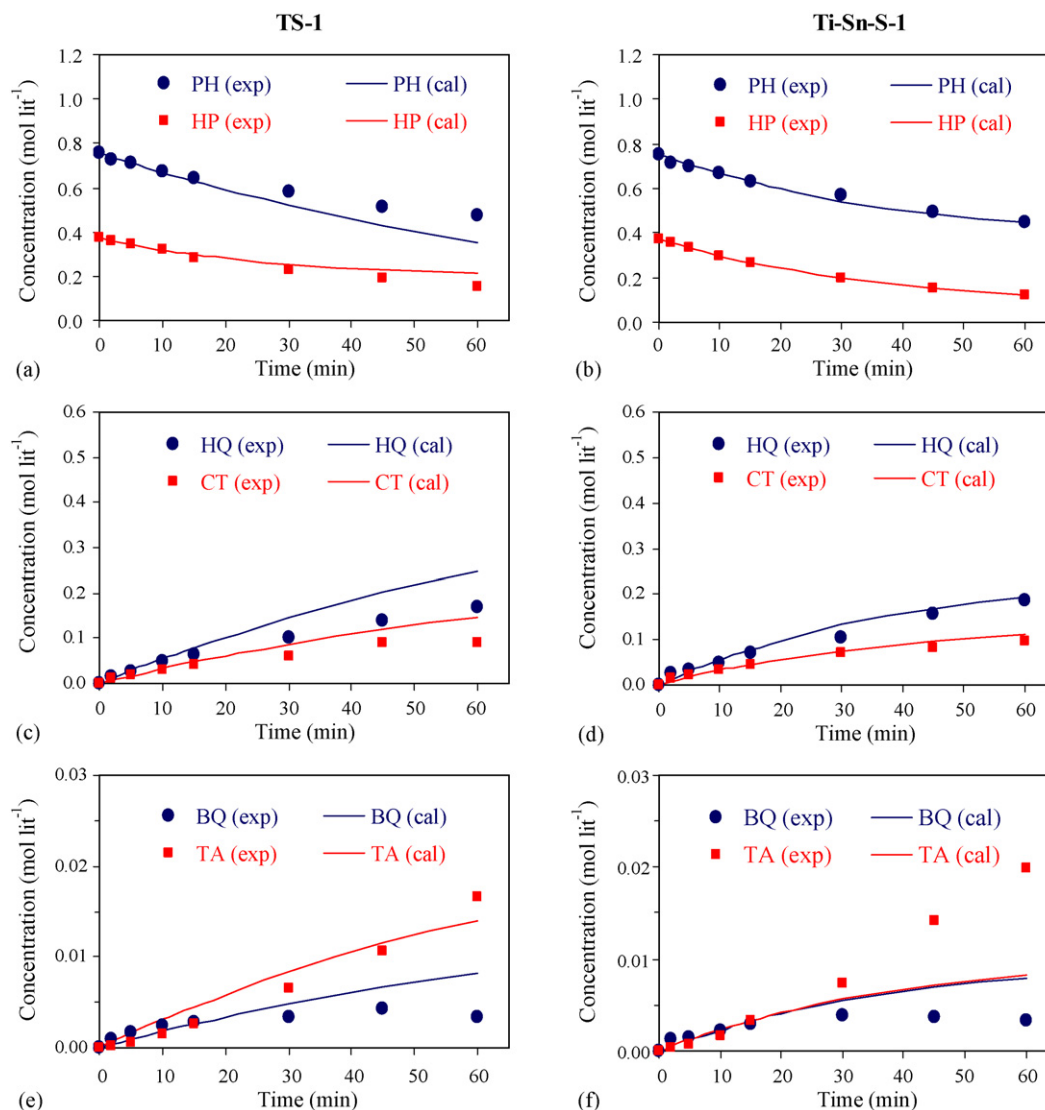


Fig. 5. Comparison of model predictions (solid line) with the experimental data (open line) of components in PH hydroxylation system using TS-1 and Ti-Sn-S-1 in water at 60 °C, 60 min (PH:H₂O₂ = 2:1): (a and b) for reactants, (c and d) for desired products, and (e and f) for by-products.

(Tables 1 and 3). Namely, the two comparisons of $K_{HP,S'} > K_{HP,S}$ and $K_{PH,S'} > K_{PH,S}$ are the important keys. Not only the equilibrium constants but also the kinetic constants are quite higher on the Ti-Sn-S-1 than those on TS-1. The value of k_1 in Table 3 is 1000 times higher than k_1 in Table 1. This shows that the incorporation of tin enhanced the reaction between the adsorbed HP and PH, not only the adsorption. These are logically provided by the Langmuir–Hinshelwood like models.

Tin incorporation in TS-1 framework also influenced the rate of intermediate reactions of products. For BQ reaction using TS-1, the rate of reaction strongly depends on the adsorption of BQ on the titanium active site ($K_{BQ,S}$) (Table 2). When tin was incorporated, an increase in HP adsorption on the tin active sites played an effect. Furthermore, it was observed that the value of k_4 in Table 4 was much higher than that of k_4 in Table 2. This indicates that a higher BQ conversion when Ti-Sn-S-1 was used instead TS-1 (Fig. 2) resulted from a higher adsorption of BQ and HP and a higher reaction between these adsorbed reactants.

For CT reaction using TS-1, the reaction rate is mainly influenced by the adsorption of HP on the titanium active site ($K_{HP,S}$ in Table 2) and the concentration of CT, due to the limitation of CT adsorption. When tin was incorporation in TS-1, the adsorption of CT was fewer limits. However, the rate of CT reaction using TS-1 was higher than using Ti-Sn-S-1 (Fig. 2). This suggests that the higher adsorptions of CT and HP on the tin active sites retard the reaction of CT.

For HQ reaction, HQ adsorption on the titanium active sites is lower than that on the tin ones, $K_{HQ,S} > K_{HQ,S'}$. However, these two values are small giving that the reaction rate of HQ was very little.

3.7. Effect of temperature and activation energy

The effect of temperature on the hydroxylation of PH using TS-1 and Ti-Sn-S-1 was also investigated. The reactions were carried out using 2 to 1 of PH to H₂O₂ molar ratio in water at

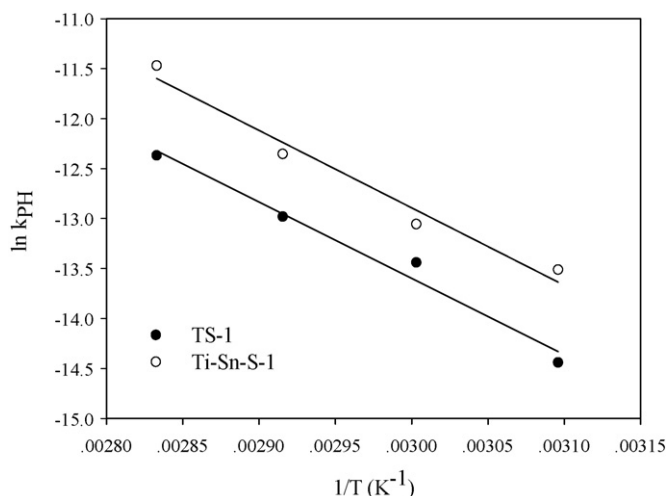


Fig. 6. Arrhenius plot of the overall rate constant “ k_{PH} ” for the PH hydroxylation with H_2O_2 (PH: H_2O_2 = 2:1) using TS-1 and Ti-Sn-S-1 in water.

different temperatures between 50 and 80 °C. The result shows that the conversion of PH increased with the increasing of the temperature due to a higher H_2O_2 activation at high temperature. The influence of reaction temperature on the reaction rate described as the Arrhenius expression:

$$k_{PH,overall} = k_{PH,f} \exp\left(\frac{-E_{a0}}{RT}\right) \quad (5)$$

where $k_{PH,f}$ is the pre-exponential factor and E_{a0} is the apparent activation energy is shown in Fig. 6. From the Arrhenius plot, the straight line represents the linear fit of the data points estimated E_{a0} for PH hydroxylation using TS-1 and Ti-Sn-S-1 equals to 63.5 and 64.3 kJ mol^{-1} , respectively.

4. Conclusion

In summary, TS-1 and Ti-Sn-S-1 are highly active and selective for PH hydroxylation and the reactions of intermediate products. Tin incorporation in TS-1 increases the rate of PH and BQ conversions; however, it does not for the HQ and CT ones. TA formed during the reaction of BQ and CT can plug the catalyst pores then decrease the catalyst activity, and consequently retard all reaction rates. As a result, the overall product selectivity was constant. A possible reaction pathway proposed based on the experimental results indicates that the PH hydroxylation is a complex reaction; PH was permanently hydroxylated to BQ, HQ, and CT, then BQ and CT converted under the same conditions to TA while HQ changed to BQ. The maximum reaction rate is the formation of TA from BQ and CT; however, as produced TA plugs the catalyst pores, these reaction rates are declined. According to the statistical analysis, the Langmuir–Hinshelwood mechanism as the surface reaction is the rate-limiting step. It yields the best model fitting for almost

all reaction with TS-1 and Ti-Sn-S-1 with exception for the CT reaction where the adsorption of CT on the surface of TS-1 is the rate-limiting step. The proposed reaction mechanisms, the established kinetic equations, and all parameters can be accepted for representing the experimental data. Based on the kinetic model, tin affects the PH hydroxylation by increasing the adsorption of reactants (HP and PH) and the reaction between these adsorbed reactants. However, tin incorporation lowered the adsorption of BQ, CT, and HQ, and retarded the reactions of HQ and CT. PH hydroxylation reaction with TS-1 and Ti-Sn-S-1 strongly depends on the reaction temperature. The apparent activation energy of this reaction is estimated 64 kJ mol^{-1} for using TS-1 and Ti-Sn-S-1.

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References

- [1] L. Krumenacker, M. Costantini, P. Pontal, J. Sentenac, Hydroquinone, resorcinol, and catechol, in: J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 13, fourth ed., John Wiley and Sons, Inc., New York, 1991, p. 1008.
- [2] M. Taramasso, G. Perego, B. Notari, US Patent 4,101,501 (1983).
- [3] A. Esposito, M. Taramasso, C. Neri, F. Buonomo, UK Patent 2,116,974 (1985).
- [4] A. Tuel, S. Moussa-Khouzami, Y. Ben Taarit, C. Naccache, J. Mol. Catal. 68 (1991) 45.
- [5] J.A. Marten, Ph. Buskens, P.A. Jacobs, A. van der Pol, J.H.C. van Hooff, C. Ferrini, H.W. Kouwenhoven, P.J. Kooyman, H. van der Bekkum, Appl. Catal. A 99 (1993) 71.
- [6] U. WilkenhÖner, G. Langhendries, F. van Laar, G.V. Baron, D.W. Gammon, P.A. Jacobs, E. van Steen, J. Catal. 203 (2001) 201.
- [7] T. Tatsumi, M. Nakamura, S. Negeshi, H. Tominaga, J. Chem. Soc., Chem. Commun. (1990) 476.
- [8] D.R.C. Huybrechts, P. Buskens, P.A. Jacobs, J. Mol. Catal. 71 (1992) 129.
- [9] G. Bellussi, A. Carati, M.G. Clerici, G. Maddinelli, R. Millini, J. Catal. 133 (1992) 220.
- [10] B. Notari, Catal. Today 18 (1993) 163.
- [11] A. Thangaraj, R. Kumar, S.P. Mirajkar, P. Ratnasamy, J. Catal. 130 (1990) 1.
- [12] A. Thangaraj, R. Kumar, P. Ratnasamy, J. Catal. 131 (1991) 294.
- [13] R. Klaewkla, S. Kulprathipanja, P. Rangsunvigit, T. Rirkosomboon, L.T. Nemeth, Chem. Commun. (2003) 1500.
- [14] L.T. Nemeth, G.J. Lewis, R.R. Rosin, US Patent 5,780,654 (1998).
- [15] <http://www.polymath-software.com>.
- [16] H.S. Fogler, Elements of Chemical Reaction Engineering, third ed., Prentice-Hall International Inc., 1999, pp. 252–255.
- [17] G.F. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, second ed., John Wiley and Son Inc., New York, 1990, pp. 94–105.
- [18] C. Perego, A. Carati, P. Ingallina, M.A. Mantegazza, G. Bellussi, Appl. Catal. A (2001) 63.