



Research Article

Oxidation of Catechol using Titanium Silicate (TS-1) Catalyst: Modeling and Optimization

Sonali Sengupta*, Debarpita Ghosal, Jayanta K. Basu

Department of Chemical Engineering, Indian Institute of Technology Kharagpur, 721302, India

Received: 22nd April 2013; Revised: 25th October 2013; Accepted: 1st November 2013

Abstract

The oxidation of catechol was studied in an eco-friendly process with commercial titanium silicate-1 (TS-1) catalyst and hydrogen peroxide as oxidant in absence of all mass transfer effects. The process was optimized by Box-Behnken design in terms of three independent process variables such as reaction temperature, moles of hydrogen peroxide per mole of catechol and catalyst amount whose optimum values of the process variables were found to be 60 °C, 13.2 and 1.24 g respectively for maximum conversion of 75.8 %. The effects of different process parameters such as mole ratio of hydrogen peroxide to catechol, catalyst particle size, catalyst amount, temperature and reaction time were studied. A pseudo first order kinetic model was fitted with the experimental rate data. The apparent activation energy for the reaction was found to be 11.37 kJ/mole. © 2013 BCREC UNDIP. All rights reserved

Keywords: Catechol; oxidation; TS-1; Box-Behnken design; kinetic study

How to Cite: Sengupta, S., Ghosal, D., Basu, J.K. (2013). Oxidation of Catechol using Titanium Silicate (TS-1) Catalyst: Modeling and Optimization. *Bulletin of Chemical Reaction Engineering & Catalysis*, 8 (2): 167-177. (doi:10.9767/bcrec.8.2.4759.167-177)

Permalink/DOI: <http://dx.doi.org/10.9767/bcrec.8.2.4759.167-177>

1. Introduction

The green process development includes the manufacture of fine chemicals as well as the reduction or elimination of formation of the hazardous and undesirable byproducts [1-5]. Different catalysts, solvents, oxidizing or reducing agents and process conditions, alone or in combination, can help to make a process environmentally green.

Titanium silicate catalyst, is an excellent oxidation catalyst for different fine chemicals production in combination with hydrogen peroxide as green

oxidizing agent [6-8]. This is the most versatile catalyst in oxidation reactions like epoxidation of olefins, e.g. allyl chloride [9], the hydroxylation of aromatic hydrocarbons [10], oxidation of aliphatic C-H bonds, i.e., saturated hydrocarbons [11], the ammoxidation of ketones [12]. TS-1 can also be used for clean processes like the oxidation of secondary amines, alcohols, thioethers and sulfoxides with hydrogen peroxide as the oxidant [13-15]. Eco-friendly synthesis of heterocyclic *N*-oxides using 30% H₂O₂ and TS-1 catalyst gives a good yield with water as the by-product [16].

The liquid phase oxidation of 2-octanol was studied and kinetics of the reaction was reported [17]. The oxidation of catechol was studied in presence of metalloenzymes as a catalyst [18]. The aerobic oxidation of catechol by polyphenol oxidase as

* Corresponding Author.

E-mail: sonalis.iitkgp@gmail.com (S. Sengupta)

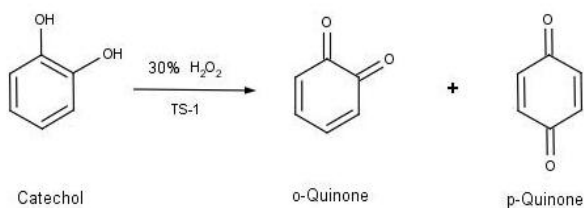
catalyst in presence of aniline gives ortho-quinone as the initial product [19]. Catechol oxidation was studied using Cu(II) complex as catalyst using molecular oxygen [20]. Silica supported Cu(II) complex was reported as a catalyst for the aerial oxidation of catechol [21]. Oxidation of catechol in the presence of H₂O₂ was studied using ruthenium complexes as catalysts [22].

The use of TS-1 as catalyst for the oxidation of alkanes, alkenes and aromatic hydrocarbons with hydrogen peroxide were carried out under mild conditions [23]. Large pore Ti-beta zeolite catalyst has been used for the oxidation of cyclic, secondary and primary alcohols in presence of hydrogen peroxide as the oxidizing agent [24].

The hydroxylation of phenol by using TS-1 as the catalyst with hydrogen peroxide produces the ortho- and para-isomers of dihydroxybenzene [25]. The application of TS-1 as oxidation catalyst was first industrially realized process by Enichem Company for conversion of phenol [26]. Moreover, TS-1 has wide range of applications in food industries and fine chemical industries where the route of oxidation of catechol is an eco-friendly method [27].

The modeling and optimization of the oxidation reaction of catechol by using titanium silicate-1 has been done in this work which is not cited in literature till now. Kinetic model which is used here is an empirical one. Statistical analysis of the data put a new light on this work.

The objective of the present study is to investigate the oxidation of catechol using commercial TS-1 as catalyst and hydrogen peroxide (30%) as oxidizing agent. The reaction is shown in Scheme 1.



Scheme 1. Oxidation of catechol with TS-1 catalyst

The process is eco-friendly as no organic solvent is used. Catechol gives quinone after oxidation reaction. Quinone is an important organic compound, used mostly in the production of hydrogen peroxide, biochemicals, dye intermediates and other different organic reagents. The catalyst TS-1 is characterised by using standard methods such as BET surface area analysis, XRD and SEM. The effects of different process parameters on conversion have also been studied. Response surface methodology

(RSM) with the Box-Behnken design with respect to three process parameters such as reaction temperature, moles of hydrogen peroxide per mole of catechol and catalyst amount is utilized for the optimization of conversion.

The Response Surface Methodology (RSM) is a statistical method, which is a useful technique for analyzing the process including the prediction of response which is under the influence of several variables and finally, the optimization of response variable through design of experiment (DOE). In this process, a series of preliminary experimental runs are conducted by changing the input variables in order to identify the ranges of the input variables and the reasons for changes in the output variable or response. The probable upper and lower limits of the input variables are determined. The minimum number of software prescribe experimental runs are to be conducted to generate the responses as function of different level of input variables. The data is to be fitted with a quadratic polynomial. The surface represented by a function of two input variables is called a response surface. The response can be represented either in the three-dimensional space with a particular shape of the response surface or as contour plots. The optimal design of experiments is the minimization of the objective function, which is a sum of square of deviation between model-predicted and experimental values.

2. Experimental

2.1. Materials

Catechol was purchased from Himedia Laboratories Pvt Ltd. India. Hydrogen peroxide (30%, volume/volume) was supplied by Merck Specialities Pvt. Ltd., India. Titanium Silicate TS-1 (1.5mm extrudate) was supplied by Sud Chemie, Ltd., India.

2.2. Apparatus and Experimental Procedure

A three-necked cylindrical glass vessel of 150 cm³ volume and internal diameter 5.5 cm was used for the reaction. The vessel reactor is fitted with a glass stirrer, a thermometer and a reflux condenser. The whole arrangement is housed in a water-bath whose temperature was controlled with ± 1 °C variation by using a digital controller cum indicator.

A typical experiment was carried out by using 0.0182 mol of catechol dissolved in 40 ml water and 10 ml hydrogen peroxide (30%) (0.1161 mol H₂O₂), using 0.5 g catalyst, at 40 °C. The reaction mixture was stirred at 1000 rpm. The sample was withdrawn from the reaction mixture periodically and analysed using High Performance Liquid Chroma-

tography (HPLC) equipped with an Agilent SB C18 column (length: 250 mm, diameter: 4.6 mm, packing size: 5 μ). The pump and detector used were Perkin Elmer Series 200 pump and Perkin Elmer Series 200 UV/VIS detector. The mobile phase used was a mixture of methanol and water (1:1v/v) at a flow rate of 1 ml/min and detection was performed at 280 nm. The conversion of catechol was calculated by the following way: $X_A = (C_{A0} - C_A) / C_{A0}$, where, X_A is the conversion, C_{A0} and C_A are the initial and final concentration of reactant A in the reaction, respectively. The optimum reaction time for maximum conversion was determined, but as the by-product formation (p-quinone) is so negligible, that the selectivity plot of the product is almost the same type as the conversion plot.

2.3. Design of Experiment with Box-Behnken Method

The conversion of catechol was optimized by response surface methodology (RSM) using Box-Behnken design with three effective variables such as, reaction temperature, A, moles of hydrogen peroxide per mole of catechol, B and catalyst amount, C by using statistical software Design-Expert 8.0.1. The response surface methodology with factorial design is an empirical optimization technique used to evaluate the relationship between a set of controllable experimental factors and observed results and it involves three major steps (i) performing statistically designed experiments, (ii) estimating the coefficients in a mathematical model, and (iii) predicting the response and checking the adequacy of the model [28-34]. Three independent variables with their levels of factorial design are presented in Table 1.

A quadratic statistical model was determined and optimized by fitting the experimental results through response surface methodology (RSM) to maximize the catechol conversion. The quadratic equation in general form which is widely used in statistical optimization process is as follows:

$$z = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (1)$$

where, z is the response and β_0 , β_i , β_{ii} , and β_{ij} are coefficients of the intercept, linear, square and interaction effects, respectively. The parameters are $x_1=A$, $x_2=B$ and $x_3=C$ as per in Table 1. It is also possible to locate the region of interest where the desirable response (optimum condition) lies in, by simultaneous variation of several factors.

3. Results and Discussion

The commercial TS-1 was used as the catalyst for the oxidation of catechol with 30 % H₂O₂ as an oxidizing agent. The products formed are two isomers, ortho-quinone (1,2 benzoquinone) and para-quinone (1,4 benzoquinone). Ortho-quinone is observed to be the major product between the two. Optimization of the process is done to find out the maximum conversion of the substrate and finally the optimal values of the selected process parameters were obtained accordingly. The commercial TS-1 catalyst was characterized and found that it possesses total surface area of 442.64 m²/g with average pore width 34.16 Å and pore volume of 0.378 cm³/g. Pore size distribution analysis shows that the majority of the pores in TS-1 are below 20 Å. The adsorption-desorption data is given in the form of a hysteresis curve in the Figure 1(a). The N₂ sorption isotherm of TS-1 is of type I, which is the characteristic of a microporous zeolite. This observation is based on standard isotherm curves. The XRD and SEM analysis of the catalyst were also done. The XRD pattern of commercial TS-1, showed in Figure 1(b), proved high crystallinity and MFI type zeolite structure. The SEM image, shown in Figure 1(c), shows agglomerated granules of the catalyst; the particle size was estimated to be in

Table 1. Experimental range and levels of process variables

Independent Variables	Range and Levels		
	-1	0	+1
Temperature, A (°C)	20	40	60
Mole Ratio ((C ₆ H ₄ (OH) ₂):n(H ₂ O ₂)), B (mole/mole)	2.5	8.75	15
Catalyst amount, C (g)	0.10	0.80	1.5

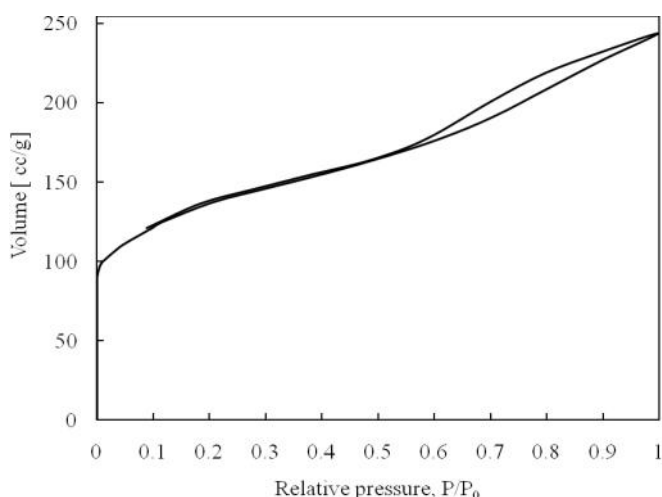


Figure 1(a). Adsorption desorption isotherm of TS-1

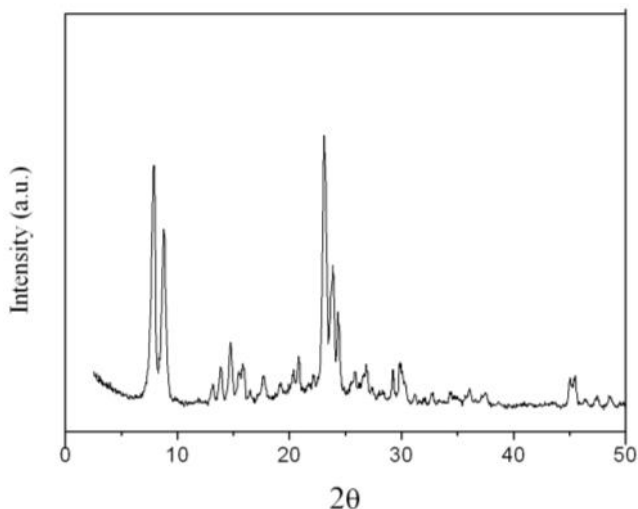


Figure 1(b). XRD pattern of commercial TS-1

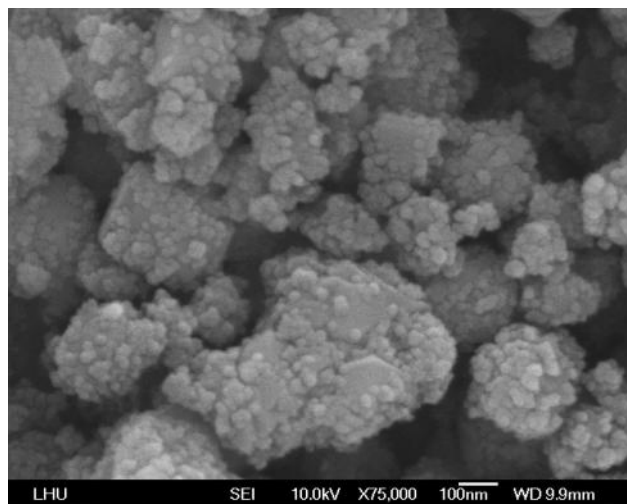


Figure 1 (c). SEM micrograph of commercial TS-1

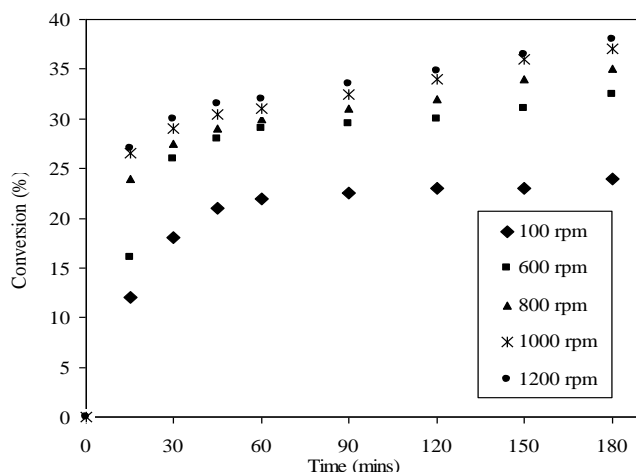


Figure 2. Influence of agitation speed (mole ratio of H_2O_2 to catechol : 5, reaction time: 180 min, temperature: 40 °C, catalyst amount: 0.50 g, catalyst particle size: 0.376 mm, oxidizing agent: 30% aqueous H_2O_2 , catalyst: TS-1)

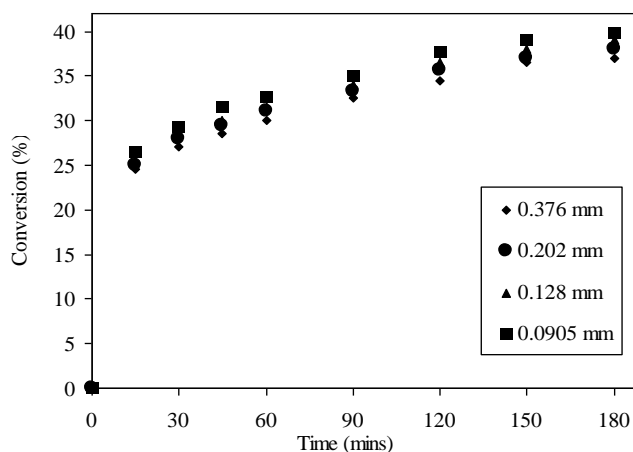


Figure 3. Variation of catalyst particle size (mole ratio of H_2O_2 to catechol : 5, reaction time: 180 min, temperature: 40 °C, agitation speed: 1000 rpm, catalyst amount: 0.50 g, oxidizing agent: 30% aqueous H_2O_2 , catalyst:TS-1)

the range of 125 to 250 nm.

3.1. Effect of variation of different parameters

Speed of agitation, catalyst particle size, temperature, catalyst amount, mole ratio of hydrogen peroxide to catechol and reaction time are the main process parameters that affect the substrate conversion. The effects of these parameters on catechol conversion are shown in Figures (2)-(7).

3.2. Influence of speed of agitation on conversion

The effect of external mass transfer on the catechol oxidation was studied by varying stirrer speed

from 100 to 1200 rpm. Figure 2 shows the time versus conversion of catechol at different stirrer speed keeping other process parameters, such as, reaction temperature, catalyst amount and moles of hydrogen peroxide to catechol constant. It depicts from the figure that the conversion of catechol using commercial TS-1 is found to be 37 % and 39% at 1000 and 1200 rpm respectively at reaction temperature 40 °C in 3 hr, thus the increase in the speed of agitation beyond 1000 rpm has insignificant effect on the conversion. This supports the fact that at or above the stirrer speed 1000 rpm all external mass transfer effects are negligible and the process is kinetically controlled. Hence all the subsequent experiments were carried out at 1000

rpm. It has been observed that during the experiment, the particle size is not reducing with stirrer speed. Besides this, as the particle size is too small, the change in solid-liquid interfacial area is negligible with change in particle size. Hence, the effect of stirrer speed with variation of particle size was not undertaken.

3.3. Variation of catalyst particle size

The effect of variation of catalyst particle size on the conversion of catechol was studied by using different size of catalyst particles in the range of 0.0905 to 0.376 mm and the results are plotted in Figure 3. It is observed that particle size of the catalyst has an insignificant effect on the conversion of catechol and so the effect of internal mass transfer resistance may be neglected. Hence an average size of 0.376 mm was used in the subsequent reactions.

3.4. Influence of temperature on reaction

The effect of temperature on the conversion of catechol was studied by varying the temperature in the range of 20 to 70 °C by keeping the agitation speed at 1000 rpm, catalyst amount at 0.50 g and hydrogen peroxide to catechol mole ratio at 5:1.

Figure 4 shows the conversion of catechol with time by varying temperature from 20 to 70 °C and it has been observed that the conversion of catechol is highly influenced by the increase in temperature.

The conversion at 60 and 70 °C are found to be 50.5 and 51.6 % in 180 min respectively and hence it is found that the increase in the reaction tem-

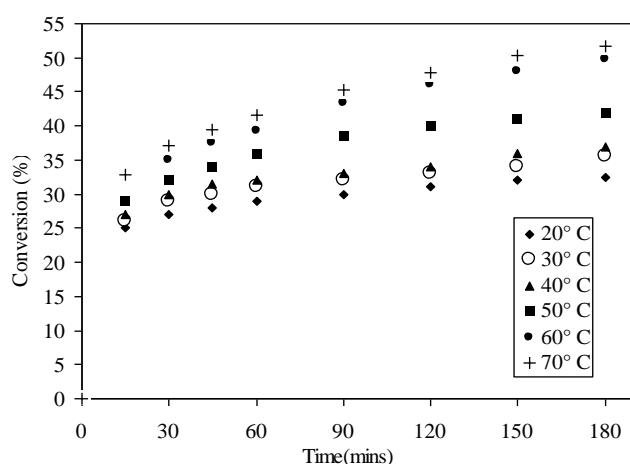


Figure 4. Temperature dependency of the reaction (mole ratio of H₂O₂ to catechol : 5, reaction time: 180 min, agitation speed: 1000 rpm, catalyst amount: 0.50 g, catalyst particle size: 0.376 mm, oxidizing agent: 30% aqueous H₂O₂, catalyst: TS-1)

perature beyond 60 °C has insignificant effect on the conversion. The reaction temperature beyond 60 °C has insignificant effect on reaction rate, which is probably due to the dissociation of hydrogen peroxide at higher temperature. Hence, 60 °C was chosen as the working reaction temperature for maximum conversion of catechol.

3.5. Effect of variation of catalyst amount

The effect of catalyst amount on the conversion of catechol was studied by varying the catalyst amount in the range of 0.1 to 1.5 g by keeping the agitation speed constant at 1000 rpm, reaction temperature at 40 °C and the mole ratio hydrogen peroxide to catechol at 5:1. Fig. 5 presents the results of variation of conversion of catechol at different catalyst amount and it is observed that the conversion of catechol is increasing by increasing the catalyst amount.

The increase in the concentration of active sites present on the catalyst surface with the increase in catalyst amount may be the reason of enhancement of conversion. The maximum conversion of catechol at 40 °C using commercial TS-1 is found to be 51.5% with 1.5 g catalyst in 3 h.

3.6. Effect of mole ratio of hydrogen peroxide to catechol

The effect of mole ratio of hydrogen peroxide to catechol on the conversion of catechol was studied by varying the mole ratio from 1:2.5 to 1:20 by keeping all other reaction parameters to be constant. The plot of conversion of catechol at different mole ratio is shown in Figure 6. From this figure, it

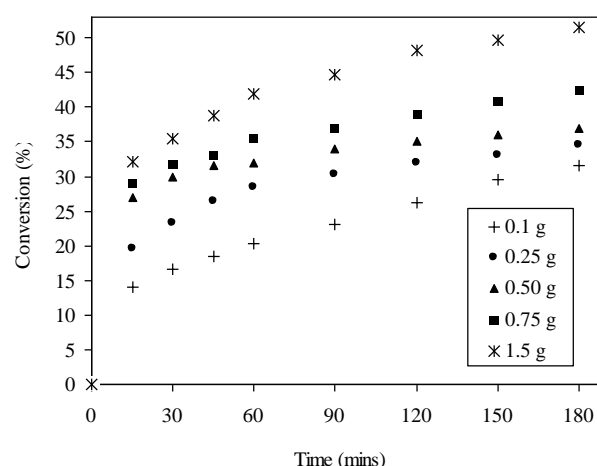


Figure 5. Variation of catalyst amount (Mole ratio of H₂O₂ to catechol : 5, reaction time: 180 min, temperature: 40 °C, agitation speed: 1000 rpm, catalyst particle size: 0.376 mm, oxidizing agent: 30% aqueous H₂O₂, catalyst: TS-1)

has been observed that the conversion of catechol is increased by increasing the mole ratio up to 15:1 and beyond that, no significant increase in conversion has been observed. This may be due to the non-availability of catechol at high hydrogen peroxide to catechol mole ratio. The maximum conversion of catechol using commercial TS-1 is found to be 57.7 % at a mole ratio of 15 : 1, at reaction temperature of 40 °C, catalyst amount 0.50 g and stirrer speed of 1000 rpm at 3 h. Therefore, the mole ratio 15 : 1 was chosen to be the optimum for catechol conversion.

3.7. Selection of reaction time span

The suitable reaction time economical to the process for obtaining maximum conversion of catechol was determined by continuing the reaction till 240 min, keeping the agitation speed at 1000 rpm, reaction temperature 60 °C, catalyst amount 0.5 g and mole ratio 5:1 and the result is shown in Figure 7. It is observed that the conversion of catechol is increased as the reaction time increases and there is a very little increase in conversion from 180 to 240 min (50.5 to 51.5%). Thus, it is not fruitful to further increase the reaction time. Moreover, H₂O₂ is unstable, thus extending the reaction time beyond 180 min is not advisable for the reaction. Hence 180 min was chosen as the optimum reaction time and all further experiments were carried out up to 180 min.

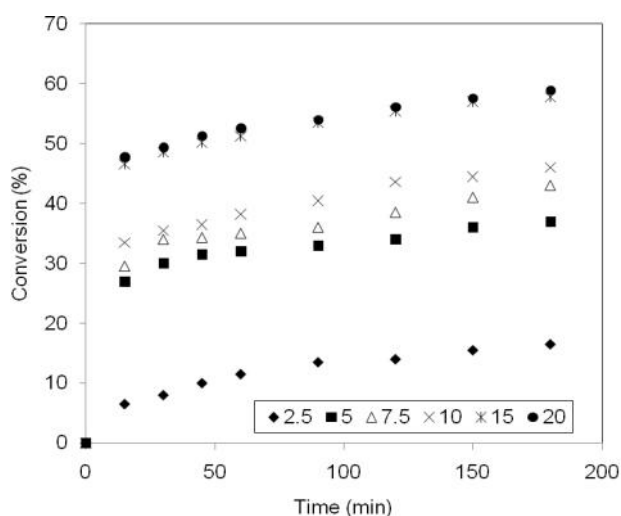


Figure 6. Influence of mole ratio of H₂O₂ to catechol. (Reaction time: 180 min, temperature: 40 °C, agitation speed: 1000 rpm, catalyst amount: 0.50 g, catalyst particle size: 0.376 mm, oxidizing agent: 30% aqueous H₂O₂, catalyst: TS-1)

4. Optimization by Box-Behnken design

A Box-Behnken design was used for optimization of conversion of catechol in order to establish the relationship between the input process parameters and reaction conversion. The input parameters for the optimization was chosen to be reaction temperature, A, moles of hydrogen peroxide per mole of catechol, B and catalyst amount, C. The Box-Behnken design [35] suggested 15 random experiments with respect to the input process parameters. The response as a function of three dependent process parameters was obtained by fitting the experimental data and it was given in the form of quadratic equation using the statistical analysis (Design-Expert 8.0.1 software).

$$Z = 43.6 + 8.14A + 19.18B + 7.24C + 0.08A^2 - 3.57B^2 + 1.95C^2 + 4.53AB + 3.2AC + 1.92BC \quad (2)$$

Table 2 shows the results of analysis of variance (ANOVA). The F-value for the regression model was found to be 218.16 which is much higher than the critical F-value $F_{95, 0.05}$. It shows that the model is more significant. However, the F-statistics values for all regressions were found to be higher which signifies that any variations in the response can be explained by the predicted model equation. The corresponding P-values in the Table 3 are used to analyze whether the F-statistics values are sufficient enough to explain statistical significance be-

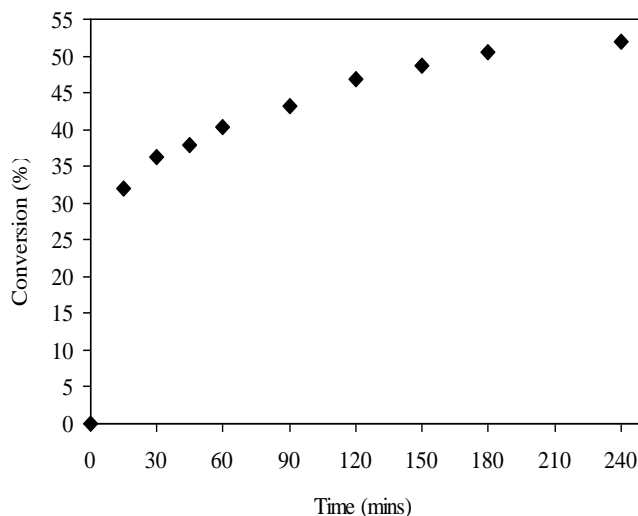


Figure 7. Influence of reaction time (mole ratio of catechol to H₂O₂: 1:5, temperature: 60 °C, agitation speed: 1000 rpm, catalyst amount: 0.50 g, catalyst particle size: 0.376 mm, oxidizing agent: 30% aqueous H₂O₂, catalyst: TS-1)

tween the predicted and actual response [35]. A P-value less than 0.05 indicate the significance of the model. It may be concluded that, the terms A, B, C, AB, AC, BC, B² and C² are significant parameters as all P-values are lower than 0.05 and the confidence level is 95%. The amount of deviation in the response is shown by the residual error in Table 3. A comparison between the experimental and predicted conversion Z_{expt} and Z_{pred} respectively are plotted in Figure 8 and a 45° line passing through origin fitted with a correlation coefficient of 0.9987 and this indicates that the predicted response correlates well with the experimental analysis.

A very high R-Squared (R-Sq) value of 0.9975 indicates that the predicted regression model is sufficiently accurate to explain the original relationship between the response and the process parameters.

4.1. Response surface plots

Response surfaces can be visualized in the form of 3-D surface plots that represent the variation of the response with two variables, keeping the other parameter fixed. The resulting response 3D surface plots for the catechol conversion is a function of (a) temperature and mole ratio (b) temperature and catalyst amount (c) mole ratio and catalyst amount which are shown in Figures 9a, 9b and 9c respectively. The central point (CP) or stationary point is the point at which slope of the contour is zero in all possible directions. The coordinates of the CP within the maximum contour levels in each of the given figures represent the optimum values of the respective parameters. The maximum predicted

conversion lies in the surface confined in the smallest curve of the 3D contour diagram.

4.2. Optimization and selection of optimum conditions

Optimization of the response was performed numerically by statistical tool. The optimization presented in Table 3 shows the optimum values of the process parameters for attaining the highest conversion. The optimum values of catechol conversion are obtained by fixing the starting values of the independent variables: temperature (60 °C), mole ratio of H₂O₂ and catechol (2.5) and catalyst amount (0.80 g). The optimum conversion (Z) was obtained as 75.84 % at the optimum temperature as 60 °C, moles of hydrogen per oxide per mole of as 13.20

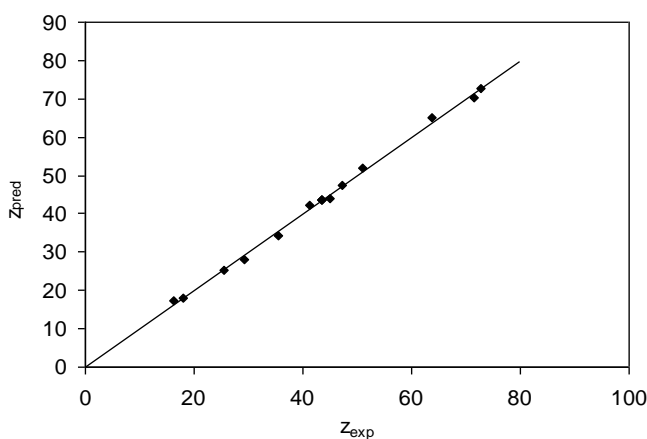


Figure 8. Comparison between experimental and predicted conversion

Table 2. Analysis of variance (ANOVA) for conversion

Source	DF	SS	MSE	F	p (Prob>F)
Model	9	4096.64	455.18	218.16	<0.0001
A	1	529.75	529.75	253.89	<0.0001
B	1	2941.44	2941.44	1409.75	<0.0001
C	1	419.05	419.05	200.84	<0.0001
AB	1	81.90	81.90	39.25	0.0015
AC	1	40.96	40.96	19.63	0.0068
BC	1	14.82	14.82	7.10	0.0446
A ²	1	2.36	2.36	1.13	0.3359
B ²	1	47.19	47.19	22.62	0.0051
C ²	1	14.04	14.04	6.73	0.0486
Residual	5	10.43	2.09	-	-
Lack of fit	3	10.43	3.48	-	-
Pure Error	2	0	0	-	-
Corr Total	14	4107.08	-	-	-

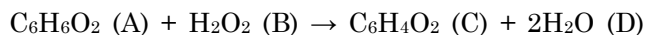
R² = 99.75%; R² = 99.29%; Pred R² = 95.94%

mol and catalyst amount as 1.24 g. Thus the RSM was successfully applied to maximize the catechol conversion for oxidation reaction using H₂O₂ as an oxidizing agent. A typical experimental reaction was performed with the optimum parametric condition obtained by RSM and the conversion (73.52 %) obtained was close to the optimum value.

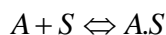
4.3. Kinetics of catechol oxidation with H₂O₂

In addition with statistical optimization, a systematic kinetic study is also important. The oxidation of catechol is a heterogeneous reaction where the liquid phase comprises a mixture of catechol and aqueous solution of H₂O₂ and TS-1 catalyst is the solid phase. The effects of mass transfer have been minimized with reasonable agitation speed and appropriate size of catalyst particles to make the reaction kinetically controlled. The reaction kinetics was studied at three different temperatures: 20, 40 and 60 °C.

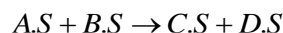
The rate model for the present heterogeneous reaction was derived based on the dual site Langmuir-Hinshelwood mechanism assuming surface reaction as the rate determining step [36]. The overall reaction may be written as



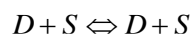
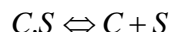
Adsorption step: (S is the active site)



Surface reaction: (rate limiting)



Desorption step:



The reaction rate for species A may be written as:

$$-r_A = \frac{mkK_A K_B C_A C_B}{(1 + K_A C_A + K_B C_B)^2} \text{ gmol.min}^{-1}\text{L}^{-1} \quad (3)$$

where, k is the rate constant; K_A and K_B are the equilibrium adsorption constants (L.gmol⁻¹) for species A and B respectively. C_A and C_B are the concentrations (gmol.L⁻¹) of species A and B in reaction mixture respectively. Where, m is the catalyst loading. The concentration of a species in a biphasic system is according to their moles in their respective phases. As all the reactions were carried out at constant catalyst loading (0.5 g), hence, the weight of the catalyst is associated with the rate constant. The rate of reaction ($-r_A$) for the case of small amount of powdered catalyst suspended in a liquid may be expressed in terms of slurry volume.

Equation (3) can be written in terms of conversion (X_A) as:

$$\frac{dX}{dt} = \frac{mC_{A0} kK_A K_B (1 - X_A)(M - X_A)}{[1 + K_A C_{A0}(1 - X_A) + K_B C_{A0}(M - X_A)]^2}$$

$$\frac{dX}{dt} = \frac{k'(1 - X_A)(M - X_A)}{[1 + k_2(1 - X_A) + k_3(M - X_A)]^2} \quad (3a)$$

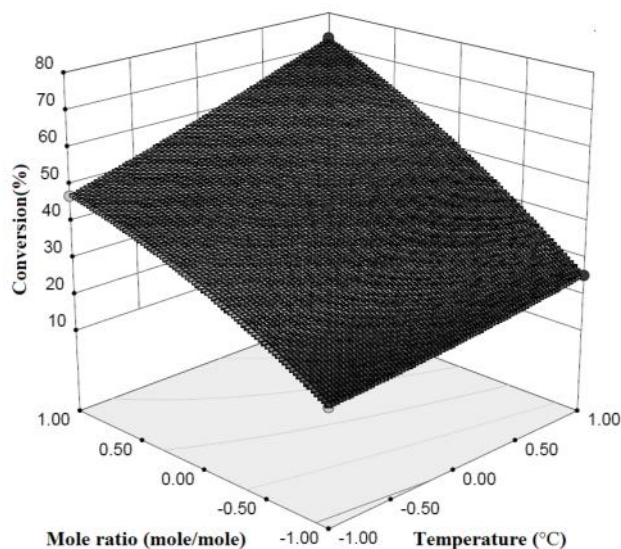


Figure 9a. Surface plot of conversion as a function of temperature and mole ratio

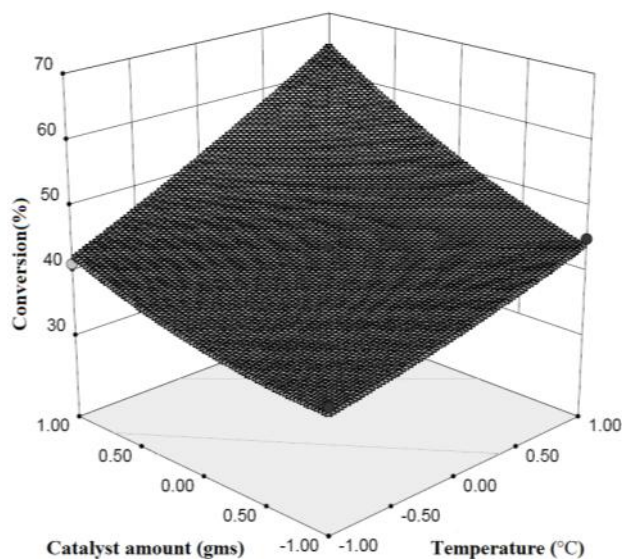


Figure 9b. Surface plot of conversion as a function of catalyst amount and temperature

where, $k'=mC_{A0}kK_AK_B$, $k_2=C_{A0}KA$, $k_3=C_{A0}K_B$ and $M=C_{B0}/C_{A0}=5$

Equation (3a) was fitted with non-linear method of analysis by using Matlab 7.1 software. The value of the parameter k_2 was found to be negative at 20 °C and k_3 is negative at 40 and 60 °C and large values of mean square error were noted.

The results of the non-linear estimation of parameters of Equation (3a) are shown in Table 4. As the values at all temperatures are found to be negative, hence, the model represented by Equation (3a) is rejected. So, an empirical rate equation of the following form has been attempted.

$$-r_A = \frac{-dC_A}{dt} = k_1 C_A C_B \quad (4)$$

where, k_1 is in $L^{-1}gmol\ min^{-1}$

As the amount of H_2O_2 was taken in excess and the change in concentration of H_2O_2 in comparison to catechol is negligible, rate is considered to be independent of C_B . Hence, the reaction may be considered as pseudo first order with respect to the catechol concentration (C_A). Hence, Eq. (4) may be simplified as:

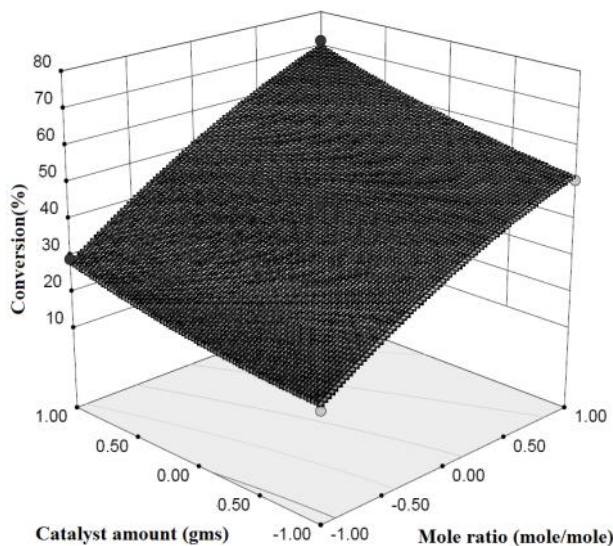


Figure 9c. Surface plot of conversion as function of catalyst amount and mole ratio

Table 3. Results of optimization of conversion

Parameter	Coded Value	Actual values	Exp. values
Conversion, %	-	75.842	73.52
Temperature, °C	+1.00	60.00	60.00
Mole ratio	+0.71	13.20	13.20
Catalyst loading, g	+0.63	1.24	1.24
Composite desirability = 1.000			

$$-r_A = -\frac{dC_A}{dt} = k_0 C_A \quad (5)$$

where $k_0 =$ apparent rate constant $= k_1.C_{B0}\ min^{-1}$

Equation (4) is integrated with limits for $t = 0, C_A=C_{A0}$ to $t=t, C_A=C_A$, on integration of Equation (5)

$$-\ln \frac{C_A}{C_{A0}} = k_0.t$$

or,

$$\ln\left(\frac{1}{1-X_A}\right) = k_0.t \quad (6)$$

where $X_A =$ fractional conversion of reactant species A at time $t = s$.

The plot of $\ln(1/1-X_A)$ versus time at different temperatures gives a linear plot as shown in Figure 10. The apparent rate constant k_0 was calculated from the slope of the straight line and fitted to the Arrhenius plot as shown in Figure 11. The apparent activation energy and the frequency factor were found to be 11.37 kJ/mole and 37.08 \min^{-1} respectively.

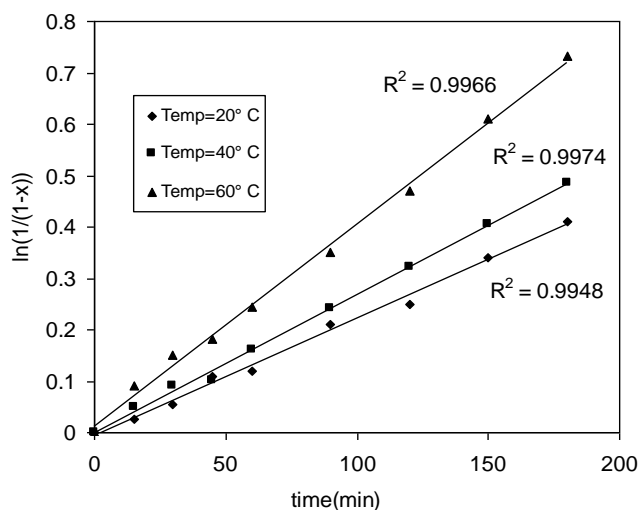


Figure 10. Fitting of kinetic data pseudo first order rate equation

Table 4. Results of the analysis of Equation 3a

Temp. °C	Parameters (X 10 ⁻²)			MSE x 10 ⁷
	k'	k_2	k_3	
20	0.0048	-5.154	0.938	5.77
40	0.1346	20.718	-3.718	9.17
60	0.0049	3.774	-0.68	16.21

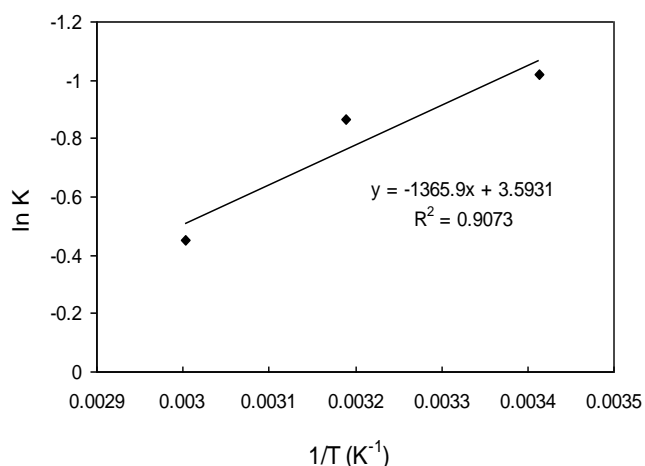


Figure 11. Arrhenius plot

5. Conclusion

The oxidation of catechol was carried out by using titanium silicate-1 as catalyst with 30 % hydrogen peroxide as oxidizing agent. The process is eco-friendly as no organic solvent is used. The process was optimized by using response surface methodology by employing Box-Behnken design and a second order quadratic equation in terms of three independent process variables such as reaction temperature, moles of hydrogen peroxide per mole of catechol and catalyst amount for the design of experiment was formed. The large value of correlation coefficient as 0.9987 indicates that the predicted response correlates well with the experimental values. The optimum values were, temperature: 60 °C, hydrogen peroxide to catechol: 13.2 and catalyst amount: 1.24 g to achieve a maximum conversion of 75.842 %. A pseudo first order kinetic rate equation was proposed for the reaction. The activation energy and the frequency factor were found to be 11.37 kJ/mole and 37.08 min⁻¹ respectively.

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