ORIGINAL RESEARCH PAPER

Application of Response Surface Methodology as an Efficient Approach for Optimization of Operational Variables in Benzene Hydroxylation to Phenol by V/SBA-16 Nanoporous Catalyst

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ABSTRACT

Herein, we prepared a V/SBA-16 catalyst using vanadyl acetylacetonate as a precursor and SBA-16 nanoporous silica as a support via an immobilization technique. The ordered mesoporous structure of catalyst was determined by X-ray diffraction and transmission electron microscopy techniques, and the catalyst was evaluated in the benzene hydroxylation to phenol with hydrogen peroxide (H_2O_2) as a green oxidant. The effects of three key factors, namely reaction temperature (°C), H_2O_2 content (mL) and catalyst amount (g) at five levels (-1.68, -1, 0, +1, +1.68), and also their interaction on the phenol yield were investigated using response surface methodology combined with central composite design. The high correlation coefficient (R^2), i.e., 0.983, showed that the data predicted using RSM were in good agreement with the experimental results. The optimization results also exhibited that high phenol yield (17.09%) was achieved at the optimized values of the operating variables: the reaction temperature of 61 °C, H_2O_2 content of 1.69 mL and a catalyst amount of 0.1 g. In addition, response surface methodology provides a reliable method for optimizing process variables for benzene hydroxylation to phenol, with the minimum number of experiments.

INTRODUCTION

Phenol is an important chemical intermediate in the manufacture of many petrochemicals, agrochemicals, polymers, and plastics [1,2]. Global production of phenol is mainly performed using the well-known cumene process, but it has disadvantages such as low yields and high energy expenditure, especially in the distillation steps [3]. Moreover, the utility of this process depends on the market demand for the by-product acetone [4]. Recently, one step process of direct hydroxylation of benzene to phenol

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has been studied as the most promising route by different clean oxidants such as N_2O [5-7], O_2 [8], and H_2O_2 [9]. Amongst these oxidants, H_2O_2 is increasingly being used as the oxidant, because it is a green oxidant and the process is simple and also, water is the only by-product of this reaction [10]. In this regard, direct hydroxylation of benzene to phenol by H_2O_2 as an oxidant, was successfully carried out with metal-based catalysts over various supports, such as molecular sieves [11-13], activated carbon [14] and carbon nanotube [15]. The development of compounds of vanadium in oxidation catalysis is significant because it has high inherent activity and remarkable stability for hydrocarbon oxidation. There have been a lot of studies related to the reaction of direct oxidation of benzene to phenol over vanadium-based catalysts, such as vanadium oxides supported on mesoporous SBA-16 [16], SBA-15 [17], clay [18], multi-walled carbon nanotubes [19] and carbon nitride [20-22].

In addition to developing suitable catalyst preparation processes, optimization of the operating variables plays a key role in achieving a good catalytic parameter such as the amount of H_2O_2, reaction temperature and catalyst amount have significant effects on the catalytic performance. Previous studies were performed using traditional one-factor-at-a-time approaches for optimizing the operating parameters in order to obtain a good catalytic activity [23-26]. Such experimental methods are time consuming and costly, especially if a large number of operating variables need to be considered simultaneously. These methods do not consider interactions among the process variables and result in poor optimum conditions. Statistical techniques such as response surface methodology (RSM), which is a more accurate method, can be used for optimization of a fixed process. RSM is a mixture of mathematical and statistical techniques and can evaluate the effects of process variables and their interactions on the response variables. This approach has been used for optimizing various processes, such as esterification reaction [27], reaction of biodiesel production [28] and advanced treatment of biologically stabilized landfill leachate [29]. In our previous work, we reported highly selective production of phenol from benzene over mesoporous silica-supported chromium catalyst and showed RSM as a reliable method for optimizing process variables

for benzene hydroxylation [30]. To the best of our knowledge, no other previous study has been conducted on the application of the RSM approach for optimizing the benzene hydroxylation process.

In the present study, a V/SBA-16 catalyst was synthesized through a low cost method by employing vanadyl acetylacetonate as a precursor and SBA-16 nanoporous silica as a support. The effect of various operational variables was optimized in benzene hydroxylation to phenol using central composite design (CCD) base on RSM technique. The main purpose of the present work was to investigate whether the interaction and quadratic effects of the operational factors such as reaction temperature (°C), H_2O_2 content (mL) and catalyst amount (g) can be significant on the catalyst performance. The optimal values of the above mentioned factors were then determined and the yield and selectivity toward phenol was obtained under the optimized conditions.

MATERIALS AND METHODS

The Pluronic F127 (EO_{106} PO_{70} EO_{106}), sodium silicate solution (SiO_2 26%, Na_2O 8%), nitric acid (65%), Vanadyl (IV) acetylacetonate, acetonitrile, benzene, hydrogen peroxide (30%) and toluene were purchased from Merck Company.

The vanadium content of the sample was measured with Varian VISTA-MPX simultaneous ICP-AES atomic absorption spectrometer. Powder XRD measurements were performed using Cu K$_á$ radiation (X'Pert-PRO X-ray diffractometer). The TEM image was obtained on Philips EM-208 at 100 kV. The liquid products were analyzed by a gas chromatography (GC) of Perkin-Elmer 8500 with a flame ionization detector (FID). The quantitative analysis of liquid products was calculated with the calibration curves which toluene was considered as an internal standard. It is noteworthy that 1,4-benzoquinone was identified as a byproduct in some of experiments.

Synthesis of SBA-16 as a support

Mesoprous silica SBA-16 was prepared by the same method described in the literature with minor modification [31]. 14.1 g F127 was dissolved in 144 mL HNO$_3$ (65%) and 900 mL deionized water by stirring at 30 °C, then 62.4 g silica source (sodium silicate solution) was added to the solution, and the reaction mixture was stirred at 300 rpm for 3 h at 70 °C. The product of the reaction was placed at 100 °C for 24 h.

then, the surfactant was extracted from ethanol and HCl (2 M), and the obtained solid was calcined in 550 °C for 5 h.

Preparation of V/SBA-16 catalyst

Deposition of [VO(acac)$_2$] complex on the SBA-16 surface was carried out by the liquid-phase immobilized method. About 2.7 g of calcined SBA-16 was stirred in 80 mL of dry toluene containing 0.739 g of [VO(acac)$_2$] complexes for 48 h at room temperature. The precipitation was filtered and washed with toluene to remove the excess metal complexes. Afterwards, it was dried at 80 °C for 8 h. The sample was calcined at 550 °C for 5 h. The resulting material was achieved as a yellow powder containing 4.7 wt.%V/SBA-16.

Experimental procedure

4.7 wt.%V/SBA-16 was applied in the direct hydroxylation of benzene to phenol by hydrogen peroxide as the oxidant. For this purpose, the benzene oxidation was carried out in a 50 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer. For all reactions, desired amount of catalyst (in the range of 0.08 to 0.1 g) was added in 6 mL acetonitrile and other parameters such as the hydrogen peroxide content (1 to 3 mL) and reaction temperature (40 to 80 °C) were adjusted according to designed experiments by using Design Expert 7.1.3 Software. When the mixture was heated to the desired reaction temperature, 1 mL of benzene (11.26 mmol) was added to the mixture and the reaction time was fixed for 6 h. After the reaction mixture was cooled, the catalyst was separated by centrifuge and low amount of ethanol was added to liquid product to be a single-phase liquid for GC analysis.

Experimental design and statistical model

RSM is an affordable and reliable method for optimizing certain processes. This technique leads to a reduction of designed experiments to investigate the effect of operation factors. In general, a second-order polynomial model is applied for the RSM analysis (Eq. 1).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j + e \quad (1)$$

Where Y is the predicted response, β_0 is the intercept term, β_i demonstrates the coefficient of linear factor,

x_i is the variable attributed to factor i, β_{ij} demonstrates the coefficient of the interaction factor, β_{ii} demonstrates the coefficient of quadratic factor, k is the number of factors and e related to random error [32].

Central composite design (CCD) is the most commonly selected method in the RSM technique. CCD is an experimental design that includes a two-level factorial design with center points, and is completed with a set of axial (or star) points to assess the curvature. For maximum efficiency, the star points should be placed a specific outside the original factor range. The distance of each factorial point from the center of the design space is ±1coded unit while the distance from the center of the design space to an axial point is ±α (Fig. 1). The value of á depends on the type of offered CCD and on the number of independent variables. In present study, α value was calculated with F=2^k base on a central composite rotatable design. Here, F is the defined number of points in the design space which is obtained from α=F$^{1/4}$ where k is the number of independent factors [33]. Then, for three factors, F and α value are equal to 8 and 1.68 respectively.

The Design Expert Software (version 7.1.3) was utilized for designing the experiments and analysis of obtained results. In this work, CCD coupled with RSM were employed to investigate the effect of operating factors, namely reaction temperature, H$_2$O$_2$ content and catalyst amount on benzene hydroxylation using a V/SBA-16 catalyst and the phenol yield was considered as a response variable. Overall, the experimental design were consisted of
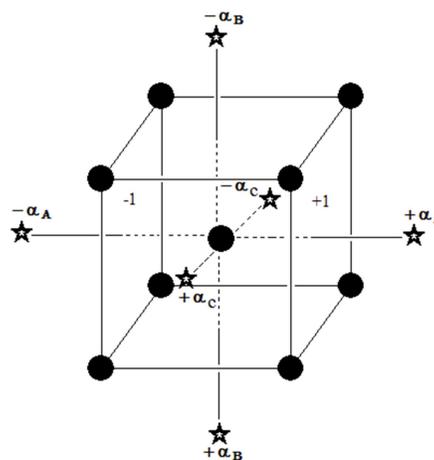

Fig. 1. Central composite design for three factors

Table 1. The actual and code levels of independent factors.

Independent factors	unit	Level				
		-α (-1.68)	-1	0	+1	+α (+1.68)
A: Reaction temperature	(°C)	26	40	60	80	93
B: H_2O_2 content	(mL)	0.32	1	2	3	3.68
C: Catalyst amount	(g)	0.07	0.08	0.09	0.1	0.11

20 experiments that were included in the following sections: (I) 8 runs by the two-level factorial design, (II) one center point and its five repeats to determine the curvature and pure errors (caused by replicating experiments) and (III) 6 runs for axial points (is shown with −α and +α). The actual and code levels of independent factors are displayed in Table 1.

RESULTS AND DISCUSSION

Characterization of catalyst

The low-angle XRD patterns of SBA-16 and V/SBA-16 are given in Fig. 2. Both patterns had one sharp reflection at $2\theta = 0.74°$ and one minor peak at $2\theta = 1.3°$; these are indexed to (110) and (211) reflections and correspond to the SBA-16 cubic structure with the Im 3 m space group. These are indicative of cage-like structures, i.e., the ordered mesoporous structure of the support was retained during catalyst preparation and did not collapse. The TEM images of SBA-16 and V/SBA-16 catalyst are shown in Fig. 3. It is obviously observed that the mesoporous structure of SBA-16 was maintained after loading of vanadium species during the preparation of catalyst.

Data analysis

The analysis of experimental results (Table 2) was proposed the second-order polynomial model for the phenol yield. The final empirical model based on the coded values after excluding the insignificant terms for the phenol yield is shown in Eq. (2). In this model, Y (phenol yield) was expressed as a function of A (reaction temperature), B (H_2O_2 content) and C (catalyst amount).

$$Y = 14.77 + 0.35\ A - 0.6\ B + 2.15C + 0.82\ AB - 0.54AC - 3.17\ BC - 2.84\ A^2 - 3.48\ B^2 - 3.02\ C^2 \qquad (2)$$

The competence of the model was assessed using analysis of variance (ANOVA) and the Fisher test (F-test), with a 95% confidence level. The statistical terms obtained from ANOVA are listed in Table 3. The ANOVA results showed that this model may be used to the considered design space. The probability value of
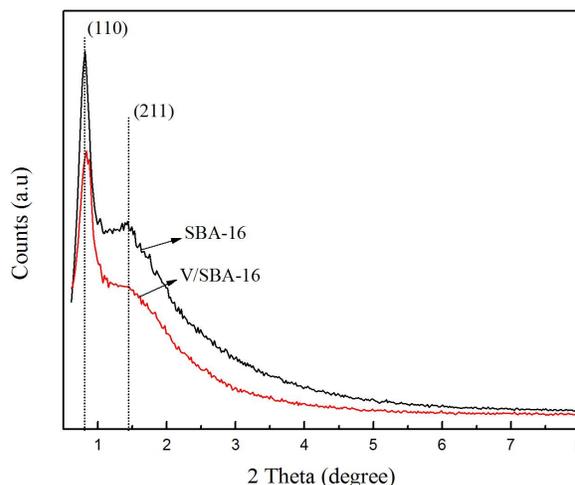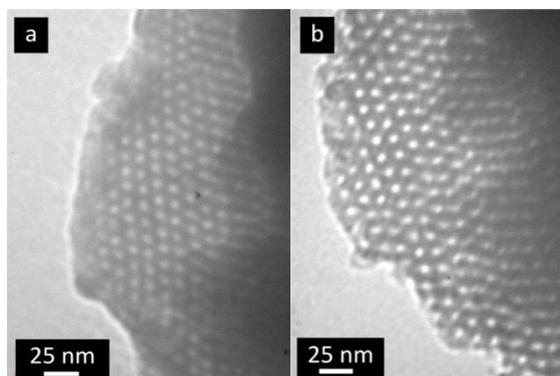

Fig. 2. Low-angle XRD patterns of SBA-16 and V/SBA-16

Fig. 3. TEM images of SBA-16 (a) V/SBA-16 (b)

phenol yield was very less than 0.05 for the model (p-value < 0.0001); it implies that the model is statistically significant. In other word, there is only a 0.01% chance that the model could occur owing to noise. But, Lack-of-fit term is the variation of the data around the fitted model. If a fixed model does not fit the data well, this will be significant. Here, the P-value of lack-of-fit was more than 0.05, indicating that the selected model was based on a statistical

Table 2. The design experiment matrix based on central composite design (CCD).[a]

Run	Block	A (°C)	B (mL)	C (g)	Observed Phenol yield (%)	Predicted Phenol yield (%)
1	1	80	1	0.1	11.18	10.87
2	1	60	2	0.07	2.22	2.62
3	1	60	2	0.11	9.71	9.84
4	1	40	1	0.1	4.11	4.43
5	1	60	3.6	0.9	12.67	11.81
6	1	80	3	0.08	7.64	8.12
7	1	93	2	0.09	4.51	5.19
8	1	60	2	0.09	14.39	14.77
9	1	80	3	0.1	4.27	4.98
10	1	60	2	0.09	14.24	14.77
11	1	40	1	008	1.17	0.082
12	1	60	2	0.09	14.11	14.77
13	1	60	0.3	0.09	4.58	5.92
14	1	60	2	0.09	15.64	14.77
15	1	40	3	0.08	3.66	3.59
16	1	60	2	0.09	15.43	14.77
17	1	80	1	0.08	1.63	1.32
18	1	26	2	0.09	4.16	5.22
19	1	40	3	0.1	7.58	7.57
20	1	60	2	0.09	14.89	14.77

[a]Other reaction conditions for all runs: benzene (1 mL, 11.26 mmol), acetonitrile (6 mL, 114.8 mmol). [b]Phenol yield = mmol product/mmol initial benzene.

Table 3: Analysis of variance (ANOVA) for response variable.

Response variable	Source	Sum of squares	Degrees of Freedom	Mean square	F-value	P-Value probability > F	
Y	Model	520.41	9	57.82	64.60	< 0.0001	Significant
	A	11.03	1	11.03	12.32	0.0056	
	B	4.86	1	4.86	5.43	0.0421	
	C	62.93	1	62.93	70.31	< 0.0001	
	AB	5.41	1	5.41	6.05	0.0327	
	AC	2.38	1	2.38	2.65	0.1343	
	BC	80.52	1	80.52	89.95	< 0.0001	
	A^2	116.33	1	116.33	129.96	< 0.0001	
	B^2	174.81	1	174.81	195.30	< 0.0001	
	C^2	131.26	1	131.26	146.64	< 0.0001	
	Residual	8.95	10	0.9			
	Lack of Fit	6.88	5	1.38	3.33	0.1063	Not Significant
	Pure Error	2.07	5	0.41			
	Total	529.36	19				

$R^2 = 0.983$, Adj-R^2=0.967, Pre-R^2 = 0.895, Adequate precision = 21.95

logic (P-value more than 0.05 is desirable). The accuracy of the proposed model was assessed with the value of correlation coefficient. The high regression coefficient of R^2=0.983 indicates that there is good agreement between the experimental and the predicted phenol yields. Desirable value of adequate precision (signal to noise ratio) is greater than 4. Here, ratio of 21.95 was obtained for Y, implying that this model can be used to navigate the design space.

The regression plot of predicted values versus actual values for phenol yield is shown in Fig. 4. As can be seen, the predicted values from Eq. (2) were close to the experimental values, demonstrating that the proposed model is credible for expressing the correlation between the effective parameters and the phenol yield. Normal distribution of data is also shown by normal probability plot (Fig. 5). It can be observed that the data were normally distributed,
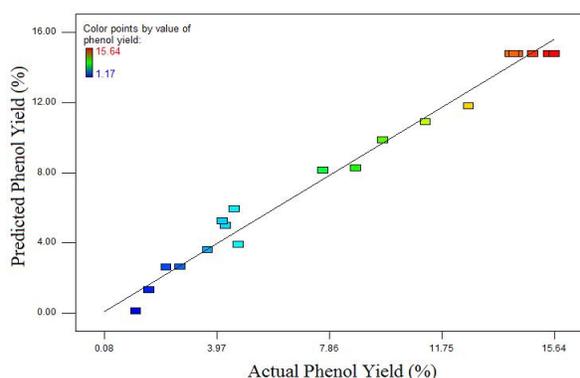
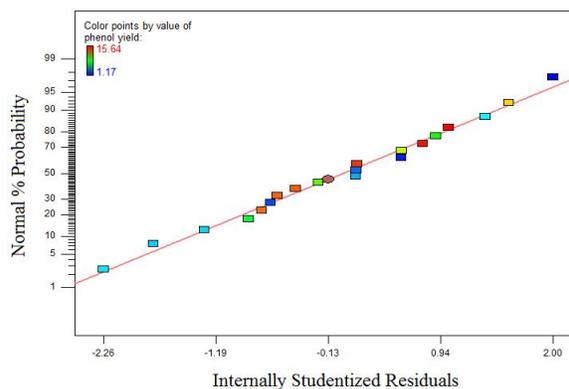Fig. 4. Plot of actual vs. predicted values of phenol yield.

Fig. 5. Normal probability plot of residuals.

Table 4. Observed and predicted results of the phenol yield at the optimum points predicted by the RSM

Temperature (°C)	H_2O_2 content (mL)	Catalyst amount (g)	Predicted phenol yield (%)	Observed phenol yield (%)	Observed[b] phenol selectivity (%)
61	1.69	0.1	15.44	17.09%	81.82%

[a]Other reaction conditions: benzene (1mL, 11.26 mmol), acetonitrile (6 mL, 114.8 mmol).
[b]Phenol selectivity= mmol phenol / mmol product.

because the data were sorted close to a straight line. In present model, the quadratic coefficients of factors (A2, B2 and C2) are equal to 2.84, 3.48 and 3.02 respectively. These results suggested that curvature is very significant for process variables in the considered reaction. In addition, the coefficients of the binary variables (AB: 3.17, BC: 2.84) show that the interaction of reaction temperature with H_2O_2 content and H_2O_2 content with catalyst amount, are very affective on the response variable.

The effect of process parameters on phenol yield
Interaction of reaction temperature with H_2O_2 content

Three-dimensional response surface and their respective contour plots were applied to more precisely investigate the interactions between operating parameters on the phenol yield. These curves show the simultaneous effects of two parameters on the response variable while other factors remain at the center point in the design space. The interaction between H_2O_2 content and reaction temperature at the center level of catalyst (0.09 g) is shown in Fig. 6a. The phenol yield is increased when the amount of H_2O_2 and temperature are increased up to 2 mL and 60 °C, respectively. It may be because of H_2O_2 decomposition to active species with increasing of temperature. Furthermore, Fig. 6a

demonstrates that the phenol yield is declined with further increasing the reaction temperature and H_2O_2 content; this can be result in self-decomposition of hydrogen peroxide to water or over-oxidation of phenol to 1,4-benzoquinone at higher temperatures that 1,4-benzoquinone was identified by using GC [34].

Interaction of reaction temperature with catalyst amount

Fig. 6b shows the interaction between reaction temperature and catalyst amount on the phenol yield, while H_2O_2 content kept at the center point (2 mL) in the design space. Initially, it can be observed that the yield of phenol is increased whereas reaction temperature and catalyst amount are increased to 60 °C and 0.09 g, respectively. The phenol yield is decreased with further increasing the reaction temperature and the catalyst amount. On the other hand, declining in the yield of phenol is attributed to phenol conversion to 1,4-benzoquinone that was observed by GC.

Interaction of H_2O_2 content with catalyst amount

Interaction between H_2O_2 content and catalyst amount on the phenol yield is presented in Fig. 6c. It can be deduced that the both parameters had a high
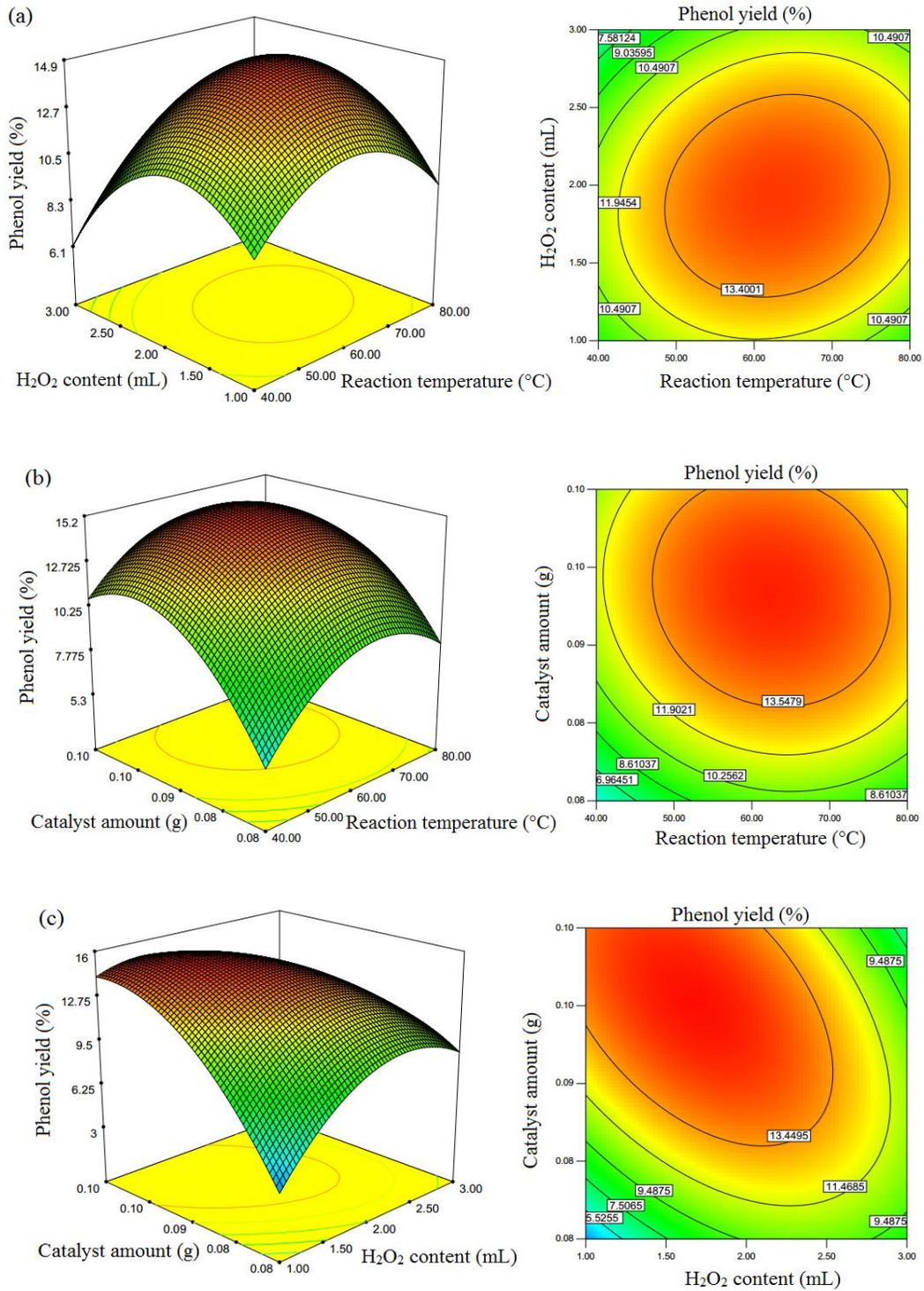
Fig. 6. The response surface and contour plots of the phenol yield for the interaction effects of the process variables. (a) reaction temperature with H_2O_2 content, (b) reaction temperature with catalyst amount, (c) H_2O_2 content with catalyst amount.

impressive effect on the phenol yield. The maximum phenol yield was achieved when the hydrogen peroxide and catalyst amount are near the central points.

Optimization of the phenol yield and validation of the proposed model

Design Expert 7.1.3 software was used to determine the optimum conditions for the direct hydroxylation of benzene to phenol. Hence, the phenol yield was defined as a maximum in the design space. In order to verify this model, the experiment was carried out under the predicted optimum conditions. The optimum operational parameters were found to be: reaction temperature of 61 °C, H_2O_2 content of 1.69 mL and amount of catalyst of 0.1 g. The predicted phenol yield from proposed model was 15.44% while the obtained phenol yield from the experimental data was 17.09% under the optimized conditions (Table 4). The result shows that there is a good agreement between second-order polynomial model of RSM and experimental data.

The prepared catalyst gave a high performance and the selectivity toward phenol was 81.82% under the optimum conditions.

CONCLUSIONS

In this study, a vanadyl acetylacetonate precursor was dispersed on mesoporous silica SBA-16 support, using an immobilization technique (V/SBA-16). The XRD and TEM results indicated that the mesoporous structure of the support was retained during catalyst preparation. The process of benzene hydroxylation to phenol by the prepared catalyst was successfully modeled using RSM base on CCD. A second-order polynomial model was developed to correlate the effective variables of reaction such as reaction temperature (A), H_2O_2 content (B) and catalyst amount (C) with the phenol yield. The high regression coefficient (R^2) of 0.983 showed that the predicted data from the model had a good agreement with the experimental data. The ANOVA of the results presented that the quadratic term of A^2, B^2 and C^2 as well as interaction between the reaction temperature with H_2O_2 content (AB) and H_2O_2 content with catalyst amount (BC) had significant effects on the phenol yield, while the interaction between reaction temperature and catalyst amount (AC) had no significant effect on the phenol yield. In addition, 3D response surface and their respective contour plots also showed that the

suitable phenol yield would achieve when the joint factors were near the central points.

Optimization results showed that maximum phenol yield (17.09%) was achieved at the operational conditions: reaction temperature of 61 °C, hydrogen peroxide content of 1.69 mL, catalyst amount of 0.1 g. The results clearly demonstrated that RSM based on CCD was one of the reliable methods to modeling and optimizing of the operational variables.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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