

Phys. Chem. Res., Vol. 3, No. 2, 111-123, June 2015.

DOI: 10.22036/pcr.2015.7879

Statistical Optimization of Liquid Phase Oxidation of Benzyl Alcohol over Efficient Cobalt Promoted Vanadyl Pyrophosphate Catalysts by Box-Behnken Design

V. Mahdavi* and H.R. Hasheminasab

Department of Chemistry, Surface Chemistry and Catalysis Division, Faculty of Sciences, Arak University, Arak 38156-8-8349, Iran

(Received 17 September 2014, Accepted 24 January 2015)

Vanadium phosphorus oxides (VPO) has been applied as a heterogeneous catalyst in gas phase oxidation reactions and its application is very limited in liquid phase. In this study a series of cobalt-doped vanadium phosphorus oxides (VPO-Co) catalysts with different loading of Co (0.01-1.0 mol ratio of Co/V) were prepared. Oxidation of benzyl alcohol was studied in the liquid phase over VPO and VPO-Co catalysts, using *tert*-butylhydroperoxide (TBHP) as an oxidant. These samples were characterized by XRD, SEM and Fourier transform infrared (FT-IR) techniques. The optimal design of experiments using Box-Behnken method was employed to evaluate the effects of individual process variables (+1, 0, -1, levels) such as, reaction temperature (30, 60 and 90 °C), reaction time (30, 255 and 480 min) and molar ratio of Co/V (0, 0.5 and 1) and their optimum values were found to be 89.86 °C, 477.8 min and 0.64 molar ratio Co/V, respectively, to achieve a conversion of 65.44%.

Keywords: VPO catalyst, Co-promoter, Optimization, Benzyl alcohol, Response surface methodology

INTRODUCTION

Vanadium phosphorus oxide (VPO) catalysts have long been recognized as the most fascinating catalyst in achieving high conversion with good selectivity in *n*-butane partial oxidation to maleic anhydride [1]. It is the most complex reaction compared to other industrially practiced selective hydrocarbon oxidations and represents the only industrially practicable selective oxidation reaction involving an alkane [2]. It is generally accepted that VPO catalysts composed mainly of vanadyl pyrophosphate ((VO)₂P₂O₇) are effective for the oxidation of *n*-butane to maleic anhydride (MA) [2-5]. One of the effective means of improving the catalytic properties is the introduction of metal ions into the lattice [6,7,8]. The effect of the dopant is to change the structure characteristics of catalyst phases [7,9]. It also plays a role in having an effect on the adsorption of oxygen and its diffusion within the lattice, by which a nonselective route of butane oxidation is suppressed [10].

One of the most studied metal dopant introduced in VPO catalysts is cobalt. Kladekova *et al.* [11] found that the catalyst modified by Co increases the specific rate of butane oxidation and maleic anhydride formation three times compared to the unmodified catalyst. Abdelouahab *et al.* [12] observed an enhancement in the VOPO₄/(VO)₂P₂O₇ dispersion at the surface of the Co doped VPO catalyst prepared by the normal organic route. However, the same catalyst prepared *via* VOPO₄·2H₂O precursor [13] gave a better catalytic performance.

Selective catalytic oxidation of alcohols to carbonyls is one of the most important chemical transformations in industrial chemistry. Carbonyl compounds such as ketones and aldehydes are the precursors for many drugs, vitamins and fragrances and they are also important intermediates for many complicated syntheses [14,15].

VPO has been applied as a heterogeneous catalyst in gas phase oxidation reactions and its application is very limited in liquid phase reactions. Recently, VPO catalyst has been used in liquid phase for cyclohexene epoxidation [16,17], esterification reaction [18,19], isopropylation of toluene [20], biomass conversion [21], cyclohexane oxidation [22],

*Corresponding author. E-mail: v-mahdavi@araku.ac.ir

and oxidation of alcohols in liquid phase in the presence of hydrogen peroxide and TBHP as oxidant [23-25].

In present study for the first time, we developed the use of cobalt-doped VPO catalyst (VPO-Co) for the oxidation of alcohols with *tert*-butylhydroperoxide (TBHP) in the liquid phase. Furthermore, it was stated that the catalytic selective oxidation efficiency of this process is dependent on numerous parameters such as amount of catalyst, cobalt loading over VPO, reaction temperature, reaction time, effect of oxidant/alcohol molar ratio and these parameters need to be carefully optimized.

One-factor-at-a-time optimization method is an intricate approach to evaluate the effects of different variables on an experimental outcome. In addition, this method is time consuming, expensive and often leads to misinterpretation of results when interactions between different components are present. Another approach to exactly evaluate the impact of the variables on the oxidation process is to change all the factors simultaneously in a systematic manner. This approach is referred to as response surface methodology (RSM).

Response surface methodology has been applied to optimize the process parameters which are not available yet in the process of benzyl alcohol oxidation. We have recently reported statistical optimization for oxidation of ethyl benzene over Co-Mn/SBA-15 catalyst by Box-Behnken design [26]. The optimization by applying factorial design in other systems is available in the literature [27-30]. Response surface methodology is used when only a few significant factors are involved in optimization. The Box-Behnken design (a type of RSM) is an independent rotatable or nearly rotatable quadratic design; it requires fewer runs (15) in a three-factor (variables) experimental design. In addition, it creates empirical model equations that correlate the relationship between the variables and the response [31]. The response surface design is classified as a simultaneous method, being used in the stage of optimization. Their application allows selecting the optimum combination of levels, to obtain the best response for a specific condition [30]. The response Y is described by a polynomial function of various independent variables X_i [31]:

$$Y = f(X_i) + \varepsilon \quad (1)$$

Where ε represents the observed error in the response Y . The response surface design and the strategic analysis implied that the response variable (μ_y) is in function of the levels of quantitative factors represented by the variables X_1, X_2, \dots, X_k . The polynomial models are used as practical approach to the real response function. The polynomial models commonly used for the analysis response surface are [32]:

The linear model of first order, applied to two factors:

$$\mu_y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 \quad (2)$$

The quadratic model, or of second order, for two factors:

$$\mu_y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (3)$$

One approach to optimal performance is to vary one factor while keeping the other factors constant to get improved response with respect to the varied factor. This often does not bring about the effect of interaction of various parameters compared to factorial design [33].

In this study, the effects of reaction temperature, molar ratio of Co/V in VPO catalyst and reaction time to produce benzaldehyde from benzyl alcohol over VPO catalyst were investigated. Box-Behnken Design was used to obtain the optimum values of variables and studying the interactions between variables. Analysis of variances (ANOVA) was used to investigate the effects of main factors and their interactions.

EXPERIMENTAL

Materials

All materials were of commercial reagent grade. All the alcohol substrates and V_2O_5 were obtained from Aldrich. H_3PO_4 (85%), *tert*-butylhydroperoxide (TBHP) 70% solution in water and cobalt(II) acetylacetonate ($C_{10}H_{14}Co.O_4$), were purchased from Merck chemical company.

Preparation of Co-promoted VPO Catalysts

For the preparation of Co-doped catalyst precursor, V_2O_5 (15.0 g) and the cobalt promoter in the cobalt(II) acetylacetonate form was suspended by rapid stirring into a mixture of isobutyl alcohol (90 ml) and benzyl alcohol (60

ml). The amount of cobalt(II) acetylacetonate was adjusted to obtain 0.01- 1.0 mol ratio of Co/V. *Ortho*-phosphoric acid (11 ml, 85%) was added in such a quantity as to obtain P:V atomic ratio of 1.0.

Catalysts Characterization

The structure of the catalysts was studied by X-ray diffraction (XRD) experiments. A diffractometer Philips model PW 1800 instrument with Cu K α radiation and Ni filter was used to collect the X-ray data. The SEM image was obtained with a Philips XL30 instrument. The infrared spectra of the catalysts were taken as KBr pellets on a Galaxy-5000 Fourier transform infrared (FT-IR) spectrometer.

Oxidation of Benzyl Alcohol

In a typical procedure, a mixture of 0.1 g catalyst (bulk VPO or VPO-Co), with a grain size of 200-230 mesh, 15 ml acetonitrile and 30 mmol of alcohol was stirred in a three-necked flask under nitrogen atmosphere at 50 °C for 30 min. The stirring rate of the solution was set at 750 cycle/min. Then 30 mmol of the oxidant (TBHP) was added. Then, the mixture was refluxed at 90 °C for 8 h under nitrogen atmosphere. After filtration, the solid was washed with ethanol and the reaction mixture was analyzed by GC. A GC (Perkin Elmer Model 8500) equipped with a flame ionization detector (FID) connected to a 3% OV-17 column with a length of 2.5 m and diameter of 1/8 in was used for product analysis.

Design of Experiment with Box-Behnken Method

The conversion of benzyl alcohol oxidation was

optimized by response surface methodology [30] using Box-Behnken design (BBD) with three effective variables such as, reaction temperature, X_1 (30-90 °C), reaction time, X_2 (30-480 min) and molar ratio of Co/V, X_3 (0.0-1.0). To minimize the number of variables, amount of catalyst and molar ratio of TBHP/benzyl alcohol for the reaction were kept constant at 0.1 g and 1 for all experiments, respectively. The parameters should be normalized before analyzing the regression. The variables were coded as +1, -1 and 0 for three levels, high, low and central, respectively. The actual variables (X_i) coded by linear transformation is shown in the Eq. (4) as follows:

$$x_i = \frac{X_i - (X_{high} + X_{low})/2}{(X_{high} - X_{low})/2} \quad (4)$$

Where x_i is the dimensionless coded value of i th factor, X_i is the uncoded value of the i th natural factor, X_{high} and X_{low} are the uncoded factor value at high and low level [34]. The statistical software Design Expert 8 was used for the analysis. Three independent variables with their levels are presented in Table 1. The following quadratic equation was used for the optimization process.

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (5)$$

Where, Y is the response and β_0 , β_i , β_{ii} and β_{ij} are coefficients of the intercept, linear, square and interaction effects, respectively. It is also possible to locate the region of interest where the desirable response (optimum condition) lies in, by simultaneous variation of several factors. The statistical significance of the model and the coefficients were judged by F-test and t-test, respectively.

Table 1. Experimental Range and Levels of Independent Process Variables

Independent variables	Coded	Range and levels		
		-1	0	+1
Reaction temperature (°C)	X_1	30	60	90
Reaction time (min)	X_2	30	255	480
Molar ratio of Co/V	X_3	0	0.5	1

RESULTS AND DISCUSSION

Characterization of the VPO-Co Catalysts

XRD patterns of all catalysts (Fig. 1) showed well crystalline materials. The appearance of lines at $2\theta = 21.8, 28.3, 29.9, 33.6, 37.7, 46.2$ and 49.5° indicates the presence of $(VO)_2P_2O_7$ (JCPDS: 41-698), while the appearance of peaks at $2\theta = 12.1, 19.3$ and 25.2° confirms the presence of β -VOPO₄ (JCPDS: 27-948). The average crystallite size of unpromoted VPO sample determined from the diffraction peak broadening by using the Scherer's formula was 18.7 nm (Fig. 1a). The X-ray lines due to $(VO)_2P_2O_7$ broadened and diminished with the increase of the Co/V molar ratio. As a result, Co promoted VPO gave poorer crystallinity compared to the unpromoted catalysts. All the patterns can be indexed to VPO catalyst although there are differences in the relative intensities of the main reflections. On the other hand, CoPO₄ (with the most representative peak at $2\theta = 24.6$) has been observed in the VPO-Co series. In this case, the intensities of the X-ray lines of CoPO₄ increased and those of the $(VO)_2P_2O_7$ and β -VOPO₄ decreased with the increase of the Co/V molar ratio. The addition of 0.01 mol% Co does not significantly affect the powder X-ray diffraction pattern. However, the addition of higher concentrations leads to a significant decrease in the intensity of the $(VO)_2P_2O_7$ and β -VOPO₄ reflection.

The surface morphology of unpromoted and promoted VPO catalysts ($P/V = 1$) is shown in Fig. 2. The unpromoted VPO catalyst (VPO-bulk) shows thin platelets with uniform crystal size and rosette plate-like structure. This data corroborates the x-ray diffractograms obtained in Fig. 1, where a dominant (001) reflection obtained is associated with an unpromoted VPO having stacked platelet morphology. The cobalt-promoted catalyst (VPO-Co) thus underwent a change in morphology compared to the unpromoted catalyst (VPO bulk). Promotion of VPO catalyst with Co-promoter also caused amorphization of the catalyst, thus giving rise the lost in rosette shape morphology and displaying nano-structured platelet and nano-rod structure morphology. VPO bulk and other Co-promoted VPO catalyst are different slightly in the shape of crystallites; the addition of cobalt decreases the sizes of crystallites. The particles of VPO are composed of lamellar crystallites, the size of them is 1-3 μm in diameter and 100-

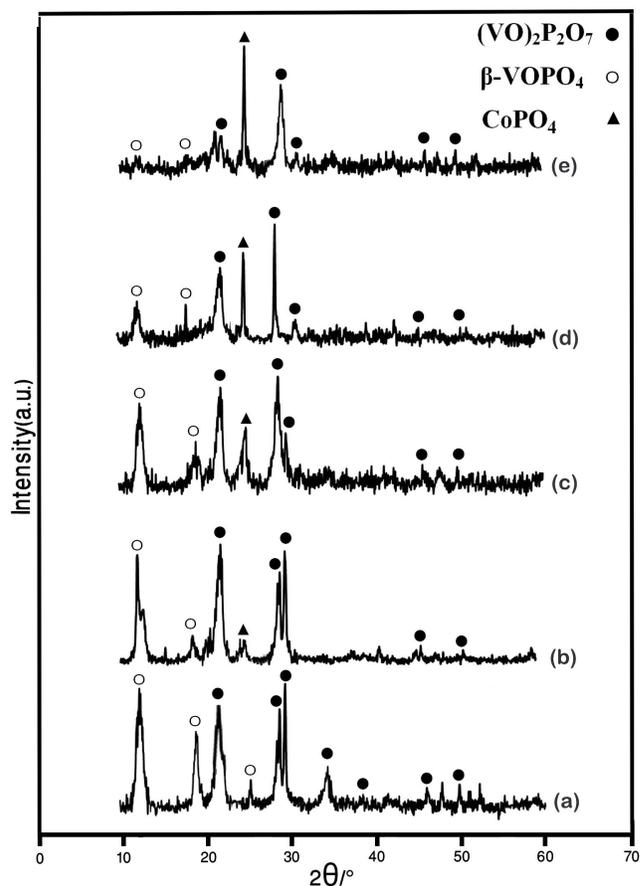


Fig. 1. XRD patterns of unpromoted and Co-promoted VPO catalysts: (a) VPO; (b) VPO-Co (0.01); (c) VPO-Co (0.03); (d) VPO-Co (0.06); (e) VPO-Co (0.1). Symbols: $(VO)_2P_2O_7$ (●); β -VOPO₄ (○); CoPO₄ (▲).

150 nm in thickness, while the VPO-Co sample is composed of the fastener-like crystallites and nano-rod structure and size of them is smaller than the former (1-1.5 μm in diameter and 50-100 nm in thickness).

The FT-IR spectra of the precursors and activated catalyst in the 250-2250 cm^{-1} region are shown in Fig. 3A and 3B, respectively. In the Fig. 3A, all of them show the characteristic vibrations of the vanadyl hydrogen phosphate hemihydrate ($VOHPO_4 \cdot 0.5H_2O$). The band centered at 1645 cm^{-1} is characteristic of coordinated water as expected from the crystalline structure, and a marked shoulder at 1600 cm^{-1} , which could be due to hydrogen-bonded uncoordinated water. In the VPO-Co precursors (Fig. 3A)

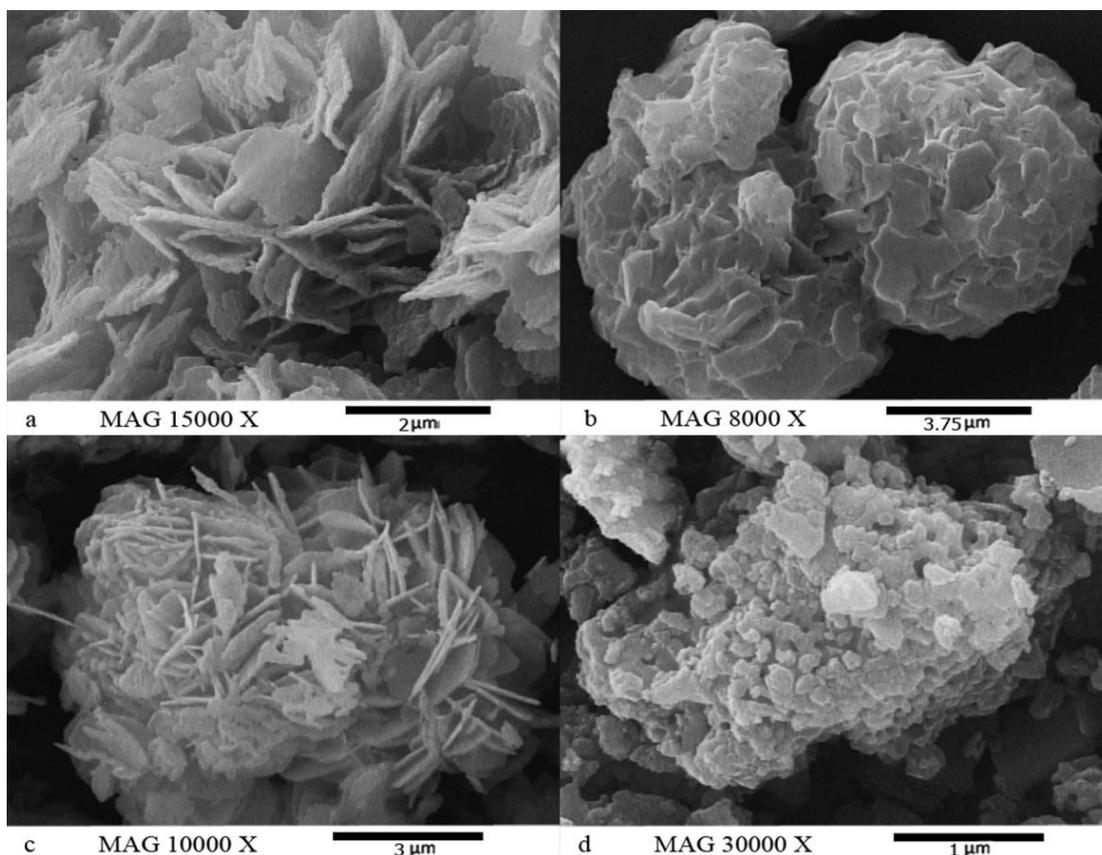


Fig. 2. Scanning electron micrographs of activated catalysts: (a) unpromoted VPO; (b) VPO-Co (0.01); (c) VPO-Co (0.06); (d) VPO-Co (0.5).

with different Co/V ratios, there appears a strong band at 975 cm^{-1} [$\text{V}^{4+}=\text{O}$]. Other characteristic bands corresponding to $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ phases are: 790 cm^{-1} (symmetric stretching of P-O-P bond), 1201 , 1105 and 1047 cm^{-1} (P-O stretching). The peaks at 929 cm^{-1} , 644 cm^{-1} , and 530 cm^{-1} were assigned to ν P-(OH) [35], δ O-P-O in β - VOPO_4 [36] and δ O-P-O, respectively. In the cases where Co has been added during the production step, the modified P-O-P vibration is observed. [37]. The ν (P-O-P) at 644 cm^{-1} has a lower intensity in the promoted catalysts compared to that in the unpromoted sample and this decreasing is independent of the Co content.

The $\text{V}=\text{O}$ absorption bands of the catalysts containing cobalt are significantly shifted to the lower wavenumber, while the P-O-P absorption bands of them are shifted to the

higher wavenumber. The introduction of promoter into the crystal lattice, in other words, the substitution of vanadium by metal brings about a shift of $\text{V}=\text{O}$ wavenumber to the lower frequencies [38], and the higher shift in P-O-P wavenumber indicates the promoter atoms affect the layer linkages [39]. So, these above results strongly suggest that cobalt promoter is located in the crystal lattice of vanadyl pyrophosphate.

The FT-IR spectra of the activated VPO catalysts are shown in Fig. 3B. Examination of the FT-IR spectrum suggests that the peaks of characteristic bands of VPO are weaker than those in cobalt-doped ones, while, the significant differences observed in the spectra are for vibrations of the linkages between the layers of the vanadyl pyrophosphates.

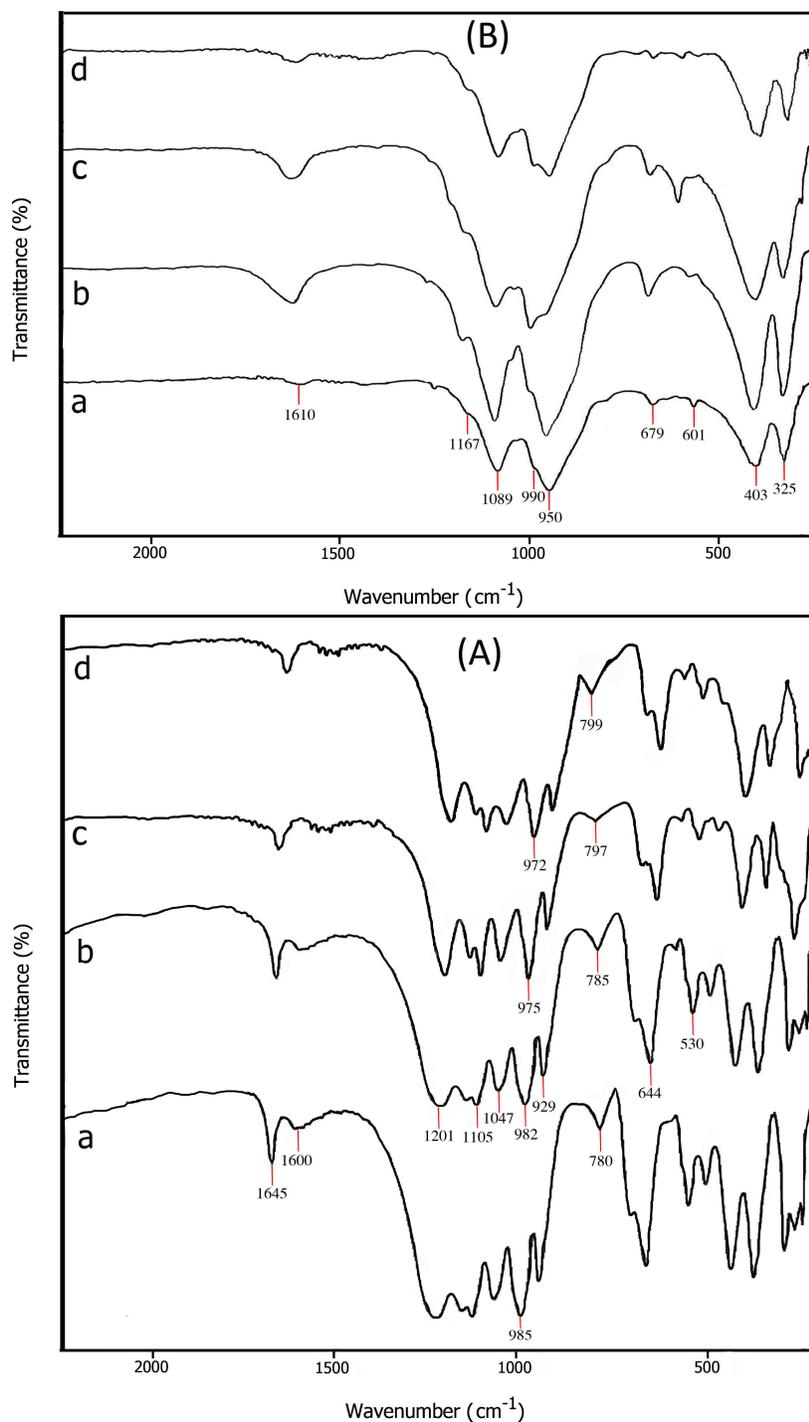


Fig. 3. FT-IR of VPO and Co-VPO, (A): before calcinations (a) VPO, (b) VPO-Co (0.01), (c) VPO-Co (0.06), (d) VPO-Co (0.1) and (B): after calcinations : (a) VPO, (b) VPO-Co (0.01), (c) VPO-Co (0.06), (d) VPO-Co (0.1).

Effect of the Amount of the Catalyst

The effect of the amounts of catalyst on the conversion was investigated. In these experiments, the amounts of VPO-Co(0.5) (with 0.5 molar ratio of Co/V) were varied from 0.01 to 0.3 g for reactions carried out at 90 °C for 8 h, with molar ratio of TBHP to benzyl alcohol 1:1, stirring rate of the reaction mixture 750 cycle/min and other reaction conditions remain constant. The results (Fig. 4) clearly demonstrate that the oxidation reaction is strongly dependent upon the catalyst amount. Without addition of catalyst, the conversion% is 5%. In the presence of catalyst, on the other hand, a general trend is observed for increasing the conversion of benzyl alcohol by rising catalyst amounts, which is due to the increase in the total number of available active catalytic sites for the reaction.

With increasing the amount of loading catalyst from 0.01 g to 0.1g the conversion of benzyl alcohol was increased from 29% to 64%. However, the conversion did not distinctly benefit from increasing the catalyst amount beyond 0.1 g.

In this reaction, the reaction rate is determined by surface reaction and mass transfer. In VPO catalysts, the pore diameters are very low. Therefore, the benzyl alcohol oxidation reaction mostly takes place on the external surface

of the catalysts and the internal diffusion has little impact on the reaction rate. In these experimental conditions, the surface reaction is the limiting step when the amount of catalyst is below 0.1 g. However, the external diffusion becomes the limiting step when the amount of catalyst is exceeded 0.1 g. Therefore, in this reaction, the optimum mass of catalyst is 0.1 g.

Analysis of Data and Development of the Response Surface Model

In the Box-Behnken design, seventeen experimental observations were undertaken at random orders for the optimization of conversion (Y) in the benzyl alcohol oxidation process. Table 2 shows the data resulting from the experiment of the effect of three variables, reaction temperature (X_1), reaction time (X_2) and molar ratio of Co/V (X_3), where amount of catalyst, molar ratio of TBHP to benzyl alcohol, amount of solvent and stirrer speed are kept unchanged at 0.1 g, 1:1, 15 ml and 750 rpm, respectively. The selectivity of benzyl alcohol in all seventeen experiments was around 76%-80%. The experimental results were analyzed through RSM to obtain an empirical model for the best response (conversion of benzyl alcohol). To investigate the effects of the main

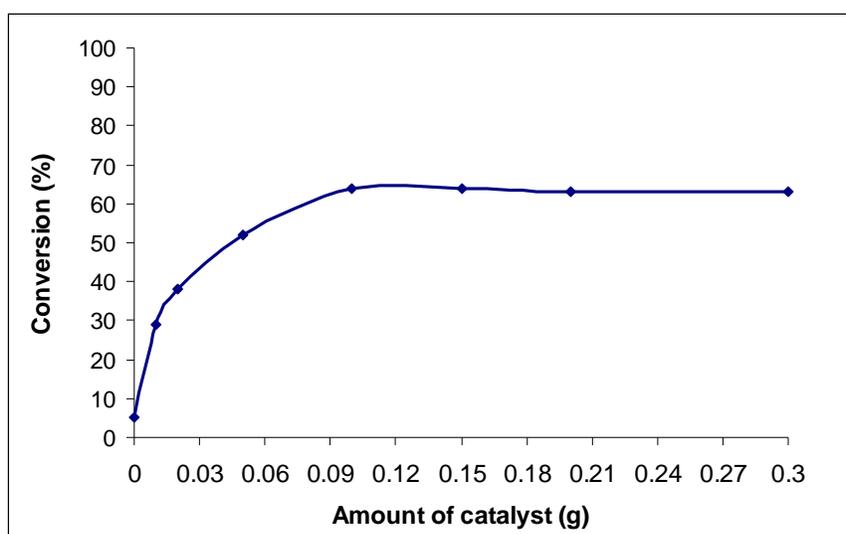


Fig. 4. The effect of the amount of VPO-Co (0.5) in the oxidation of benzyl alcohol Reaction condition: benzyl alcohol 30 mmol; TBHP 30 mmol; acetonitrile 15 ml; Reflux temperature (90 °C); stirring rate of the reaction mixture 750 cycle/min; reaction time 8 h.

Table 2. Box-Behnken Design Matrix

Run	Coded values			Actual values			Conversion (%)		
	X ₁	X ₂	X ₃	X ₁	X ₂	X ₃	Y _{exp}	Y _{pred}	Residual
1	-1	0	+1	30	255	1	28.70	29.06	-0.36
2	0	0	0	60	255	0.5	49.80	49.76	0.04
3	-1	0	-1	30	255	0	27.00	27.76	-0.76
4	0	-1	+1	60	30	1	31.00	31.17	-0.17
5	0	0	0	60	255	0.5	50.00	49.76	0.24
6	+1	+1	0	90	480	0.5	64.00	64.61	-0.61
7	+1	0	+1	90	255	1	48.50	47.82	0.68
8	0	0	0	60	255	0.5	50.20	49.76	0.44
9	0	0	0	60	255	0.5	49.30	49.76	-0.46
10	-1	+1	0	30	480	0.5	41.80	41.25	0.55
11	+1	-1	0	90	30	0.5	46.00	46.55	-0.55
12	0	+1	+1	60	480	1	54.50	54.63	-0.13
13	+1	0	-1	90	255	0	47.00	46.52	0.48
14	-1	-1	0	30	30	0.5	33.00	32.39	0.61
15	0	-1	-1	60	30	0	40.00	39.87	0.13
16	0	0	0	60	255	0.5	49.50	49.76	-0.26
17	0	+1	-1	60	480	0	43.50	43.33	0.17

Table 3. Analysis of Variance (ANOVA) for Benzyl Alcohol Conversion (%)

Source	Sum of squares	Freedom degree	Mean square	F-Value	P-Value
Model	1538.75	8	192.34	456.33	<0.0001
X ₁	703.13	1	703.13	1668.15	<0.0001
X ₂	361.81	1	361.81	858.37	<0.0001
X ₃	3.38	1	3.38	8.02	0.0221
X ₁ X ₂	21.16	1	21.16	50.20	0.0001
X ₂ X ₃	100.00	1	100.00	237.25	<0.0001
X ₁ ²	67.54	1	67.54	160.23	<0.0001
X ₂ ²	0.83	1	0.83	1.98	0.1972
X ₃ ²	266.45	1	266.45	632.15	<0.0001
Residual	3.37	8	0.42		
Lack of fit	2.84	4	0.71	5.34	0.0668
Pure error	0.53	4	0.13		

R-Sq = 99.78%; R-Sq (adj) = 99.50%.

factors and their interactions, analysis of variance (ANOVA) was used. The stepwise regression method is to add variables in the earlier stage and eliminate unimportant variables subsequently. Backward elimination method was applied, and statistically insignificant terms ($p > 0.05$) were deleted from the full quadratic model to obtain a final response surface model. The model was refitted after successive elimination until an unsatisfactory fit occurred indicated by a decrease in the adjusted R-square value. Backward elimination was adopted in this study since it is less probable to miss significant predictors exhibiting significant effect only in the presence of some other variables [40]. The results of the second-order response surface model fitting in the form ANOVA are given in Tables 3.

The F-value of 456.33 implies that the model is significant. In addition, the P-value of the model is less than 0.05, indicating that it is a significant and desirable model. The F-value is defined as $F = MSF/MSE$, where MSF and MSE are the mean squares of factors or interactions, and errors, respectively. In this model with high F-value, the P-value of <0.0002 indicates that there is only 0.02% chance for noise product in the experiments. The large value of F indicates that most of the variation in the response can be explained by the regression equation [41].

The equation indicates that conversion of benzyl alcohol (Y) has linear and quadratic relationships with the three variables. Regression analysis revealed a coefficient of determination (R^2) value of 0.9978, indicating that the model does not explain only 0.22% of total variations. The adjusted determination coefficient ($AdjR^2 = 0.9950$) was also high, implying that the model has high significance. After the ANOVA test, it was observed that the factors X_1 , X_2 and X_3 and interactions $X_1 \times X_2$, $X_2 \times X_3$, X_1^2 and X_3^2 proved to be the statistically most significant effect on the conversion of benzyl alcohol (Y). A quadratic model with statistical significance from a combination of estimates for the variables and the ANOVA results can be produced. The quadratic model was used to explain the mathematical relationship between the independent variables and dependent responses which is represented by Eq. (6).

$$Y = 49.76 + 9.38X_1 + 6.73X_2 + 0.65X_3 + 2.30X_1X_2 + 5.00X_2X_3 - 4.01X_1^2 + 0.45X_2^2 - 7.96X_3^2 \quad (6)$$

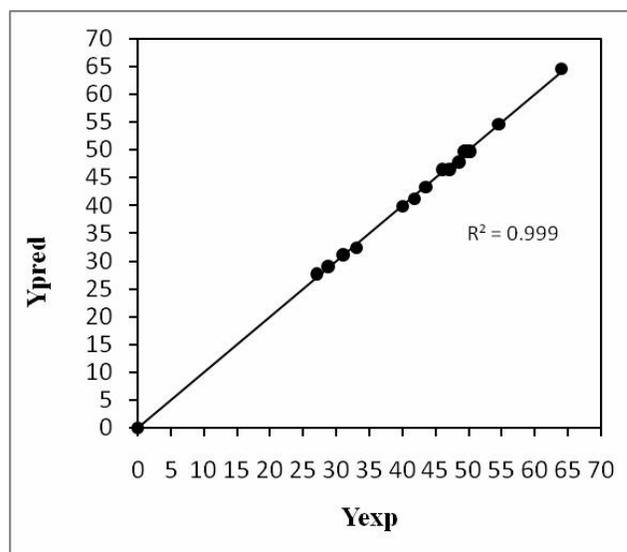


Fig. 5. Comparison between experimental and predicted Y.

A positive sign before a term indicates a synergistic effect, while a negative sign indicates an antagonistic effect [42]. The presence of the significant XX cross terms in the model confirms that responses depend on both single and mixture variables. According to Eq. (6) the binary terms indicate that there is a synergistic effect between reaction time (X_2) and two other variables (X_1 and X_3) for Y.

Using data given in Table 2, the experimental conversion of benzyl alcohol (Y_{exp}) vs. predicted values (Y_{pred}) are plotted (Fig. 5) and R^2 of the linear plot was 0.999.

Effect of Process Variables on the Conversion of Benzyl Alcohol

The effect of the three factors on the response variable is shown in Fig. 6. In contrast to the traditional trial and error method, the prediction profiler provides an efficient way of changing one variable while keeping others constant to study the individual effects on the response [43].

Main effects of factors (X_1 , X_2 and X_3) on the conversion of benzyl alcohol (Y) have been presented in Fig. 6. Reaction temperature plays an important role in the reaction progress. The temperature of reaction can influence reaction rate and benzaldehyde yield, because rate constants are strong functions of temperature. Therefore, the study of the

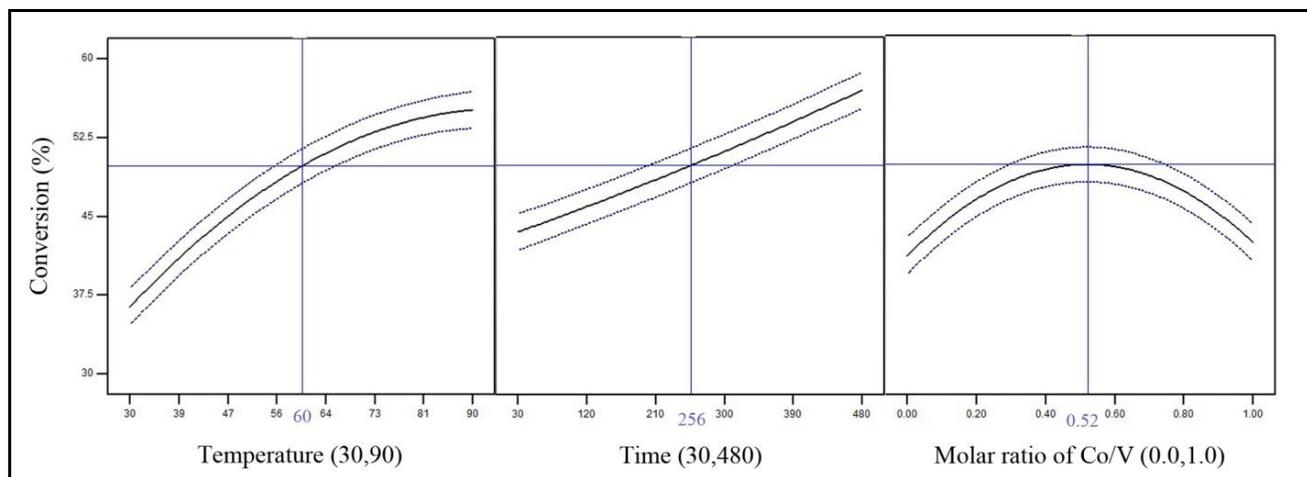


Fig. 6. Prediction profiler showing the influence of each variable on the response.

effect of temperature is very important for a heterogeneously catalyzed reaction. The conversion of benzyl alcohol is significantly increased with the increase of temperature.

Reaction time also plays an important role in the reaction progress. An increase in reaction time will also increase the conversion of benzyl alcohol. The reaction occurred fast at first, and gradually reached to the steady state after 8 h. The conversion changed little after 8 h.

From Fig. 6, the conversion of benzyl alcohol was increased by increasing the molar ratio of Co/V (X_3) and then decreased in higher than 0.52 molar ratio of Co/V. XRD characterization of Co-promoted VPO catalysts with different Co/V molar ratio (Fig. 1) shows that the vanadium phosphorous oxides exit as poor crystalline $(VO)_2P_2O_7$ phase when Co/V molar ratio is 0.1. When Co/V molar ratio is lower than 0.1 the crystalline phase emerged, which has been proved to be $(VO)_2P_2O_7$ mostly. From Fig. 2, the SEM of VPO-Co with Co/V = 0.5, shows that the VPO structure was not retained after Co promotion and rosette shape morphology of VPO breaks down to irregular and aggregated particles. In fact, variation in Co/V molar ratio produces significant changes in phase composition, textural properties, morphology and relative content of $(VO)_2P_2O_7/VOPO_4$ species, of the VPO-Co catalysts. Such alterations in catalyst characteristics should account for the

observed difference in performance.

Response Surface and Contour Plots

Other than the individual effect contributed by each main variable, the response was also influenced by the interaction variables. To gain a better understanding of the interaction effects of variables on yields, contour plots for the measured responses were formed based on the model equations (Eq. (6)). The effects contributed by these interactions can be observed from the response surface plots generated by the contour profiler. The contour profiler is an interactive facility used to optimize response surface graphically. The three dimensional response surfaces and contour plots were used to facilitate a straightforward examination of the influence of experimental variables on the response [44-46]. Each response surface and contour plot was created by keeping two out of three variables constant at their center points. They can be also used for designing an optimum catalyst for the conversion of benzyl alcohol vs. reaction temperature, reaction time and molar ratio of Co/V. Note that only the contour profilers of significant interaction variables will be studied here because insignificant interaction variables do not result in much variation in the response within the factor region. In general, the shape of the contour plots are either straight, circular, elliptical or in the form of minimax [44]. If the shape of the

contour is elliptical or inclined, the interaction between variables is evident.

Figure 7 shows the response surface plot of conversion of benzyl alcohol over the process parameters (reaction temperature and reaction time) with other variable fixed at

center point. The response surface plot reveals useful information for optimization in a qualitative way. Figure 7 exhibits that conversion of benzyl alcohol increase due to both increase in the reaction temperature and reaction time. The contour plot in Fig. 8 shows that maximum conversion

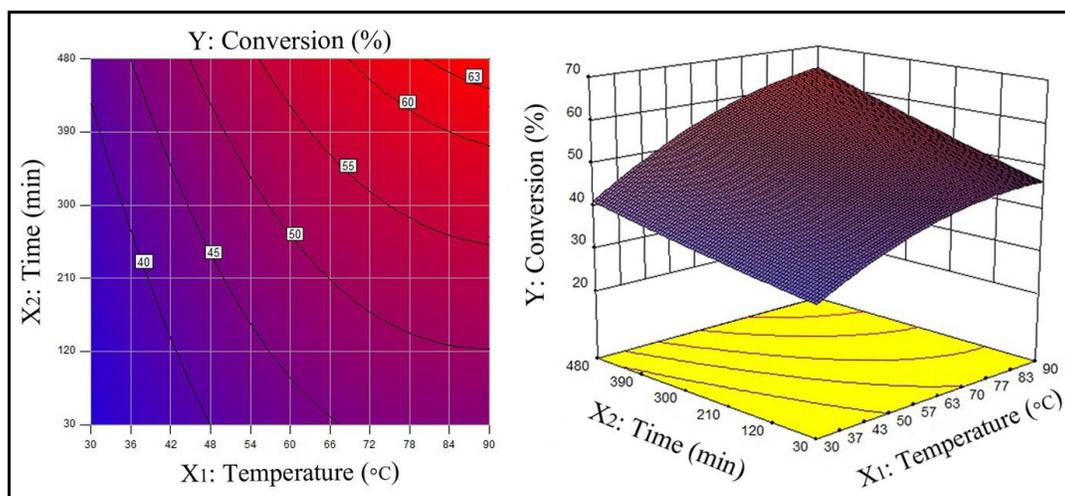


Fig.7. Contour plot (left) and surface plot (right) of conversion of benzyl alcohol as a function of reaction temperature and reaction time at molar ratio of Co/V = 0.5.

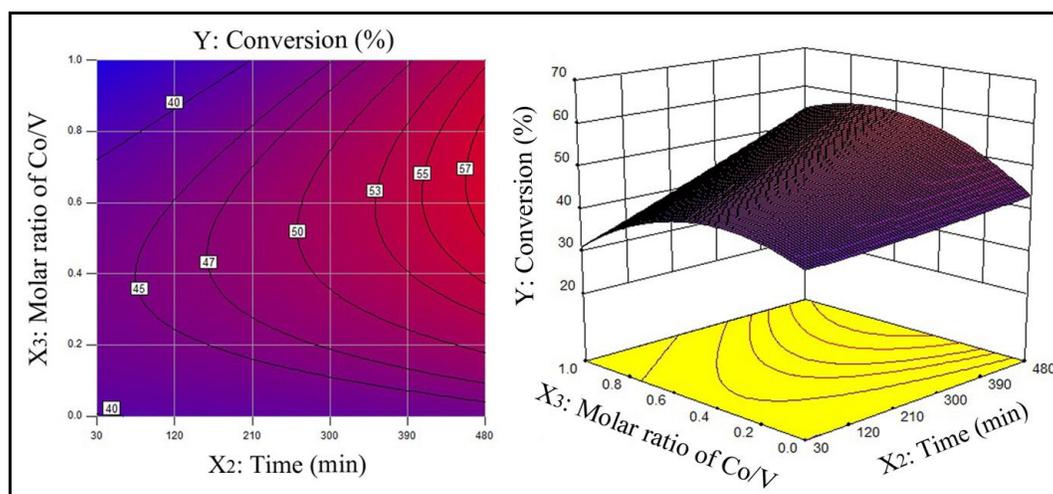


Fig. 8. Contour plot (left) and surface plot (right) of conversion of benzyl alcohol as a function of reaction time and molar ratio of Co/V at reaction temperature = 60 °C.

Table 4. Comparing the Experimental and Predicted Values for Maximum Conversion

Parameter/Response	Predicted values	Experimental values
Conversion (%)	65.44	64.23
X ₁ : Reaction temperature (°C)	89.86	90
X ₂ : Reaction time (min)	477.8	477
X ₃ : Molar ratio of Co/V	0.64	0.64

of benzyl alcohol at middle level of molar ratio of Co/V was produced. The conversion of benzyl alcohol decreased to 42.5% from 49.8% by further increase of molar ratio of Co/V to 1.0. From Fig. 6, at constant reaction temperature, the conversion of benzyl alcohol is significantly increased with the increase of reaction time.

As mentioned, the conversion of benzyl alcohol has an optimum amount with respect to reaction temperature, reaction time and molar ratio of Co/V. At 89.86 °C reaction temperature, 477.8 min reaction time and 0.64 molar ratio of Co/V the conversion of benzyl alcohol reached to a maximum amount, 65.44% (Table 4). Also, to show the validity of predictions, an experiment with optimized independent variables was carried out and data is presented in Table 4. These results confirm that the predicted results are matching satisfactorily with the experimental values. Thus the RSM was successfully applied to maximize the conversion of benzyl alcohol.

Response optimizer helps to identify the combination of input variable settings that jointly optimize a single response or a set of responses [47]. The factor setting can be adjusted to get the initial solution. The values of the process variables for the maximum conversion of benzyl alcohol are shown in Table 4. The optimum values of the independent variables are obtained considering the initial and final values of reaction temperature, reaction time and molar ratio of Co/V.

CONCLUSIONS

A response surface model, based on the Box-Behnken technique, was developed to describe the oxidation of benzyl alcohol in liquid phase. The obtained results from

ANOVA showed that the most significant factors affecting the conversion of benzyl alcohol were reaction temperature and reaction time, respectively. In addition, the interaction between reaction time and molar ratio of Co/V ($X_2 \times X_3$), had significant effects on the conversion of benzyl alcohol. Coefficient of determination (R^2) value of 0.9978 obtained from Eq. (5) showed that quadratic polynomial regression model could properly interpret the experimental data. At 89.86 °C reaction temperature and 477.8 min of reaction time and 0.64 molar ratio of Co/V, we could achieve the highest conversion of benzyl alcohol (65.44%).

REFERENCES

- [1] G. Centi, F. Trifirò, J.R. Ebner, V.M. Franchetti, Chem. Rev. 88 (1988) 55.
- [2] G. Centi, Catal. Today 16 (1993) 1.
- [3] J.B. Benziger, V. Gulians, S. Sundaresan, Catal. Today 33 (1997) 49.
- [4] M. Oconnor, B.K. Hodnett, Appl. Catal. 42 (1988) 91.
- [5] Y. Kamiya, S. Ueki, N. Hiyoshi, N. Yamamoto, T. Okuhara, Catal. Today 78 (2003) 281.
- [6] B.K. Hodnett, Catal. Rev-Sci. Eng. 27 (1985) 373.
- [7] G.J. Hutchings, Appl. Catal. 72 (1991) 1.
- [8] M. Brutovský, S. Gerej, Collect. Czech. Chem. Commun. 47 (1982) 403.
- [9] M. Brutovský, S. Gerej, F. Vasilco, J. Gerejová, J. Collect. Czech. Chem. Commun. 47 (1982) 1290.
- [10] G.J. Hutchings, R.J. Higgins, Catal. 162 (1996) 153.
- [11] D. Kladekova, A. Hanudel, M. Brutovsky, J. Novak, Collect. Czech. Chem. Commun. 60 (1995) 457.
- [12] F.B. Abdelouahab, R. Olier, M. Ziyad, J.C. Volta, J.

- Catal. 157 (1995) 687.
- [13] M.T. Sananens-Schulz, F.B. Abdelouahab, G.J. Hutchings, J.C. Volta, *J. Catal.* 163 (1996) 346.
- [14] R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1981.
- [15] M. Hudlicky, *Oxidations in Organic Chemistry*, ACS, DC, Washington, 1990.
- [16] E. Mikolajska, V. Calvino-Casilda, M.A. Banares, *Appl. Catal. A: Gen.* 164 (2012) 421.
- [17] G.C. Behera, K.M. Parida, *Appl. Catal. A: Gen.* 364 (2013) 464.
- [18] K.M. Parida, G.C. Behera, *Catal. Lett.* 140 (2010) 197.
- [19] G.C. Behera, K.M. Parida, *Dalton Trans.* 41 (2012) 1325.
- [20] G.C. Behera, K.M. Parida, D.P. Das, *J. Catal.* 289 (2012) 190.
- [21] G.C. Behera, K.M. Parida, *Catal. Sci. Tech.* 3 (2013) 3278.
- [22] U.R. Pillai, E. Sahle-Demessie, *Chem. Commun.* 25 (2002) 2142.
- [23] G.C. Behera, K.M. Parida, *Appl. Catal. A: Gen.* 245 (2012) 413.
- [24] U.R. Pillai, E. Sahle-Demessie, *Appl. Catal. A* 276 (2004) 139.
- [25] V. Mahdavi, H.R. Hasheminasab S. Abdollahi, *J. Chin. Chem. Soc.* 57 (2010) 189.
- [26] V. Mahdavi, A. Monajemi, *Korean J. Chem. Eng.* 30 (2013) 2178.
- [27] M. Daroux, H. Zamani, J.L. Greffe, J. Bordet, *Chem. Eng. J.* 22 (1981) 125.
- [28] K. Ravikumar, K. Pakshirajan, T. Swaminathan, K. Balu, *Chem. Eng. J.* 105 (2005) 131.
- [29] F. BuYuKsoNmez, T.F. Hess, R.L. Crawford, A. Paszczynski, R.J. Watts, *Appl. Environ. Microbiol.* 65 (1999) 2784.
- [30] D.C. Montgomery, *Design and Analysis of Experiments*, John Wiley & Sons, Inc: New York, 1991.
- [31] R.H. Myers, *Response Surface Methodology*, Allyn and Bacon: Boston, 1971.
- [32] G.E.P. Box, K.B. Wilson, *J. R. Stat. Soc. Ser.* 13 (1951) 1.
- [33] W.G. Cochran, G.M. Cox, *Experimental Design*, John Wiley & Sons, Inc: New York, 1957.
- [34] D. Bas, I.H. Boyac, *J. Food Eng.* 78 (2007) 836.
- [35] G. Busca, G. Centi, F. Triroand, V. Lorenzelli, *J. Phys. Chem.* 90 (1986) 1337.
- [36] E. Bordes, P. Courtine, *J. Catal.* 57 (1979) 236.
- [37] L.M. Cornaglia, C.R. Carrara, J.O. Petunchi, E.A. Lombardo, *Appl. Catal. A*, 183 (1999) 177.
- [38] Y. Takita, K. Tanaka, S. Ichimaru, Y. Mizihara, Y. Abe, Y. Ishihara, *Appl. Catal. A: Gen.* 103 (1993) 281.
- [39] R.L. McCormick, G.O. Alptekin, A.M. Herring, T.R. Ohno, S.F. Dec, *J. Catal.* 172 (1997) 160.
- [40] G. Du, Y. Yang, W. Qiu, S. Lim, L. Pfefferle, G.L. Haller, *Appl. Catal. A: Gen.* 313 (2006) 1.
- [41] P. Tripathi, V. Chandra Srivastava, A. Kumar, *Desalination* 249 (2009) 1273.
- [42] S.Y. Lu, J.Q. Qian, G.W. Zhang, D.Y. Wei, G.F. Wu, B.P. Yi, B. Pan, K.Y. Zhang, *J. Biochem. Technol.* 1 (2009) 79.
- [43] Q. Tang, Y. Chen, C. Jasmine Zhou, T. Chen, Y. Yang, *Catal. Lett.* 128 (2009) 210.
- [44] I. Istadi, N.A. Saidina Amin, *Fuel Process Technol.* 87 (2006) 449.
- [45] N.A. Saidina Amin, D.D. Anggoro, *Fuel.* 83 (2004) 487.
- [46] C. Ye, J. Liu, F. Ren, N. Okafo, *J. Pharm. Biomed. Anal.* 23 (2000) 581.
- [47] N. Jose, S. Sengupta, J.K. Basu, *Fuel.* 90 (2011) 626.